STUDIES ON THERMOPLASTIC ELASTOMERS BASED ON POLYETHYLENE / ELASTOMER BLENDS

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CERTIFICATE

This is to certify that this thesis is a report of the original work carried out by **Ms. Rajalekshmi. S** under my supervision and guidance in the Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology. No part of the work reported in this thesis has been presented for any other degree from any other institution.

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Declaration

I, **Rajalekshmi.S.** hereby declare that the thesis titled ***"STUDIES ON THERMOPLASTIC ELASTOMERS BASED ON POLYETHYLENE / ELASTOMER BLENDS"*** is a bona fide record on research done by me and that no part of this thesis has been presented / reported for any degree or diploma of any other University.

COCHIN, **05-11-2001.**	**RAJALEKSHMI.S.** Dept. of Polymer Science and Rubber Technology, Cochin University of Science and technology, Cochin – 682 022.

...........to my husband
who taught me to take life as it comes

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It never happens without help:

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LIST OF ABBREVIATIONS USED

POLYMERS

ATNR	- Amine Terminated (Liquid) Natural Rubber
Chl. PIB	- Chlorinated Poly iso butylene
CIIR	- Chloro Butyl Rubber
GW (P)	- Modified Powdered Glove Waste
GW	- Modified Glove Waste
HDPE	- High Density Polyethylene
IIR	- Isoprene Isobutylene (Butyl) Rubber
ISNR	- Indian Standard Natural Rubber
LDPE	- Low Density Polyethylene
LLDPE	- Linear Low Density Polyethylene
LNR	- Liquid Natural Rubber
NR	- Natural Rubber
PE	- Polyethylene
PIB	- Polyisobutylene
RR	- Reclaimed Rubber
TPEs	- Thermoplastic Elastomers
TPNR	- Thermoplastic Natural Rubber
TW	- Modified Thread Waste

CHEMICALS

CBS	- N-cyclohexyl benzothiazole-2-sulfenamide
CCl_4	- Carbon tetra chloride
HCl	- Hydrochloric Acid
MBT	- Mercapto benzo thiazole
MBTS	- Dibenzthiazyl disulphide
S	- Sulphur
ZDC	- Zinc dithio carbamate
ZnO	- Zinc Oxide

MISCELLANEOUS

ASTM	- American Standard for Testing Materials
DMA	- Dynamic Mechanical Analysis
DSC	- Differential Scanning Calorimetry
E'	- Storage Modulus
IS	- Indian Standards
RRII	- Rubber Research Institute of India
RRIM	- Rubber Research Institute of Malaysia
SEM	- Scanning Electron Microscopy
Tanδ	- Loss Tangent
UTM	- Universal Testing Machine

CHAPTER I

INTRODUCTION

A polymer blend is a combination of two or more polymers, resulting from common processing steps. Almost all polymers in industrial and transportation applications are used as polymer blends. The science and technology of polymer blends is advancing at a rapid rate. One of the main advantages of polymer blends is the great regulatable variability of their properties, despite the limited number of initial components. Among the various blends, the elastomer-thermoplastic blends have become technologically useful as thermoplastic elastomers in recent years (1-3). They have many of the properties of elastomers, but they are processable as thermoplastics (4). They exhibit the characteristics of thermoplastics at processing temperature and those of elastomers at service temperature (5-7). They contain a soft rubbery phase and hard thermoplastic phase. Thermoplasticity results from the melting characteristics of the hard thermoplastic phase at the high temperatures of processing, where as the elastic properties arise from the soft rubbery phase at the low temperatures of use. The ideal elastomer-plastic blend comprises finely divided elastomer particles dispersed in the plastic phase. At low temperatures, this plastic phase will act as crosslinks or as reinforcing filler particles between the soft rubbery phase. This unique combination of properties of vulcanized rubber and the easy processability of thermoplastics bridge the gap between conventional elastomers and thermoplastics. The usual methods of preparation of elastomer-plastic blends are melt-mixing, solution blending or latex mixing (8).

All materials attract interest on the basis of their property-processing cost-performance relationship. The properties of miscible blends will follow relationships that are functions of compositions and to some extent, the degree of interaction between the components (9-10). The properties of immiscible blends will depend on the phase morphology, phase interaction as well as composition. The practical utility of a polymer blend is decided by compatibility, which is considered as the fundamental property (11-13). In miscible polymer blends, the property (P) depends on average properties of the constituents and can be described by the following equation:

$$\mathbf{P = P_1C_1 + P_2C_2 + IP_1P_2}$$

where, **P** is the property of the blend, $\mathbf{P_1}$ and $\mathbf{P_2}$ are the properties of the isolated components and $\mathbf{C_1}$ and $\mathbf{C_2}$ are the respective concentrations of the constituents and **I** is the interaction parameter which can be positive, zero or negative.

Intermolecular bonding force is considered to be the most important factor that governs the ultimate properties of a polymer blend. Phase separation under various conditions like stress, blend ratio, temperature etc. occurs due to the low interaction of the interface. Also, poor adhesion between the components of the blend at the interface in a heterogeneous system does not allow efficient transfer of stress across the interface and this leads to premature failure under stress. Though many immiscible systems form useful products and are being successfully commercialized, the applicability of such blends is limited because of the inferior macroscopic properties. Hence, if incompatible polymer systems can be effectively blended with retention of macroscopic properties of the component polymers, that can be very successful and that is why such blends are gaining importance both in the academic and industrial fields.

In these types of blends, one polymer may be regarded as 'reinforcing' the other. This 'reinforcing' effect enhance tensile strength, tear strength, modulus etc. of the elastomer by thermoplastic and improves impact strength, environmental stress-cracking etc. of the thermoplastic by elastomer (14). Several studies have been done in this subject. Corish and Powell (15) has made a review of thermoplastic elastomer blends. Polymer blends have been discussed by Fettes and Maclay (16), who observed that such blends are usually heterogeneous, since most polymers are incompatible with each other. It can be assumed that the useful properties of thermoplastic-elastomer blends are frequently those which arise from their incompatibility. Several blends have been prepared and studied using low and high crystalline thermoplastics like polyvinyl chloride, polystyrene, polyethylene, polypropylene etc. as the plastic phase and nitrile rubber, polybutadiene rubber, natural rubber, butyl rubber etc. as the elastomer phase (17-20).

Methods of preparing polymer blends

Mechanical blending of polymers is the easiest and most direct method of preparing a polymer blend. This may be accomplished on two-roll mill or internal mixers like Banbury. The nature of the resulting dispersion depends on the time of mixing, the shear field in equipment, temperature, rheological properties of the component polymers etc. Also, there is a possibility of chemical effects being produced by the milling operation.

When the individual components can be obtained in latex form, they may be conveniently combined by blending the lattices. The polymer is then recovered by coagulation or spray-drying. This method results in an intimate, uniform dispersion. However, one drawback is the difficulty in completely removing the non-polymer material (emulsifier etc.) present in the lattices.

Mixing of polymer solution is, in practice, mainly used for coatings as it permits rapid and easy mixing of the components at low energy and costs. Hence it can be used for simple applications at normal temperature. This does not cause any degradative colour changes or premature crosslinking reactions. But for the preparation of the solid polymer blends, this method requires removal of the solvent, which usually leads to phase separation. Further more, the use of solvents creats problems connected with their price, toxicity, flammability, pollution and the economics of the whole process. Usually only laboratory samples of solid polymer blends are prepared by this method. Blends may also be prepared by dissolving a polymer in the monomer of the other component and then polymerizing the second component. This may result in appreciable grafting of the polymer in addition to good dispersion.

Processing characteristics of polymer blends

Rheological studies of polymer blends are important because of the reasons outlined below.

1. Most of the processing techniques involve some form of direct flow of polymer solutions or melts. This will help to identify the defects in processing, if any, and thus adjustments can be done on the processing conditions to minimize the defect.
2. Process and equipment can be designed by deriving qualitative and to some extent quantitative relations between factors like output, power consumption, machine dimension, material properties and operational variables such as temperature and pressure.
3. The best polymer that can be used under a given set of conditions can be selected.
4. Identification and characterization of the molecular structure of polymer solutions can be done with their flow properties.

A variety of methods and instruments have been devised to measure viscosity and other flow properties of liquids in all cases (21). Almost all viscometric systems can be classified into two: those in which flow is caused by a difference in pressure from one part of the liquid to other and those in which flow is caused by controlled relative motion of the confining solid boundaries of the liquid. Capillary type viscometers fall in the first class and rotational types in the second class.

Of the many devices available to study the rheological properties of polymer melts, Capillary Rheometer is the most important one (22), because it can be used to cover the shear rate ranges encountered in factory processes such as compression moulding (1 - 10 s^{-1}), milling and calendering (10 - 100 s^{-1}), Extrusion (100 - 1000 s^{-1}) and injection moulding (1000 - 10000 s^{-1}).

One of the important aims of blending of polymers is to obtain a better processing material. This betterment may be attained by lowering the stock viscosity or producing a material that is less prone to fracture or crumbling when subjected to flow. The elastic behaviour and related phenomena of die swell and shrinkage can also be altered by blending. Generally, it is expected that the processing behaviour of the polymer blend will be intermediate to those of the component polymers. However, polymer blends sometimes display anomalous rheological properties. The viscosity of a polymer blend may exhibit minima or maxima as a function of the composition. Very complex dependencies of rheology on composition have been observed.

Thermoplastic elastomers: effect of dynamic vulcanization

Vulcanization is the process of chemically producing network junctions by inserting crosslinks between polymer chains (23). There are two different types of vulcanizations: conventional vulcanization and dynamic vulcanization. Originally it was required that vulcanization takes place after the uncured rubber part or article has been formed and has flown into its final shape. This is what is occuring in a heated mould. But now it has been proved that rubber can be processed by mixing, extruding, calendering or moulding both before and after vulcanization. Vulcanization during melt mixing is called 'dynamic vulcanization' (24-27). Useful products can be produced by dynamic vulcanization only if the mix contains enough of a molten non-vulcanizing polymer like polyethylene, polypropylene etc. A.Y Coran has defined dynamic vulcanization as the process of vulcanizing rubber during its intimate melt mixing with a non–vulcanizing thermoplastic polymer (28). This process results in the formation of a particulate vulcanized rubber phase of stable domain morphology during further melt processing (29).

Dynamic vulcanization is a method to produce new thermoplastic elastomers which have properties as good or even better, in some cases, than those of block copolymers. The commercial importance of dynamic vulcanization has been increased since the introduction of proprietary products like 'SANTOPRENE' thermoplastic elastomers prepared by the dynamic vulcanization of blends of olefin rubber with polyolefin resin. If the elastomer particles of the blends are small enough and if they are fully vulcanized, then the properties of the blends are greatly improved. These improvements include enhanced ultimate mechanical properties, reduced permanent set, improved fatigue resistance, greater impact resistance, improved high temperature utility, greater melt strength, more reliable thermoplastic fabricability and so on. A factor contributing to the enhanced high temperature utility of dynamically vulcanized blends is that, during fabrication of a finished part, many of the vulcanized rubber particles physically, interact with one another to form a 'network' of vulcanized elastomer. Melt processability of the blend is restored on regrinding and remelting, as the 'network' of loosely bound together particles disintegrates. Briefly, dynamic vulcanization provides blends that are very elastomeric in their performance characteristics, at the same time they can be rapidly fabricated into finished parts in thermoplastic processing equipment.

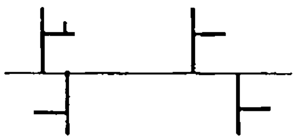
Polyethylene/Elastomer blends

Many thousands of tons of plastics are produced yearly all over the world. Among these materials, polyethylene plays a very important role as the most extensively used polymer. Since their discovery in 1933, there has been a continuous rise in the consumption to the present level of around 25 million tons per annum or 42 % of all plastics (30). This extended period of growth originates in continuous development and modification of these resins, resulting from a wide range of polymerization techniques. The history of polyethylene can be classified in to three periods.

1. The initial period characterized by predominance of the radical polymerization of ethylene C_2 at high temperature and pressure
2. Development of co-ordination copolymerization of C_2 monomer with other α-olefins
3. Development of polymer blending technology

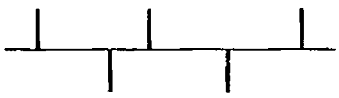
Discoveries in the laboratories of Ziegler and Natta in the early 1950's caused a revolution in polymer and organo-metallic chemistry (31-34). Natta discovered that Ziegler catalysts containing highly ordered transition metal salts in a low valence state (eg: Titanium trichloride, Vanadium trichloride) polymerize α-olefins to crystalline stereoisomeric polymers. This discovery led to the commercialization of HDPE, which had to be toughened by copolymerization with butene C_4. This was followed by the development of LLDPE, by Du Pont, Canada in the 1950's. The polymer was prepared by co-ordination polymerization in solution of ethylene with 10 to 20 mol % of C_4, C_6 or C_8 comonomers. The impact of this technology on the plastic industry has not only made LLDPE popular around the world, but also has led to an ingress of blending methods for obtaining new polymers with a range of properties for specific end use applications.

HDPE is pictured as a linear molecule with a relatively few or no branches and LDPE is pictured as a highly branched molecule with branches of varying lengths. LLDPE can be described as molecules having a linear configuration with many short side-chains, all of uniform length (35). Structure of HDPE, LDPE and LLDPE are,



LDPE-long chain branching

HDPE-linear structure



LLDPE-short chain branching, (Frequency higher than that for HDPE)

Properties of HDPE, LDPE and LLDPE are as follows

MFI (g/10 min)	0.4-0.6	1.6-2.2	0.8-1.2
Density (g/cm^3)	0.950	0.920	0.918
Melting Temperature (^{0}C)	135-140	110	125-130
Crystallinity (%)	75-80	60-65	65-70
Max. Stretch ratio at 190^{0}C		120-160	800-1000
Processability	Fair	Good	Fair
Impact strength (J/cm)			
transverse	15	25	40
Longitudinal	2	6	25

When the properties of LDPE and LLDPE are compared, LLDPE has several positive features than LDPE, which are

a. Heat resistance is considerably higher
b. Higher crystallinity and so greater degree of stiffness
c. Excellent stretchability which permits thinner films to be obtained
d. Higher and better balanced impact resistance properties

France *et al* have proved that LLDPE exhibited greater tensile strength, tear strength, higher environmental stress crack resistance and better flexibility than high or low pressure polyethylenes (36).

On the other hand, the high melt viscosity of LLDPE associated with its long regular molecular chains makes the processability difficult. Melt fracture may also occur due to the high shear stress in the die.

Thermoplastic elastomers can successfully be prepared based on polyolefins, like polyethylenes, and they are considered to be an important family of engineering materials (37-39). The combination of rubbery properties along with thermoplastic nature of polyethylene/elastomer blends makes it a very useful material in industrial applications. Since polyethylene is based on co-ordination catalysts, it does not lend itself to block or multi-segmented copolymer synthesis. However, since polyethylene has many important attributes favourable to useful elastomeric systems, there was considerable incentive to produce thermoplastic elastomers based on polyethylene by some means. The low density, chemical stability, weather resistance and ability to accept compounding ingredients without compromising physical properties are highly desirable. These considerations led to the development of polyethylene thermoplastic elastomer blends.

As a class of materials, thermoplastic elastomers based on polyethylene blends exhibit a number of highly useful properties. They can be processed using standard injection moulding, blow moulding, extrusion and thermoforming methods. Their chemical composition results in good resistance to many solvents and can be stabilized for good out door ageing. By dynamically vulcanizing the elastomer phase, physical properties are improved due to the stable chemical crosslinks (40-45).

Polyethylene / Modified NR Waste blends

Over recent years, blends of natural rubber with polyolefins have been studied (46-54). The thermoplastic elastomers prepared by blending natural rubber with crystalline polyolefins such as polyethylene have been given the name 'Thermoplastic Natural Rubber' (TPNR). Properties have been reported for thermoplastic elastomers based on natural rubber and polyethylene by several workers (55-59). Michaeli *et al* studied the mechanical properties and morphology of NR / LLDPE blends and found that the ozone resistance of the TPE was very high (60). The structure and properties of NR / HDPE based TPEs were studied by Xiang *et al* using extension rheometer, DSC, SEM etc. The effect of dynamic vulcanization was also discussed (61).

Recycling and reuse of the rubber products after their useful life is one of the solutions for minimizing the effect of threat arised by the waste rubber. This has been practiced by the rubber industry for many years, almost entirely by conversion of the waste products to reclaimed rubber (62-66). Reclaiming process imparts the necessary degree of plasticity to vulcanized rubber (67-70). Reclaiming process is not exactly devulcanization. The combined sulphur still present after reclaiming is an evidence for this. The process of reclaiming involves degradation of the vulcanizate structure, induced by chemical and thermal means followed by mechanical working. Several methods have been developed for the reclamation of latex product waste including those by Rubber

Research Institute of India (71) and Rubber Research Institute of Malaysia (72-73). Since latex product waste is a source of high quality rubber hydrocarbon, it is a potential candidate for generating reclaimed rubber of much superior quality.

Modified latex product waste can be utilized more effectively for the replacement of NR phase in Polyethylene/NR blends than other rubber reclaims. R.S.George and R.Joseph studied the properties of thermoplastic elastomers based on reclaimed latex waste products/Polypropylene blends and found that the mechanical properties were comparable with those of conventional TPEs based on NR / Polypropylene blends (74).

Utilization of reclaimed rubber as the elastomer phase in PE/elastomer blends was practiced by the industry in recent years. Several combinations have been tried in this field. A study on reclaimed rubber/PE blend thermoplastic elastomers by static vulcanization method was done by Chen Zhanxun *et al* (75). Statically vulcanized LLDPE/reclaimed rubber blends showed domain morphology, with LLDPE being the continuous phase. High melt viscosity and improved creep resistance were exhibited by these blends.

Mechanical properties and ageing of thermoplastic elastomers based on NR/reclaimed rubber/PP systems and their role as solid phase dispersants in PP/PE blends were studied by Malaik *et al* (76). Reclaimed Rubber (RR)/PE thermoplastic compositions were examined by Chen Li *et al* (77) and found that the compounds exhibit tensile strength in the range 4.0 - 7.5 MPa, Elongation at break 200 – 400 % and shore A hardness 60 – 85. Chen Li *et al* studied the dynamically vulcanized RR/LDPE blends (78) and observed that the properties of these TPEs were similar to those prepared from general purpose rubber and LDPE. TP composites containing different ground rubber tyre materials and LLDPE were prepared and impact energy studies were conducted by Rajalingam *et al* (79). Michal Duhaime *et al* (80) studied the reactive blending of polyethylene and scrap rubber. In this study, prior to blending, the rubber phase and LLDPE phase were modified with small amounts of chemical functionality, capable of interacting in the melt blending process. Impact and tensile properties of these reactive blends were compared with simple mechanical melt blends of similar compositions. All blends, whether reactive or nonreactive, showed a decrease in over all mechanical properties at all proportions of rubber phase content.

Polyethylene / Butyl Rubber blends

The earliest polyolefinic TPE to be introduced consists of blends of butyl rubber (IIR) with polyethylenes. In 1970, Hartman and coworkers (81) reported on a series of elastomeric thermoplastics called ET polymers which were prepared by grafting butyl rubber on to polyethylene. Four compositions were available from Allied Chemical Corporation, including the grafts based on high density and low density polyethylenes with butyl rubber at 3/1 and 1/1 butyl rubber/PE ratios. Deanin and coworkers (82) have reported on the properties of blends of butyl rubber with high and low density polyethylene. These blends were neither vulcanized nor grafted. Kumbhani (83) has shown butyl rubber to be beneficial in improving environmental stress-cracking resistance and impact resistance at normal and low temperatures in PE. Structure and property peculiarities of butyl rubber and HDPE copolymers have been evaluated by Aliguliyev *et al* (84). The peculiarities of copolymers at molecular and super molecular level were studied. Thermal oxidation of high pressure polyethylene blends with IIR in presence of thermal stabilizers was studied by Listov *et al* (85). The blends exhibited good impact strength and resistance to cracking. Imoto and coworkers (86) examined blends of polyethylene and butyl rubber and suggested that the blends would have great industrial value. Cooke, Edwards and Walker reviewed the properties of butyl/PE blends (87). Rodrigues and Winding (88) had shown that addition of substantial amounts of polyethylene to butyl rubber resulted in excellent resistance to degradation by water and high temperature and also stability of electrical properties. Igron *et al* (89) studied the vulcanizate properties of unreacted blends of high pressure polyethylene and butyl rubber. They found that 20 phr polyethylene increased the tensile strength and improved heat stability, electrical insulation properties and tan δ of butyl rubber. In later work, Igron and coworkers (90) found that blends of high and low pressure PE in butyl rubber gave some what higher strength than high pressure PE alone. The blend vulcanizates were more resistant to ozone and swelling in oils and seawater than were typical cable insulation and hose vulcanizates.

Compatibilizers in PE/Elastomer blends

The mechanical properties of TPEs can be enhanced several fold by using physical or chemical modifiers (59 & 91). The practical utility of a polymer blend is determined by the compatibility of the component polymers, which is considered as the fundamental property (11-13). But it has been observed that majority of TPE systems are incompatible (17-20), though most of their useful properties arise from their incompatibility. Physical and chemical modifiers can improve these properties by making the blends more compatible than before.

Low molecular weight Liquid Natural Rubber (LNR) has been used as a compatibilizer in LLDPE//NR systems (92-93). Ahamad *et al* studied the effect of LNR as compatibilizer in HDPE/NR blends (94). In all the cases, the tensile properties, hardness etc. were found to increase on the addition of the compatibilizer. A single glass transition temperature was observed via Dynamic Mechanical Analysis (DMA). The compatibilizers were found to enhance the inter phase reaction between the elastomeric and plastic phases which resulted in mutual wetting of the two phases due to which the blends became more compatible.

Thermal properties of TPE blends

Homogeneity of polymer blends can be found out with the help of thermal, analytical methods like Differential Scanning Calorimetry (DSC), Dynamic Mechanical Analysis (DMA) etc. The glass transition temperatures of the component polymers can be found out and their variations on blending can be studied. Several studies have been done in this regard (93,94,95-97). DMA studies were conducted for sulphonated butyl rubber ionomers and their blends by Xie *et al* (98). Thermal characterization of NR/PP blends was done using DMA, DSC etc. by Choudhury *et al* (99) and studied the variations in T_g and T_m of the rubber and plastic phases on blending.

From the foregoing, it is clear that reclaimed rubber, especially that from waste latex products, is a promising material for developing industrially important thermoplastic elastomers. Since the rejection rate from the latex products industry is very high (as high as 15%) and since the cost of development of thermoplastic elastomers based on polyethylene and modified latex product waste is lower compared those based on PE/NR blends, the primary objective of the present investigation is to develop low cost TPEs based on PE/modified latex waste.

Objectives of the work

PE/butyl rubber blends are gaining more industrial importance in recent years. The advantages of melt-blending of butyl rubber and PE have not been fully recognized and only a few studies have been done in this area. Hence, another objective of this study is the development of TPEs from PE/butyl rubber blends. The specific objectives of the study are the following:

1. To develop a method for the modification of latex product waste materials such as glove waste and thread waste and to evaluate the properties of the modified waste.
2. To prepare thermoplastic elastomers by blending the modified latex waste materials with high density, low density and linear low density polyethylenes.
3. To prepare thermoplastic elastomers based on butyl rubber and polyethylenes.
4. To investigate the effect of dynamic vulcanization of the elastomer phase on the mechanical properties of PE/modified waste and PE/butyl blends.
5. To investigate the use of LNR, chlorinated polyisobutylene and chlorobutyl as compatibilizers in PE/NR waste and PE/butyl blends.
6. To study the thermal properties of selected blends.

This thesis is divided into the following Chapters:

Chapter **I** Introduction ; Chapter **II** Experimental Techniques ; Chapter **III** Modification of Waste Latex Products.

Mercapto benzothiazole

Chapter **IV (a)** Studies on the TPEs from MBT modified latex product waste and HDPE, **IV (b)** Studies on the blends of LDPE and LLDPE with MBT modified latex product waste, **IV (c)** TPE based on HDPE and latex product waste modified with Thiocarbanilide, **IV (d)** Studies on TPE based on LDPE and latex product waste modified with Thiocarbanilide,

Chapter **V (a)** TPEs from HDPE and butyl rubber, **V (b)** blends of LDPE with butyl rubber, **V (c)** Studies on LLDPE / butyl rubber blends.

Chapter **VI (a)** Effect of compatibilizers on the mechanical properties of PE / elastomer blends, **VI (b)** Thermal analysis of 80/20 PE / butyl rubber blends,

Chapter **VII** Summary and conclusion.

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CHAPTER II ooooooooo

CHAPTER II

EXPERIMENTAL TECHNIQUES

The materials used and the experimental procedures adopted in the present investigations are given in this chapter.

MATERIALS USED

Elastomers

1. Natural Rubber (NR)

ISNR-5 was supplied by the Rubber Research Institute of India, Kottayam, Kerala. The Indian Standard specifications for this grade of rubber are given below

Parameters	**Limit**
Dirt content, % by mass, max	0.05
Volatile matter, % by mass, max	1.00
Nitrogen, % by mass, max	0.70
Ash, % by mass, max	0.60
Initial plasticity (P_o), min	30.00
Plasticity Retention Index (PRI), min	60.00

2. Butyl Rubber

Butyl Rubber (IIR) was Exxon 065 having a Mooney viscosity [ML (1+8) at 100°C] of 50.

3. Latex product waste

Waste examination gloves were supplied by Midland Rubber Products Ltd., Kakkanad, Kerala, India.

Waste latex thread was supplied by Rubfila International, Kanjikode, Palakkad, Kerala.

4. Liquid Natural Rubber (LNR)

Amine terminated liquid natural rubber (ATNR) was used in the study and it was prepared in the laboratory according to the procedure out lined below.

Natural rubber was masticated for 30 minutes at 50^{0}C. 100 g masticated rubber was dissolved in 450 ml Toluene and the solution was charged into a flat bottomed borosilicate flask. 50 ml of ethylene diamine together with 50 ml of tetrahydrofuran was added and thoroughly mixed with rubber solution. This solution was kept in sunlight for irradiation. After about 60 hours of irradiation, the product was precipitated using methanol and dried in vacuum. The sample for analysis was purified by repeated precipitation using methanol from toluene solution and dried in a vacuum oven. ATNR used in the present study had an average molecular weight (M_w) 2100 and functionality 1.79. Average molecular weight was measured using get gel permeation chromatograph (water associates, model 6000) and functionality by end group analysis (10).

5. Chlorinated Polyisobutylene (Chl.PIB)

Polyisobutylene (PIB) was supplied by Cochin Refineries, Balmer Lawrie Ltd., Ambalamugal, Kerala. Chlorination of PIB was done in the laboratory according to the procedure given below 11).

PIB was dissolved in Carbon tetrachloride (CCl_4 - 50% solution) and pure, dry chlorine gas was passed through it for 5 hours. The resulting solution was poured into water at 80^{0}C and excess chlorine and CCl_4 were removed. Then it was filtered and dried. This sample was dissolved in toluene and reprecipitated using methanol. The sample was dried in a vacuum oven. The chlorine content of this sample was found to be 7.6% and molecular weight was 1000.

6. Chlorobutyl Rubber (CIIR)

Polysar chlorobutyl grade 1240 was used having Mooney viscosity [ML (1+8) at 125^{0}C] of 38, chlorine content 1.3 %, basic polymeric unsaturation 2.49 mol % and volatility 0.2.

Polyethylenes

1. High Density Polyethelene (HDPE) of grade Indothene HD was supplied by Indian Petrochemical Corporation Ltd., Vadodara and had the following specifications

Melt Flow Index (MFI, g/10 min)	5.2
Density at 23^{0}C, g/ cm^3	0.950

Melting point	127-135^{0}C

2. Low Density Polyethelene (LDPE) of grade Indothene 24 FS 040 was supplied by Indian Petrochemical Corp. Ltd., Vadodara and had the following specifications

Melt Flow Index (MFI, g/10 min)	4.0
Density at 23^{0}C, g/cm^{3}	0.919
Melting point	105-110^{0} C

3. Linear Low Density Polyethylene (LLDPE) used was Indothene LL 20 FS 010

Melt Flow Index (MFI, g/ 10 min)	1.0
Density at 23^{0}C (g/ cm^{3})	0.920

Compounding Ingredients

1. Zinc Oxide (ZnO)

ZnO was supplied by M/s Meta Zinc Ltd., Mumbai. The specifications for ZnO were as follows.

Specific gravity	5.5
Zinc Oxide content	98.0%
Acidity	0.4%
Heat loss max 2 hrs at 100^{0}C	0.5%

2. Stearic Acid

Stearic acid used in the study, supplied by Godrej Soaps Pvt. Ltd., Mumbai had the following specification

Specific gravity	0.85 ± 0.01
Melting point	50-69^{0}
Acid number	185-210
Iodine number	9.5 max
Ash content	0.1 % max

3. Zinc Diethyl dithio Carbanate (ZDC)

ZDC was supplied by Polyolefins Industries Ltd., Mumbai. It had specifications as follows

Melting point	178°C
Specific gravity	1.50

4. Sulphur

Sulphur was supplied by Standard Chemical Company Pvt. Ltd., Madras, India, having the following specifications

Specific gravity	2.05
Acidity	0.01
Ash	0.01
Solubility in CS_2	98.00 %

5. Dibenzthiazyl Disulphide (MBTS)

MBTS was supplied by Bayer India Ltd., Mumbai and had the following specifications

Specific gravity	1.34
Melting point	165^{0}C

Reclaiming Chemicals

1. Mercapto benzothiazole

Mercapto benzothiazole having the following specifications was supplied by Bayer India Ltd., Mumbai.

Specific gravity	1.45- 1.52
Melting point	160°C- 180°C

2. Diaryl Sulphide

Diaryl Sulphide is supplied by Rubber Reclaim Co. of India Pvt. Ltd., New Delhi.

3. Wood Rosin

Wood rosin used was commercial grade, having the following specifications

Solubility in water	Insoluble
Acid number	163.00
Softening point	73^{0}C
Saphonification Number	168.00
Refractive Index at 20^{0}C	1.545

Specific gravity	1.067

4. Benzoyl Peroxide

Benzoyl Peroxide was supplied by CDH Pvt. Ltd., Mumbai and had the following specifications

Solubility in water	slightly soluble
Melting point	102 – 105^{0}C

5. N- Cyclohexyl benzothiazole-2- sulfenamide (CBS)

CBS was supplied by Polyolefins India Ltd., and had the following specifications

Specific gravity	1.27
Melting point	101^{0}C

6. Thiocarbanilide(13)

Thiocarbanilide was prepared in the laboratory according to the method given below. 40 g of aniline, 50 g of carbon disulphide and 50 g of ethanol were heated in a 1 litre round bottomed flask fume cupboard for 8 hours. Heating was continued until the contents were solidified. Excess carbon disulphide was distilled off. Then it was shaken well with excess of 1:10 dilute HCl, filtered and drained well. Pure needles of thiocarbanilide were recrystallized from rectified spirit. Melting point was 154^{0}C.

7. Naphthenic Oil

Naphthenic Oil was supplied by M/S Hindustan Petroleum Ltd., India and the specifications are as follows

Colour	Light coloured oil
Viscosity gravity constant	0.85 - 0.9

8. Hydroquinone

Hydroquinone used was of commercial grade.

Solvent

Toluene of commercial grade was used as the solvent.

EXPERIMENTAL METHODS

1. Mixing and Homogenization

(a) Using the mixing mill

Mixing and homogenization of elastomers and compounding ingredients were done on a laboratory size (15 x 33) two-roll mill at a friction ratio of 1:1.25. The elastomer was given one pass through the nip (0.002 x 100)$^{\prime\prime}$. Then it was given two passes through the nip (0.002 x 10)$^{\prime\prime}$. The temperature of the rolls was maintained at 70 ± 5^0 C during the mastication. After the nerve had disappeared, the compounding ingredients were added as per ASTM D 3184 (1980) and ASTM D 3182 (1982) in the order of activators, accelerators and curing agents. After completion of the mixing, the compound was homogenized by passing six times endwise through a tight nip and finally sheeted out at a nip gap of 3 mm.

(b) Using a Brabender Plasticorder (14)

A Brabender Plasticorder (torque rheometer) model PL 3S was used for various investigations. It is a device to measure the torque during processing under pre-selected conditions of shear and temperature. The mixing chamber of 40 cc capacity is the central part of the machine which is heated by oil circulating thermostat heating tanks. High temperature silicone oil is used as heating liquid and the temperature on the mixer can be varied up to 300^{0}C. The measuring head is equipped with a stock temperature thermocouple, coupled with a temperature recorder for temperature measurement. The mixing or shearing of the material in the mixing chamber is done by two rotors. Various types of rotors can be used, depending upon the nature of the polymers. A speed controlled DC drive thyristor allows the rotor speed adjustment between 0 to 150 rpm. The measurement is based on the fact that the resistance which is put up by the material against the rotors in the chamber is made visible as a means of viscosity in the dynamometer. The torque is plotted continuously against time. Torque up to 20,000 meter grams can be measured by the torque rheometer.

In the present study, Brabender Plasticorder was used for blending polyethylene with natural rubber/latex reclaim and butyl rubber to develop thermoplastic elastomers. It was also used to assess the rheological behavior of thermoplastic elastomer blends based on polyethylene and latex reclaim polyethylene/NR and polyethylene/butyl rubber.

Thermoplastic elastomer blends were prepared in the Brabender Plasticorder equipped with roller mixing heads according to ASTM D 3184 (1980) and ASTM D 3182 (1982). Blending parameters were selected based on torque-temperature data of the individual components and the particular blends. The basic principle followed in every blending was to ensure the melting of the polymers and to keep polymer degradation to the minimum.

2. Determination of cure characteristics

The cure characteristics of the modified waste materials were determined on a Goettfert elastograph model 67.85. It is a microprocessor-controlled rotorless cure meter with(15) quick temperature control mechanism and well defined homogeneous temperature distribution in the dielectric constant or test chamber. In this instrument, a specimen of definite size is kept in the lower half of the cavity which is oscillated through a small deformation angle ($\pm 0.2^0$). The frequency is 50 oscillations per minute. The torque is measured on the lower oscillating dielectric constant half. From the torque-time curve, the time taken for attaining 90 % of the maximum torque, T_{90} (Optimum cure time) and the time taken for attaining 10 % of the maximum torque, T_{10} (Scorch time) are obtained.

3. Moulding of test specimens

The test specimens were prepared in standard moulds by compression moulding on an electrically heated hydraulic press having 30×30 cm platens at a pressure of $120 kg/cm^2$ on the mould. The rubber compounds were vulcanized up to their respective optimum cure times at 150^0C.

The test specimens for determining the physical properties of the thermoplastic elastomers were prepared in specially fabricated moulds, by compression moulding, in the electrically heated hydraulic press. The moulding temperature and time for thermoplastic elastomers were determined according to ASTM D 3182 (1982).

Physical Test Methods

1. Tensile stress-strain behaviour

Tensile stress-strain behaviour is determined according to ASTM D 412 for rubber samples and ASTM D638 for thermoplastic elastomer samples on a Zwick Universal Testing Machine model 1445 at cross-head speeds 500 mm/min and 50 mm/min respectively. All tests were carried out at room temperature 28 ± 2^0C. Samples were punched out from compression moulded sheets using a dumbell die (C-type). The thickness of the narrow portion was measured by bench thickness gauge. The sample was held tightly by the two grips of which the upper grip was fixed. The rate of separation of the power- actuated lower grip was fixed at 500 mm/min for rubber samples and 50 mm/min for TPE samples.

2. Tear resistance

This test was carried out as per ASTM D 624 on a Zwick UTM at a cross-head speed of 50mm/min. The test temperature was 28 ± 2^0C.

3. Hardness

Hardness is measured in accordance with ASTM D 2240 (1981). The tests were performed on the hardness tester using mechanically unstressed samples of 300 mm diameter and minimum 6 mm thickness. A load of 12.5 N was applied and the readings were taken after 10 seconds of intendation after firm contact has been established with the specimen.

4. Permanent set

Dumbell shaped test specimens were kept under tension for 24 hrs and the length of the specimen before and after were measured. It was calculated as follows:

Permanent set (%) = (Change in length × 100)/original length

5. Melt Flow Index (MFI)

MFI of the TPE samples were determined according to ASTM D 1238. An extrusion plastometer was used for measuring the MFI of the blends. The rate of extrusion through a die of specified length and diameter was measured under prescribed *conditions of temperature, load and piston position in the barrel as a function of time. Melt index was calculated and reported as g/10min. This index is inversely related to molecular weight.

*190^{0}C, 2.16 kg and 298.2 kPa

6. Impact resistance

Impact resistance was measured on an Izod Impact Tester using ASTM D 256 method. The relative susceptibility of a standard test specimen to the pendulum-type impact load is measured. Notched samples were used to provide a stress concentration area that promotes a brittle rather than ductile failure.

7. Ageing studies

Ageing studies were done according to ASTM D 573-88 procedure. Dumbell shaped samples were punched out from the moulded sheet and kept in air oven at predetermined temperatures for specified periods. The percentage retention of the physical properties were evaluated for assessing the effect of ageing.

8. Initial Plasticity

The initial plasticity of the samples was measured according to ASTM D 3194-73 method. A test portion of about 30 g of rubber sample was taken and passed three times between mill rolls at room temperature with the opening adjusted so that the final sheet thickness is approximately 1.7 mm. Immediately the sheet was doubled and the two halves were pressed tightly together to avoid the formation of air bubbles. The test pieces were cut from the doubled sheet with a punch and their thickness were measured until three test pellets were obtained with a thickness of 3.4 mm having a volume of 0.4 cm^3. Then the sample was placed between a bleached, unglazed, acid free tissue paper and then inserted between the heated platens of the Wallace Rapid Plastimeter. The medium values of the three results of the test pieces were taken as initial plasticity (P_o).

9. Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analysis can be used to study the thermal behaviour of polymer blends. Determination of the T_g's of the component polymers using DMA helps to find out the compatibility of the blend. Storage Modulus and loss tangent obtained from the analysis are helpful in studying the thermal behaviour of the blends. In the present investigation, Rheovibron Viscoelastometer DDV- III- C is used for the dynamic mechanical analysis.

10. Mooney Viscosity measurements

The Mooney Viscosity of the raw rubbers were measured on a Mooney Viscometer which is designed for measuring the shearing viscosity of rubber and rubber like materials by a disc, rotating (2 rev/min) in a cylindrical cavity set at 100^0C and filled with rubber under test. In running a viscosity test, the sample was allowed to warm up for 1 minute, after the platens were closed and the rotation of the die was then started. Reading after 4 minutes was reported as the Mooney Viscosity [ML (1+4) at 100^0C]. The procedure followed was as given in ASTM D 1646 (1981).

Rheological Evaluation

1. Using Brabender Plasticorder

Brabender Plasticorder (torque rheometer) has been widely used for measuring processability of polymers, rheological properties of polymer melts, blending of polymers etc. (1-2). The torque rheometer is essentially a device for measuring the torque generated due to the resistance of a material mastication or flow under preselected conditions of shear and temperature.

The Brabender Plasticorder model PL 3S was used in this study for evaluating the rheological behavior of the polymer blends. The nature of shear in the plasticorder is similar to that encountered in practical processing operations such as extrusion or milling. Blyler and Daane (3) observed that the power law relationship between rotor torque and rotor speed is the reminiscent of the power law relationship, often found between shear stress and shear rate and with a few assumptions derived the equation

$$\mathbf{M = C\ (n)\ K\ S^n}$$

Where, **M** is the torque, **n** is the power law index, **C (n)** is a function weakly dependent on **n**, **K** is constant and **S** the rotor speed.

The slope of the plot of log M Vs. log S gives the power law index. The torque / rpm value of the Brabender represents viscosity and rpm represents the shear rate.

2. Using a Capillary Rheometer

Capillary Rheometer is widely used for determining the rheological properties of polymer melts (4) since they cover a shear rate range up to 10,000 S^{-1} with good rheological behavior of polymers and polymer blends. The capillary rheometer used in this study was Geottfert Viscotester model 1500.

The barrel of the rheometer was filled with 30 g of the sample in the form of small pieces or granules. Then it was forced down to the capillary by a plunger attached to the moving cross-head. Then the sample was extruded through the capillary at different speeds viz., 0.05, 0.1, 0.5, 1.0, 2.0 mm/min and so on. The shear stress, shear rate and viscosity values corresponding to specific plunger speeds were recorded using a chart recorder.

In the present investigation, the extrudates emerging from the capillary was collected at different shear rates taking care to avoid any deformation. Optical photographs of these extrudates were taken to study the non-laminar flow and surface imperfections.

Morphology Studies

1. Using Optical microscope

The morphology of the Thermoplastic elastomeric extrudates was investigated using an optical microscope model Carl Zeiss Stemi 2000 C with magnification 2.5.

2. Using Scanning Electron Microscope

Scanning electron microscopic studies were found to be a very powerful tool in polymer research for studying morphology (5,6). Scanning Electron Microscope model S 2400 was used to investigate the morphology of fractured surfaces. In this technique, an electron beam is scanned across the specimen resulting in back scattering of electrons of high energy, secondary electrons of low energy and X-rays. These signals are monitered by detectors (photo multiplier tube) and magnified. An image of the investigated microscopic region of the specimen is thus observed in cathode ray tube (CRT) and photographed using 120-roll, black and white film.

The SEM observations reported in the present study were made on the fracture surface of tensile specimens. A thin specimen of the samples was prepared and mounted on a metallic stub with the help of a silver tape and conducting paint in the upright position. The stub with the sample was placed in an Ion Sputter for gold coating of the sample to make it conducting. Gold-coated sample was observed in the SEM.

Reprocessability Studies

The moulded samples were remelted in the Brabender Plasticorder and remoulded in the hydraulic press, adopting the same procedure used for the preparation of the original samples. The mechanical properties of these reprocessed samples were measured according to the ASTM methods.

Chemical Test Methods

1. Crosslink density

The concentration of chemical crosslinks was estimated from the equilibrium swelling data. The volume fraction of rubber (V_r) in the swollen network was then calculated by the method reported by Ellis and Welding (7) from the following equation:

$$V_r = \frac{[(D - FT)\,\rho_r^{-1}]}{(D - FT)\,\rho_r^{-1} + A_0\,\rho_s^{-1}}$$

Where,

T = weight of the test specimen

D = deswollen weight of the test specimen

F = weight fraction of insoluble components

A_0 = weight of the absorbed solvent corrected for the swelling increment

ρ_r = density of the rubber

ρ_s = density of the solvent

The crosslink density (½MC) was then determined from V_r using the Flory-Rehner equation (8,9)

$$½\,MC = \frac{-[\ln(1-V_r) + V_r + \chi V_r^2]}{2\,\rho_r\,V_s\,(V_r)^{1/3}}$$

Where,

V_s = molar volume of solvent

χ = Parameter characteristics of interaction between rubber and solvent

2. Free sulphur estimation

Free sulphur in the crosslinked product was determined according to ASTM D 297-72 A method. The principle of this method is based on the reaction of free sulphur with sodium sulphite to give sodium thiosulphate which is finally titrated against standard solution.

$$S + Na_2SO_3 \quad Na_2S_2O_3$$

$$I_2 + 2Na_2S_2O_3 \quad Na_2S_4O_6 + 2NaI$$

2 g of the sample was digested gently with 100 ml of aqueous sodium sulphite solution (5g/litre) for 15 hrs in presence of 5 ml of sodium stearate suspension in water (1g/litre) to assist wetting and approximately 1 g of paraffin wax to avoid aerial oxidation. 100 ml of strontium chloride (5g/litre) solution was added to precipitate fatty acids and 10 ml of cadmium acetate solution (30g/litre) to remove accelerators. The precipitate was separated by filtration. It was then washed twice with 75 ml portions of cadmium acetate solution (1.2g/litre). To the filtrate, 10 ml 40% formaldehyde solution was added with vigorous stirring and subsequently it was acidified with glacial acetic acid (10 ml). The solution was cooled below 10^0C by adding enough crushed ice and titrated with 0.02 N iodine solution using starch as indicator.

A blank run was taken without sample and the free sulphur content was calculated using the following equation:

$$\textbf{Free sulphur (\%)} = \frac{(x-y)\ N \times 0.032 \times 100}{W}$$

Where **x** is the volume of iodine solution required for titration of the sample in cc, **y** the volume of iodine solution required for the titration of the blank in cc, **N** the normality of iodine solution and **W** the weight of sample taken.

3. Acetone extract determination

The procedure adopted was according to BS 1673 part 2, 1967. About 1 gm of the sample of 1.6 mm thickness was weighed to the nearest milligram and wrapped in a filter paper in such a manner that the pieces were separated from each other. The test pieces were kept in the Soxhlet type apparatus and sufficient acetone was poured to fill the extraction cup. The apparatus was assembled and the extraction vessel was heated continuously on a thermostatically controlled water bath for 12 to 16 hrs, the rate of evaporation being controlled to 5 to 8 extractions per hour. After the extraction period was over the combined acetone from the extraction flask and cup was recovered by distillation. After most of the acetone was recovered, the contents of the flask was dried in an oven at 70^0C for about 1 hour to remove the last traces of acetone. The flask was cooled to room temperature in a desiccator and weighed. Heating, cooling and weighing were repeated until concordant values were obtained. Acetone extract was calculated from the equation

$$\textbf{Acetone extract (\%)} = \frac{(B-C) \times 100}{A}$$

Where, **A** is the weight of the sample taken in g., **B** the weight of extraction flask and extracted residue in g., **C** the weight of empty flask in g.

4. Volatile matter determination

Volatile matter of the sample was determined according to IS specifications for analysis of dry rubber. About 30 g of the sample was cut and wrapped airtight in a polyethylene bag. Then 10 g was weighed from this and passed through the mill rolls set 0.5 mm apart and at a friction ratio 1:1.4. Then the test pieces were placed on an aluminium tray and kept inside the oven at 100^{0}C for 4 hrs. At the end of heating each test pieces were inserted in a polyethylene bag and clipped quickly. The test pieces were allowed to cool for half an hour and then removed from the bag and weighed. The volatile matter was calculated from the equation

$$\textbf{Volatile matter (\%)} = \frac{(A-B) \times 100}{A}$$

Where **A** is the weight of test piece in g., **B** is the weight of test piece after drying in g.

5. Ash content determination

Ash content was determined according to ASTM D 1278 68 a (1969). About 5 g of the sample was weighed, wrapped in an ashless filter paper and placed in a silica crucible, which had been previously ignited for 15 minutes and weighed. Then the crucible was introduced into a muffle furnace at 550^{0}C and heated for 4-5 hours. When ignition was completed, the crucible was allowed to cool in a desiccator and then weighed. Ash content was calculated as

$$\textbf{Ash content (\%)} = \frac{(A-B) \times 100}{C}$$

Where,

A = weight of crucible + ash in g

B = weight of empty crucible in g

C = weight of sample taken in g

6. Rubber hydrocarbon content determination

The rubber hydrocarbon content was calculated using BS 903 : Part B 11(1960). It was determined by difference after the other constituents have been determined.

Rubber hydrocarbon content = 100 – (Acetone extract + Volatile matter + Ash content)

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CHAPTER III oooooooooo

CHAPTER III

MODIFICATION OF WASTE LATEX PRODUCTS

Introduction

Latex products generally contain superior quality rubber compared to dry rubber products since they are not masticated or subjected to high temperature during vulcanization. For example, waste examination gloves contain lightly crosslinked rubber hydrocarbon of very high molecular weight without any filler. Hence the factory rejects of the glove industry represent a source of high quality rubber hydrocarbon for reclamation and reuse.

Rubber Research Institute of India (1) and Rubber Research Institute of Malaysia (2-3) have developed techniques for reclaiming waste latex products. The process reported by Rubber Research Institute of India involves reclaiming waste condoms by thermo-mechanical method using Renacit-7 as the reclaiming agent. The latex reclaim produced by this method can replace raw rubber upto about 25% of its weight in filled NR compounds without much deterioration in mechanical properties. The details of the process adopted by Rubber Research Institute of Malaysia are not available. Another technique of swelling the waste latex products in organic solvents followed by mechanical break down has been developed in our laboratory (4). Latex reclaim produced by this method can replace the natural rubber upto about 50% of its weight in filled compound without reduction in mechanical properties.

Acetta and Vergnaud (5-6) have studied vulcanization of reclaimed rubber powder with vulcanizing agents, with out adding fresh rubber. They found that rubber powder could be converted to a plastic or elastomeric material according to the percentage of vulcanizing agents. Phadke and co-workers (7) have studied the vulcanization of reclaimed rubber and found that the physical properties of reclaimed rubber are inferior to those of the NR vulcanizates and the reclaim compound exhibit comparatively poor processing characteristics.

From the forgoing discussion it is clear that the reclaiming of waste latex product and its utilization has not achieved its full potential. In contrast to other rubber reclaims, latex reclaim contains rubber hydrocarbon of very high quality.

This chapter deals with the development of two new processes for reclaiming latex product waste, which do not adversely affect the quality of the rubber. The mechanical properties of the modified waste materials have been evaluated. Ageing studies were also done.

Experimental

In this study four different chemicals viz., 1) Mercapto benzo thiazole (MBT) 2) Diaryl sulphide 3) Benzoyl peroxide and 4) Thiocarbanilide are proposed as reclaiming agents.

First of all the latex product wastes such as thread and gloves were wetted with toluene and kept tightly closed for 16 hrs. This waste was mixed with other ingredients as per the formulations given below.

In the first process the waste was passed through a laboratory two-roll mill with a nip gap of 1 mm at room temperature for 3 minutes. Further plastication was achieved using the reclaiming agent and process oil as in the following formulation.

Thread waste/glove (masticated)	100.0 phr
NR (masticated)	10.0
ZnO	2.0
Stearic acid	2.0 "
MBT	0.5 "
Naphthenic oil	3.0 "
Hydroquinone	0.2 "

The above ingredients were added in the order given above. Mixing was done for 10 minutes and the material was obtained in the form of a sheet.

In the second process, MBT was replaced by Diaryl sulphide and wood rosin was used as the process aid. The formulation was as follows and mixing was done for 10 minutes.

Latex waste	100.0 phr
NR (masticated)	10.0 "

ZnO	2.0 "
Stearic acid	2.0 "
Diaryl sulphide	1.0 "
Wood rosin	3.0 "
Hydroquinone	0.2 "

In the third process, the reclaiming agent tried was benzoyl peroxide and compounding was done as per the following formulation.

Latex waste	100.0 phr
NR (masticated)	10.0 "
ZnO	2.0 "
Stearic acid	2.0 "
Benzoyl peroxide	0.5 "
Naphthenic oil	3.0 "
Hydroquinone	0.2 "

In the fourth process two changes have been made. The wetted latex waste was heated at 70⁰C in a hot air oven for 1 hr and then masticated for 3 minutes. To this 20 phr masticated NR was added instead of 10 phr NR as in the other cases. The formulation is given below.

Latex waste (heated at 70⁰C for 1 hr)	100.0 phr
NR (masticated)	20.0 "
ZnO	2.0 "
Stearic Acid	2.0 "
MBT	0.5 "
Naphthenic Oil	3.0 "
Hydroquinone	0.2 "

In the fifth process, 10 phr NR reclaim (commercial) was used along with 10 phr NR and mixed as per the formulation below.

Latex Waste	100.0 phr
NR	10.0 "
NR Reclaim	10.0 "

ZnO	2.0 "
Stearic Acid	2.0 "
MBT	0.5 "
Naphthenic Oil	3.0 "
Hydroquinone	0.2 "

In the sixth process, the only change made was the heating of the latex waste at 70^{0}C for 1 hr. The formulation was same as in the fifth process.

In the seventh and the last process the reclaiming agent used was thiocarbanilide, which has been synthesized in the laboratory. Powdered latex waste was heated at 70^{0}C for 1 hr in a hot air oven .The formulation is as follows.

Latex Waste (Powdered and heated at 70^{0}C, 1 hr)	100.0 phr
NR	20.0 "
ZnO	5.0 "
Stearic Acid	2.0 "
Thiocarbanilide	3.0 "
CBS	0.6 "
Naphthenic Oil	3.0 "
Hydroquinone	0.2 "

The Mooney Viscosity, initial plasticity and plasticity retention index of the above compounds were measured. The modified thread waste, glove waste and powdered glove waste are hereafter mentioned as TW, GW and GW (P) respectively.

Results and Discussion

Table III 1 shows the Mooney Viscosity and initial plasticity values of the modified waste materials obtained from different processes. It is found that the Mooney Viscosity and initial plasticity of compounds based on formulations I, II, III, V and VI are high. This may be due to inadequate chain breakdown and plasticity. The compounds based on formulations IV and VII have Mooney Viscosity, initial plasticity and plastic retention index in the processable range, which can be compared with those of natural rubber. Other properties of these compounds are shown in Table

III 2. Since these modified materials exhibited better properties, compared to the other mixes prepared with other reclaiming agents, they were selected for further studies.

Table III 1 Mooney Viscosity and Initial Plasticity of modified wastes

Formulation No.	Mooney Viscosity			Initial Plasticity		
	TW	GW	GW (P)	TW	GW	GW (P)
I	91.1	94.0		60	63	
II	98.0	97.2		65	60	
III	94.4	91.4		63	58	
IV	57.4	55.1		41	40	
V	85.0	90.0		52	59	
VI	86.0	82.3		54	49	
VII			29.0			32.0

Mechanical properties of the Modified Waste

The mechanical properties of the vulcanized TW, GW and GW (P) were tested. The compounds were vulcanized upto their respective cure times in an electrically heated hydraulic press at 150^{0}C. Dumbell shaped test specimens were punched out of these compression moulded sheets. The tensile properties were measured on a Zwick Universal Testing Machine model 1445 at a cross-head speed of 500 mm/min according to ASTM D 412-80.

Tear resistance of the samples was measured on the Zwick UTM according to ASTM D 624. The aging resistance of the samples were also studied at 100^{0}C for 24 and 48 hours in a laboratory air oven. Hardness was also tested.

Table III 3 shows the mechanical properties of the modified waste materials. It can be seen that all the properties show the highest values for the waste modified with

Table III 2 Properties of TW, GW and GW (P) based on formulation IV and VII

Property	Formulation IV		Formulation VII
	TW	GW	GW (P)
Volatile matter, % by mass	0.58	0.60	0.63
Acetone extract, % by mass	4.66	5.10	5.81
Ash content, % by mass	5.76		3.22
Rubber hydrocarbon content, % by mass	88.45	91.14	92.84
Free sulphur content, % by mass	0.55	0.70	0.90
Mooney viscosity ML (1+4) 100^{0}C	57.40	52.00	29.00
Initial Plasticity, P_0	41.0	38.00	32.00
Plasticity retention index,PRI	59.0	54.00	46.00
Crosslink density (g mol/cc)	$1.1x10^{-3}$	$4.1x10^{-5}$	$1.9x10^{-3}$
Cure characteristics			
Scorch time, T_{10} (Min)	0.058	0.051	0.065
Optimum cure time, T_{90} (Min)	1.250	1.230	1.320

Thiocarbanilide [GW (P)]. This may be attributed to its higher crosslink density compared to the other two. All the properties are compared with those of NR.

Table III 4 shows the mechanical properties of the aged samples at 100^{0}C for 24 hrs and 48 hrs. Some variations are observed after 48 hrs of ageing. All the properties of the modified waste were compared with those of NR compounds.
The values decrease with increase in aging time only slightly. This may be due to the presence of residual antioxidants in TW GW and GW (P).

Conclusion

The study shows that the two methods of modifying latex products waste outlined in this chapter are promising ones for generating good quality rubber which can be used to replace raw natural rubber without much deterioration in mechanical properties

Table III 3 Mechanical Properties of the modified waste

Material	Tensile strength (MPa)	Tear strength (N/mm)	Elongation at break (%)	Hardness (Shore A)
TW	12.8	32.1	271	52
GW	10.2	31.4	322	47
GW (P)	16.9	45.1	540	62
NR	20.1	37.7	580	40

Table III 4 Mechanical Properties of the aged samples of the modified waste

Ageing time (hrs)	Material	Tensile strength (MPa)	Tear strength (N/mm)	Elongation at break (%)	Hardness (Shore A)
24	TW	8.9	30	210	43
	GW	7.5	28.4	280	39
	GW (P)	10.2	41.2	350	57
	NR	13.5	29.4	420	35
48	TW	6.7	25.1	190	40
	GW	5.3	21.7	215	35
	GW (P)	8.5	38.3	280	51
	NR	10.1	22.2	340	32

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CHAPTER IV

CHAPTER IV (a)

STUDIES ON THE THERMOPLASTIC ELASTOMERS FROM MBT MODIFIED LATEX PRODUCT WASTE AND HIGH DENSITY POLYETHYLENE

Introduction

Thermoplastic elastomers are materials having the characteristics of thermoplastics at processing temperature and those of elastomers at service temperature (1-3). They contain a soft rubbery phase and a hard thermoplastic segment. Thermoplasticity results from the melting characteristics of the hard thermoplastic phase at the high temperatures of processing, where as, the elastic properties arise from the soft rubbery phase at the low temperatures of use (4-5). At low temperatures, the hard thermoplastic phase will act as crosslinks or as reinforcing filler particles between the soft rubbery phase (6). This unique combination of properties of vulcanized rubber and the easy processability of thermoplastics, bridge the gap between conventional elastomers and thermoplastics.

Over recent years, blends of natural rubber with polyolefins have widely been studied (7-8) and are found to behave very well as thermoplastic rubbers, within the category of olefinics.

Blending of an elastomer with a thermoplastic in an internal mixer at a temperature, above the melting point of the thermoplastic has certain definite advantages (9). The desired properties can be achieved by proper selection of elastomer and thermoplastic components and their ratios in the blend. In polyolefin /elastomer blends, the effect of the characteristics of the components and blend ratios on the technical properties, processing characteristics and failure mechanism of the resulting thermoplastic elastomers have already been reported (10-14).

Scrap latex products contain rubber hydrocarbon of very high quality, which is only lightly crosslinked. These waste materials can effectively be utilized by reclaiming processes and may be blended with other polymers. Various processes have been developed for reclaiming latex products.

This part deals with the preparation of Thermoplastic Elastomers (TPEs) by blending latex product waste modified with Mercapto benzothiazole (MBT) and High Density Polyethylene (HDPE). The mechanical properties, rheology and morphology of these TPEs are compared with those of the HDPE/NR based TPEs.

Experimental

The latex thread waste and glove waste were modified into processable materials by a novel economic process described earlier using the formulation given in Table IV (a) 1. The additives used were Zinc oxide, Stearic acid, MBT, Naphthenic oil and Hydroquinone. The modified thread waste and glove waste are hereafter referred to as TW and GW respectively.

Table IV (a) 1 Formulation

Ingredients	Phr
Thread waste / Glove waste	100.0
NR	20.0
ZnO	2.0
Stearic Acid	2.0
MBT	0.5
Naphthenic Oil	3.0
Hydroquinone	0.2

Blends of HDPE with TW and GW or NR were prepared as follows. Mixing was done on a Brabender Plasticorder model PL 3S at 150^{0}C and 50 rpm. HDPE was melted in the mixer for 4 minutes and then TW, GW or NR containing the additives was added and the mixing was continued for 6 more minutes. The mix was then taken out and sheeted on a laboratory mixing mill at 20 mm nip gap setting. The sheeted material was cut into small pieces and again mixed in the plasticorder at 150^{0}C for 4 minutes so as to get a uniform dispersion of the ingredients. After mixing, the blend was compression moulded in an electrically heated hydraulic press at 160^{0}C for 6 minutes. Specially fabricated mould with nuts and bolts was used for this purpose so as to hold the material inside under pressure. The mould with sample was cooled by circulating cold water. Polyester sheets were used in between the mould surfaces to reduce shrink marks on the sheets.

Measurement of mechanical properties

A Zwick Universal Testing Machine model 1445 was used for the mechanical property measurements. All tests were performed at room temperature at a cross-head speed of 50 mm/minute as per ASTM D 638.

Rheological measurements

The rheological behaviour of the blends was investigated using the Brabender Plasticorder as well as a Capillary Viscotester Goettfert model 1500 at 150^{0}C. In the Brabender plasticorder, processability evaluation was done at different rotor speeds at 150^{0}C. The dependence of the viscosity (torque/ rpm) of the blends with shear rate (rpm) was measured.

In the Capillary Viscotester, the variation of viscosity with shear rate of each blend was directly measured.

Morphological study

The morphological studies of the extrudates from Capillary Viscotester were done with the help of optical microscope.

Scanning Electron Microscopic study

The tensile fracture surfaces of LDPE/rubber blends were studied using a Scanning Electron Microscope.

Reprocessing

The blends were remelted and remoulded and their mechanical properties were evaluated and compared with those of the conventional Polyethylene/Natural rubber blends.

Results and Discussion

Fig IV (a) 1 Variation of tensile strength with rubber content of HDPE/rubber blends

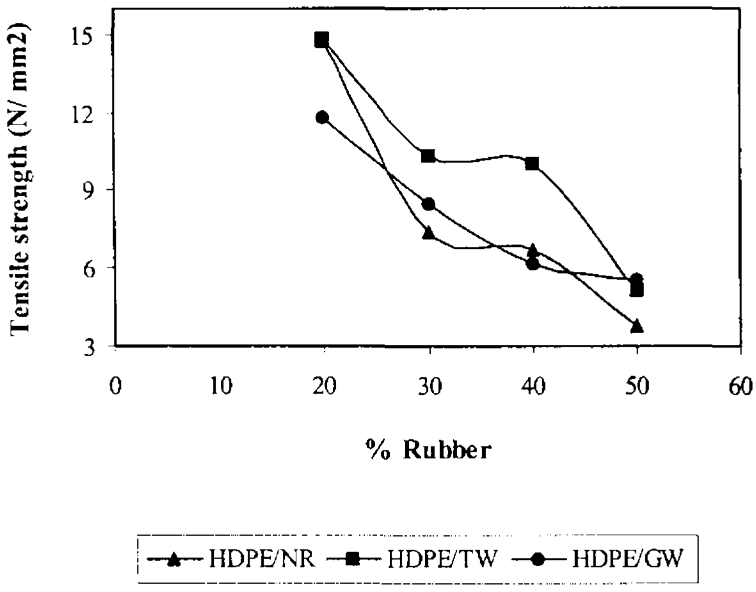


Fig IV (a) 1 shows the variation in tensile strength of the blends with the percentage of rubber. For all the three blends, the tensile strength decreases with increase in the rubber content as expected (13) and the maximum tensile strength is obtained at 20 parts of rubber. [illegible]. The decrease in strength with increase in rubber may be due to the drop in crystallinity (15-16). High tensile strength and low elongation on decreasing the rubber content implies that the continuous phase is the polyolefin for all the compositions. In blends containing a higher proportion of HDPE, the elastomer phase remains as dispersed particles. Smaller size and uniform dispersion of the dispersed phase improve the tensile properties of the blends (17)[*]. It is seen that the tensile strength of the blends with TW or GW is slightly higher than that of the blends with NR. This may be due to the partially crosslinked nature of the

[*] This can be observed in the SEM photograph (Fig IV (a) 4).

TW and GW (18). Of the two blends HDPE/TW and HDPE/GW, the former shows higher tensile strength values than the latter. This is due to the higher crosslink density of TW compared to that of GW. The values were calculated to be 4.1×10^{-5} g mol/cc for GW and 1.1×10^{-3}g mol/cc for TW.

Fig IV (a) 2 Variation of Elongation at break with Rubber content of HDPE/Rubber blends

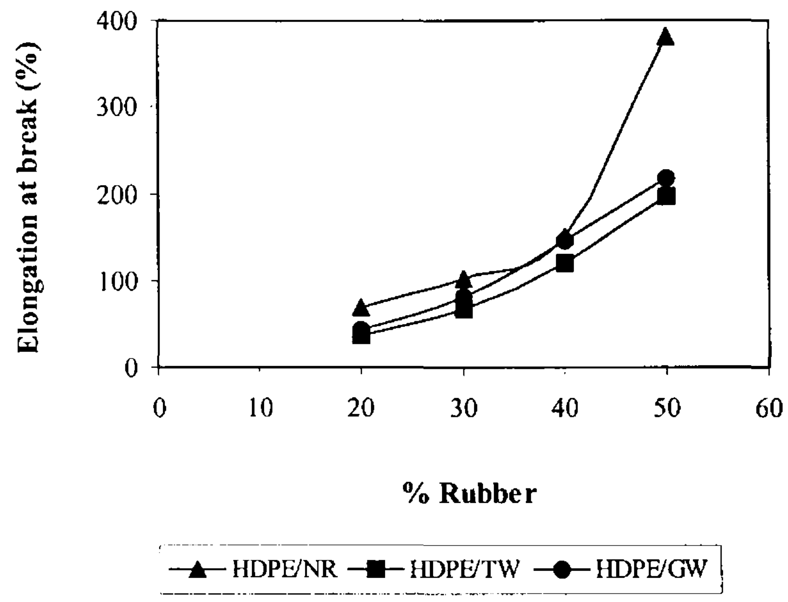


Fig IV (a) 2 shows the variation of elongation at break with rubber content. Elongation generally increases with increase in rubber content, though the increment is only marginal for HDPE/TW and HDPE/GW blends. The HDPE/NR blend shows a higher elongation because of the uncrosslinked nature of the NR phase.

Fig IV (a) 3 shows the variation of tear strength with % of rubber. The behaviour is similar to that of tensile strength and the reason is again the drop in crystallinity of the plastic phase as the rubber content is increased.
HDPE/NR shows better properties, which may be due to the lesser degradation of NR.

Table IV (a) 2 shows the values of modulus and hardness of the blends. The modulus decreases with increase in rubber content and hardness increases with plastic content. Plastic materials have comparatively higher hardness and modulus than elastomers.

Fig IV (a) 4 shows the tensile fractographs of 80/20 HDPE/NR, HDPE/TW and HDPE/GW blends. For HDPE/TW and HDPE/GW blends, the initiation of fracture is propagated as short curved lines as the shear advances. . The resistance to high deformation of these crosslinked particles restricts the flow under stress. This is shown by the presence of many short curved shear lines on the fracture surface. But in the case of 80/20 HDPE/NR blend, the uncrosslinked NR phase undergoes much higher deformation, resulting in the multidirectional shear lines.

Fig IV (a) 3 Variation of Tear strength with Rubber content of HDPE/Rubber blends

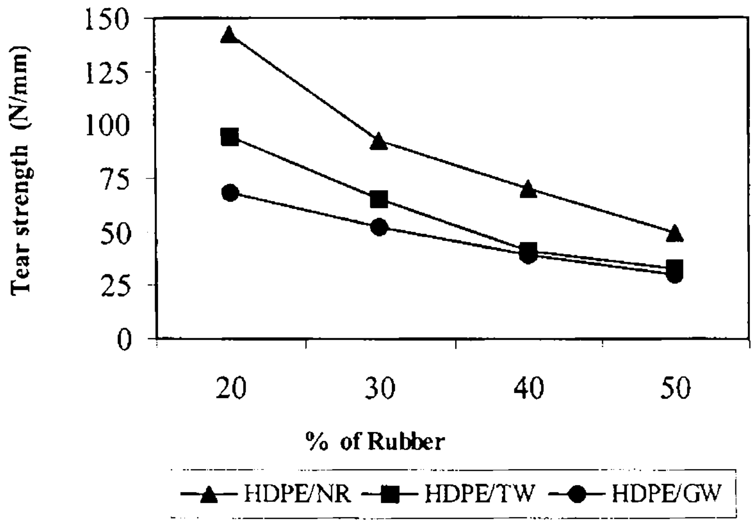
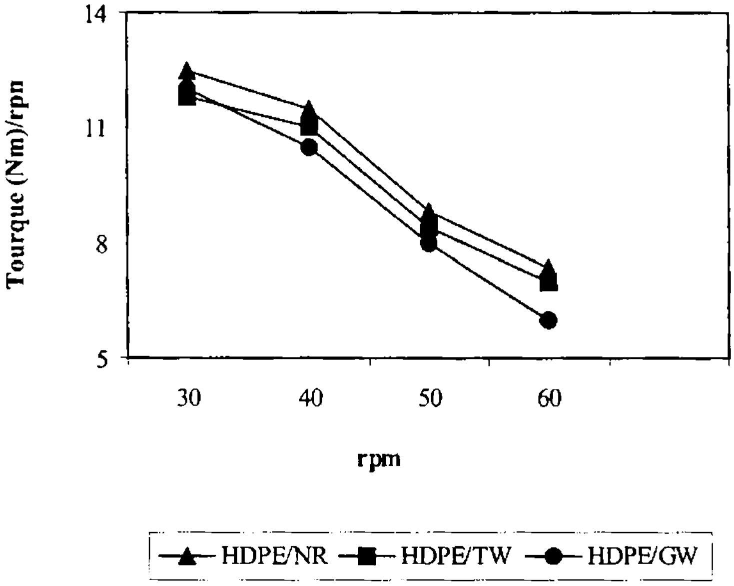


Fig IV (a) 5 shows the variation of viscosity (torque/rpm) with shear rate (rpm) of 80/20 HDPE/rubber blends. The torque/rpm representing viscosity decreases with increase in shear rate (rpm) at constant temperature, viz., 150^{0}C. From the figure it is seen that

Table IV (a) 2 Physical properties of HDPE/Rubber blends

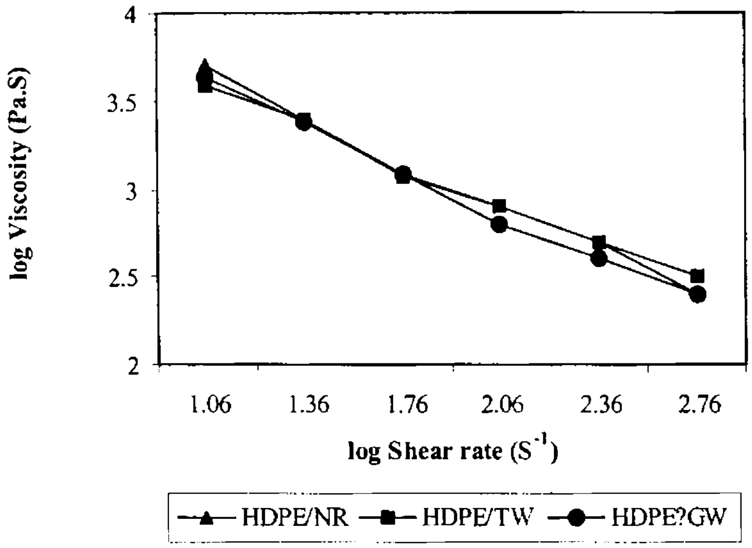
Blend	Ratio	Young's Modulus (MPa)	Hardness (Shore D)
HDPE/NR	50/50	92	26
	60/40	113	29
	70/30	141	35
	80/20	160	43
HDPE/TW	50/50	101	25
	60/40	127	30
	70/30	156	34
	80/20	198	43
HDPE/GW	50/50	97	23
	60/40	119	25
	70/30	151	29
	80/20	195	41

Fig IV (a) 5 Variation of Torque/rpm with rpm of HDPE/Rubber blends



HDPE/TW and HDPE/GW blends show lower viscosity compared to HDPE/NR blend. This may be due to the partial devulcanization and molecular break down during the preprocessing of the waste material. HDPE/GW blends have lower viscosity than those of HDPE/TW blends due to the lower crosslink density of GW when compared to that of TW.

Fig IV (a) 6 Variation of Viscosity with Shear rate of HDPE/Rubber blends



In Fig IV (a) 6, log viscosity is plotted against log shear rate of 80/20 HDPE/rubber blends. It shows that as the shear rate increases viscosity decreases. From this curve also it can be seen that there is no increase in the viscosity of HDPE/TW and HDPE/GW blends compared to the HDPE/NR blend even though the former blends were slightly crosslinked. The reasons are again the partial devulcanization and molecular breakdown during the preprocessing. The decrease in viscosity with increase in shear rate shows that the blends are pseudoplastic in nature (19).

Fig IV (a) 7 shows the relationship between shear stress and shear rate. It is clear that as the shear rate increases, shear stress also increases as expected. It confirms the non-Newtonian behaviour of the blends.

Fig IV (a) 7 Variation of Shear stress with Shear rate of 80/20 HDPE/Rubber blends

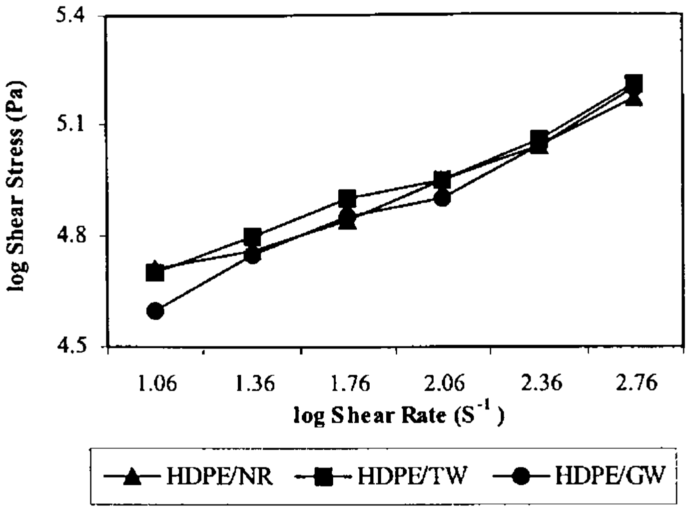


Fig IV (a) 8 shows the optical photographs of the extrudates from the Capillary Viscotester. It shows that as the shear rate increases, the roughness of the extrudate surface increases. This implies that there is difference in the rate of flow of the plastic and the rubber phases at various shear rates. The increase in the roughness of the surface with the increase in the shear rate may be due to the difference in the melt viscosity of the two phases. This difference is still higher for systems based on HDPE/TW and HDPE/GW compared to HDPE/NR because of the crosslinked nature of TW and GW.

Table IV (a) 3 shows the values of tensile strength, elongation, modulus and hardness of the reprocessed samples. It can be seen that even after reprocessing, the materials could retain the mechanical properties to a great extent, which implies that they are very much reprocessable.

Table IV (a) 4 shows the variation of die swell ratio (d_e/d_c) with shear rate of HDPE/TW and HDPE/GW blends. As the shear rate increases, the d_e/d_c also increases, but the difference between the values is very small. The orientation of the rubber particles will be more at higher shear rates and this may be the reason for the increase in the swell ratio with shear rate. Also the resistance of the crosslinked rubber phase to higher deformation resulting from the greater elastic recovery of the rubber causes only a small difference between the swell ratios.

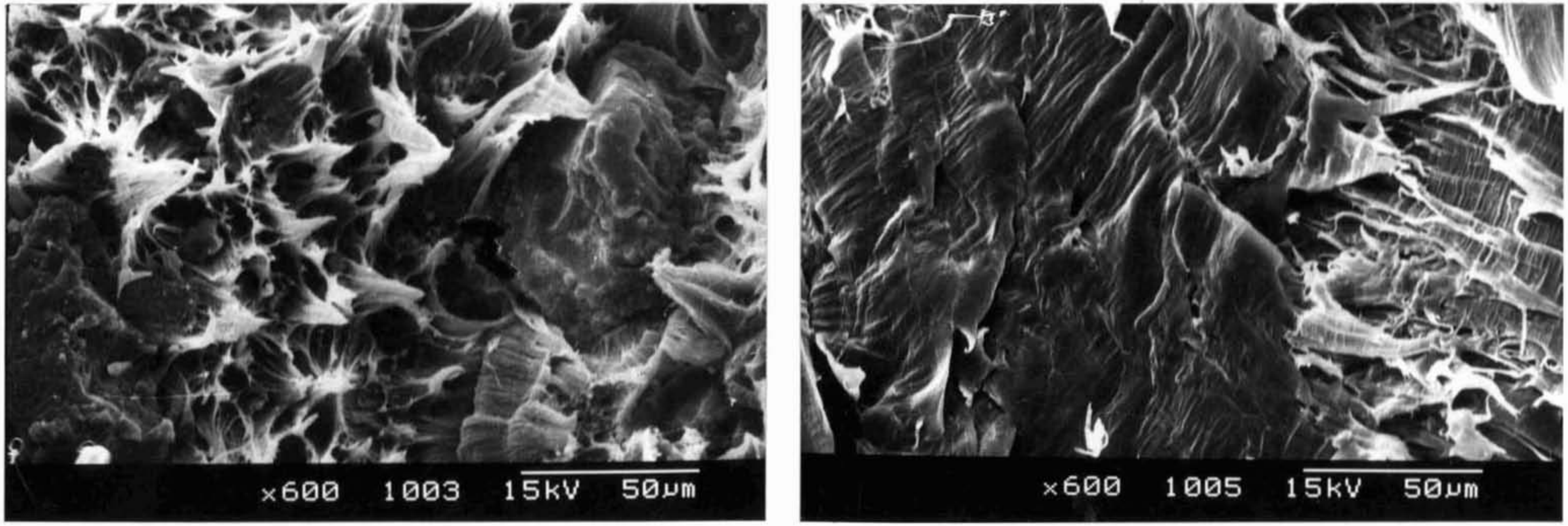
Table IV (a) 3 Mechanical properties of the reprocessed samples

Blend (80/20)	Tensile Strength (MPa)	Elongation at break (%)	Young's Modulus (MPa)	Hardness (Shore D)
HDPE/NR	8.0	77	11.6	40
HDPE/TW	13.9	60	18.9	39
HDPE/GW	12.9	89	19.5	39

Table IV (a) 4 Variation of d_e/d_c with shear rate of HDPE/TW, GW blends

Shear rate	**Die swell ratio**	
	HDPE/ TW	**HDPE/ GW**
11.52	1.62	1.57
23.04	1.64	1.59
57.60	1.67	1.63
115.2	1.69	1.64
230.4	1.71	1.66
576.0	1.72	1.67

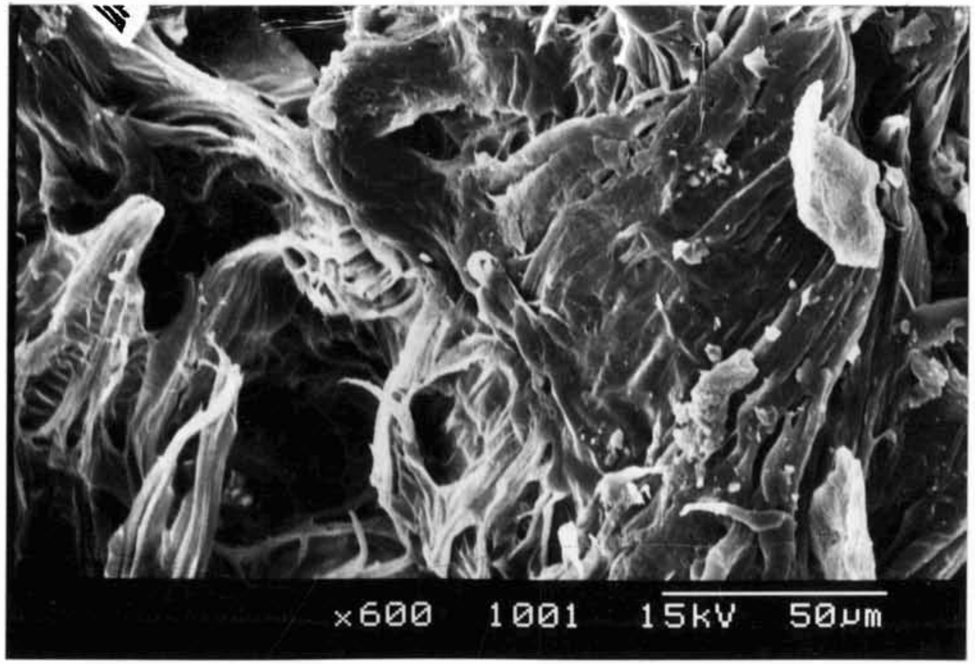
Fig IV(a) 4 Tensile fractographs of 80/20 blends of



HDPE / TW

HDPE / GW

Fig IV(a) 4 Tensile fractograph of 80/20 blend of



HDPE / NR

Fig IV(a) 8 Optical photographs of extrudates of 80/20 blends of

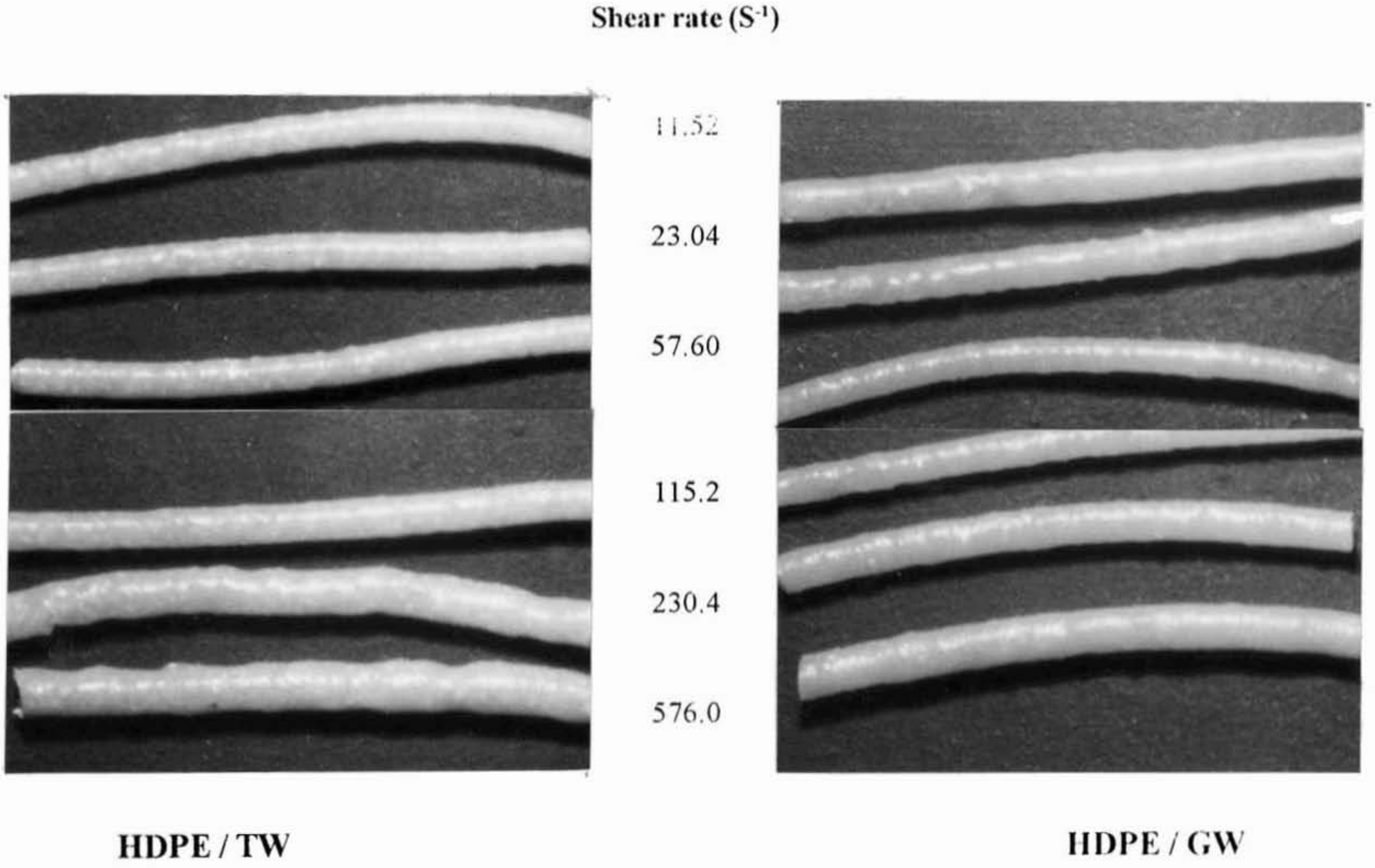
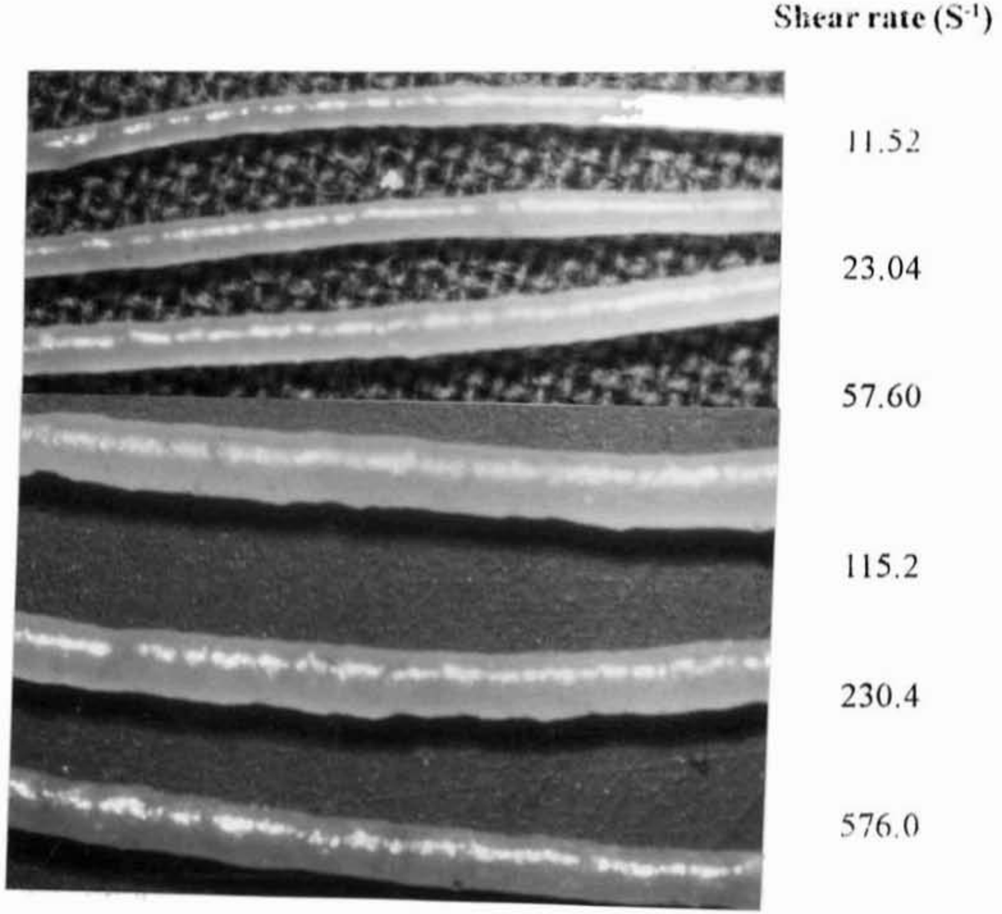


Fig IV(a) 8 Optical photographs of extrudates of 80/20 blends of



HDPE / NR

CHAPTER IV (b)

STUDIES ON THE BLENDS OF LOW DENSITY POLYETHYLENE AND LINEAR LOW DENSITY POLYETHYLENE WITH MBT MODIFIED LATEX PRODUCT WASTE

Experimental

In this part, the properties of thermoplastic elastomers prepared from modified latex waste and LDPE and LLDPE in the 80 plastic/20 rubber blend ratio have been evaluated. The mechanical, rheological and morphological properties of these blends were compared with those of the conventional natural rubber/polyethylene blends. The properties of the reprocessed samples were also evaluated.

Preparation of blends

Blends were prepared on the Brabender Plasticorder according to the procedure mentioned in Chapter IV (a). Measurement of mechanical properties, rheological behavior, morphological behavior, Scanning Electron Microscopic study, reprocessability studies etc. also were done as per the standard procedures given in IV (a).

Results and Discussion

The modified waste materials are prepared as per the formulation given in Table IV (a) 1.

Table IV (b) 1 shows the mechanical properties of the LDPE/rubber and the LLDPE/rubber blends. It can be seen that the tensile strength of the blends based on TW and GW are comparable with those of NR based blends. Since the plastic content is high, the elastomer phase tends to remain as dispersed phase. Smaller size and uniform dispersion of the dispersed phase improve the tensile properties of the blends (17). This may account for the comparable tensile strength for all the blends. As the percentage elongation of the blends is considered, a lower elongation is shown by the blends with TW and GW. This is due to the slightly crosslinked nature of TW and GW. The crosslink densities of TW and GW are 1.1 x10^{-3} g mol/cc and 4.1 x 10^{-5} g mol/cc respectively. Also, the blends based on LLDPE show very high elongation as expected (20). Tear strength shows the same trend as of tensile strength and the reason is also the same. Young's Modulus and hardness are also comparable to those of the conventional blends. Impact strength values of the blends based on TW and GW are found to be higher and those of LLDPE blends are very high (>1 KJ/m.) The presence of soft and flexible rubber particles in polyethylene leads to absorption of more energy during fracture. Also, this probably reflects the longer path of the propagating crack around the rubber particles. This effect will be more for TW and GW that results in higher impact strength values.

Table IV (b) 1 Mechanical properties of 80/20 LDPE/Rubber and LLDPE/Rubber blends

Blend	Tensile Strength (MPa)	Tear strength (N/mm)	Elongation at break (%)	Young's modulus (Mpa)	Hardness (Shore D)	Impact strength (KJ/m)
LDPE/NR	7.6	86.4	107	93	30	0.40
LDPE/TW	8.04	62.4	41	102	27	0.61
LDPE/GW	7.43	73.6	60	95	24	0.56
LLDPE/NR	12.2	104.5	589	94	30	>1
LLDPE/TW	10.8	80.2	495	112	25	>1
LLDPE/GW	8.1	69.4	547	99	24	>1

Fig IV (b) 1 and Fig IV (b) 2 show the tensile fractographs of the 80/20 LDPE/TW and LDPE/GW respectively. Here in both the cases the fracture pattern is propagated concentrically as the shear advances. Plastic phase appears to be the continuous phase and rubber remains as the dispersed phase. The crosslinked nature of the latex reclaim reduces the deformation of the rubber phase.

Fig IV (b) 3 shows the variation of viscosity (torque/rpm) with shear rate (rpm) of the 80/20 LDPE/TW, LDPE/GW and LDPE/NR blends. The torque/rpm, representing the viscosity, decreases with increase in shear rate (rpm) at constant temperature, viz., 150^{0}C. The comparatively lower viscosity of blends based on TW and GW may be attributed to the partial devulcanization and molecular breakdown during the processing of the waste material.

Fig IV (b) 3 Variation of Torque/rpm with rpm of 80/20 LDPE/Rubber blends

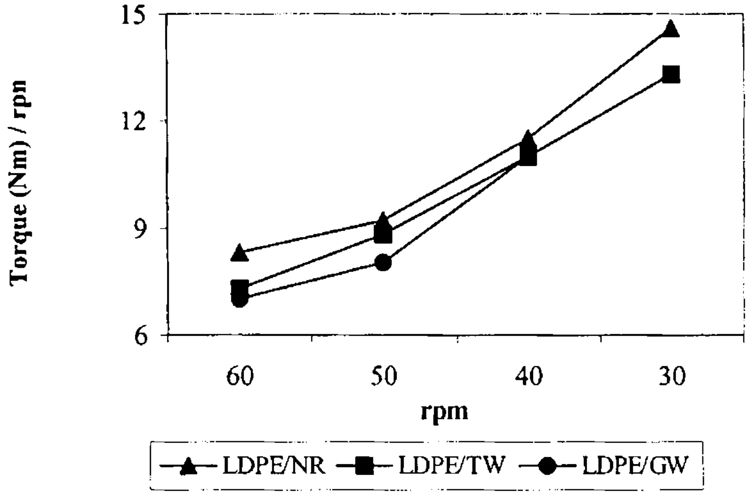


Fig IV (b) 4 shows the relationship of log viscosity with log shear rate of 80/20 LDPE/rubber blends. It can be seen that as the shear rate increases, viscosity decreases. It is also clear that, in spite of the slightly crosslinked nature of the TW and GW, all the blends show more or less same viscosity over a range of shear rates. The reasons are again the partial devulcanization and molecular breakdown during the preprocessing. The decrease in viscosity with increase in shear rate shows that the blends are pseudoplastic in nature (19).

In Fig IV (b) 5, log shear stress is plotted against log shear rate for 80/20 LDPE/rubber blends. As the shear rate increases, shear stress also increases as expected. It confirms the non-Newtonian behaviour of the blends.

Fig IV (b) 6 shows the variation of torque/rpm with rpm of LLDPE/rubber blends. The viscosity values are higher than those of the LDPE/rubber blends. This may be attributed to the higher crystallinity of LLDPE compared to LDPE.

Fig IV (b) 4 Variation of Viscosity with Shear rate of 80/20 LDPE/Rubber blends

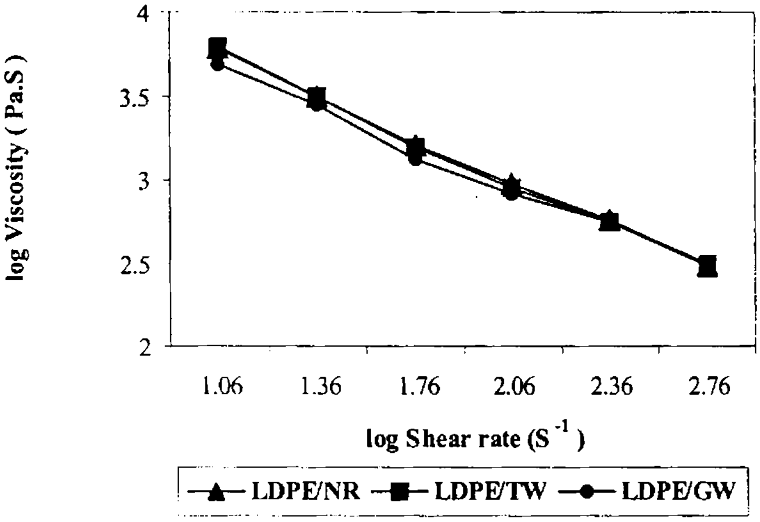


Fig IV (b) 5 Variation of Shear stress with Shear rate of 80/20 LDPE/Rubber blends

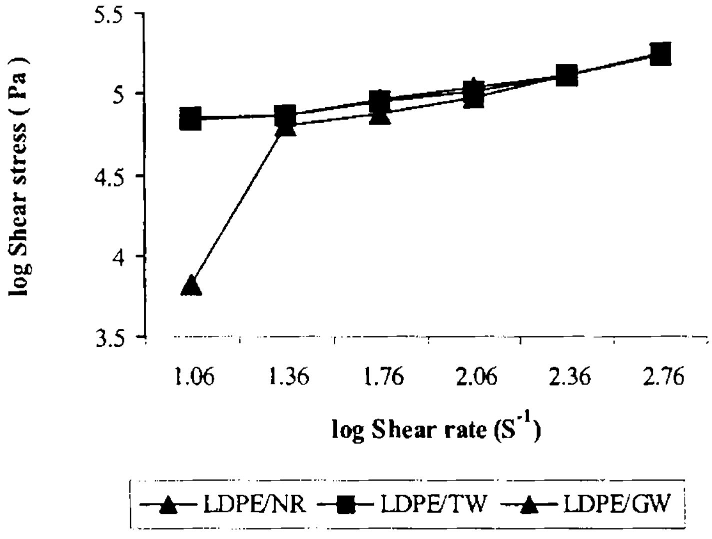


Fig IV (b) 7 shows the relationship between log viscosity and log shear rate of LLDPE/rubber blends. The trend is the same as in the case of LDPE/rubber blends.

In Fig IV (b) 8, log shear stress is plotted against log shear rate. Here also the behaviour is similar to that of LDPE/rubber blends.

Fig IV (b) 6 Variation of Torque/rpm with rpm of LLDPE/Rubber blends

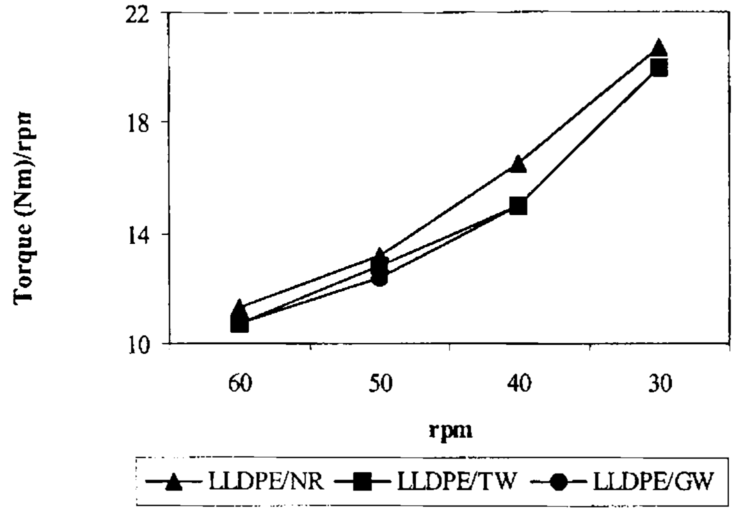


Fig IV (b) 7 Variation of Viscosity with Shear rate of LLDPE/Rubber blends

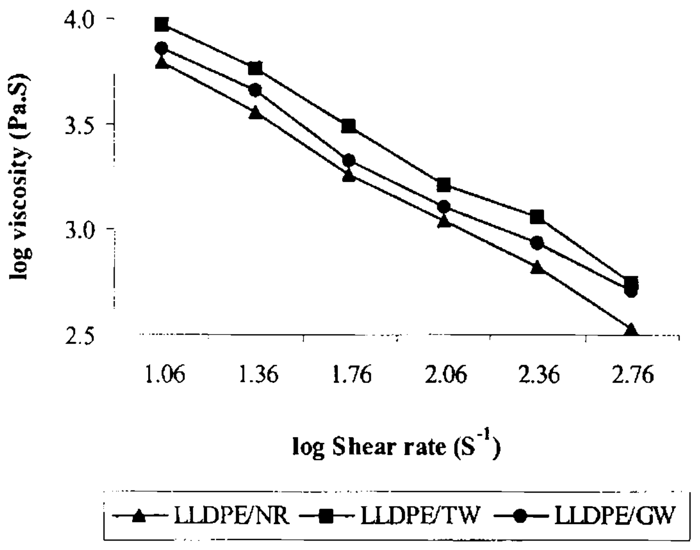


Table IV (b) 2 shows the mechanical properties of the remoulded samples. There is not much reduction in the values on remoulding and testing. This shows that the blends are reprocessable.

Fig IV (b) 9 and Fig IV (b) 10 show the optical photographs showing the morphology of the extrudates from Capillary Viscotester of 80/20 LDPE/rubber and LLDPE/rubber blends respectively. It can be seen that as the shear rate increases the deformation of the extrudate surface increases. At lower shear rates the surface of the extrudates appear smoother. Generally, the melt rheology of an elastomer-plastic blend composition is related to that of the plastic material. At higher shear rates, the viscosity-shear rate profile of the blend resembles that of the plastic material. Here there is a difference in the rate of flow of the rubber and plastic phases at various shear rates. At higher shear rates, this difference becomes higher and results in more roughness to the surface. This difference is still higher in the case of systems based on TW and GW since they are partially crosslinked. The surface roughness is more for systems based with LLDPE as plastic phase. This may be attributed again to the higher crystallinity of the same, which in turn causes higher melt viscosity.

FIG IV (b) 8 Variation of Shear stress with Shear rate of LLDPE/Rubber blends

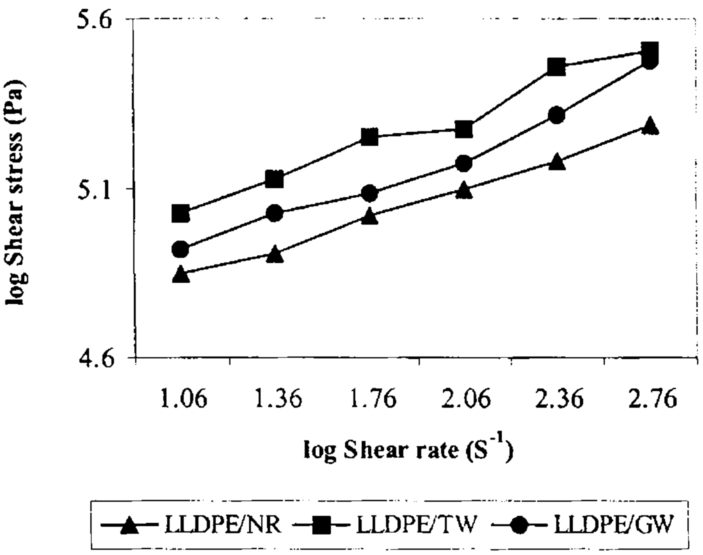


Table IV (b) 3 shows the variation of die swell ratio, d_e/ d_c with shear rate of the LDPE/TW, GW and LLDPE/TW, GW blends. As in the case of HDPE/rubber blends, die swell increases slightly with increase in the shear rate. Of the three types of blends, LLDPE blends exhibit the highest die swell ratio, which may be attributed to its higher melt viscosity compared to HDPE and LDPE.

Table IV (b) 2 Mechanical properties of the reprocessed 80/20 LDPE/rubber and LLDPE/rubber blends

Blend	Tensile strength(MPa)	Elongation at break (%)	Young's modulus(MPa)	Hardness (ShoreD)
LDPE/NR	6.5	85	93	30
LDPE/TW	7.1	38	102	27
LDPE/GW	6.4	51	95	24
LLDPE/NR	7.8	425	94	30
LLDPE/TW	6.2	386	112	25
LLDPE/GW	8.5	402	99	24

Table IV (b) 3 Variation of d_e/d_c with shear rate of LDPE, LLDPE blends with TW and GW

Shear rate	**Die swell ratio**			
	LDPE/TW	**LDPE/GW**	**LLDPE/TW**	**LLDPE/GW**
11.52	1.38	1.32	1.71	1.54
23.04	1.43	1.35	1.74	1.58
57.6	1.45	1.37	1.78	1.60
115.2	1.46	1.38	1.82	1.63
230.4	1.48	1.41	1.85	1.66
576.0	1.49	1.44	1.94	1.67

Fig IV(b) 1 Tensile fractograph of 80/20
LDPE / TW

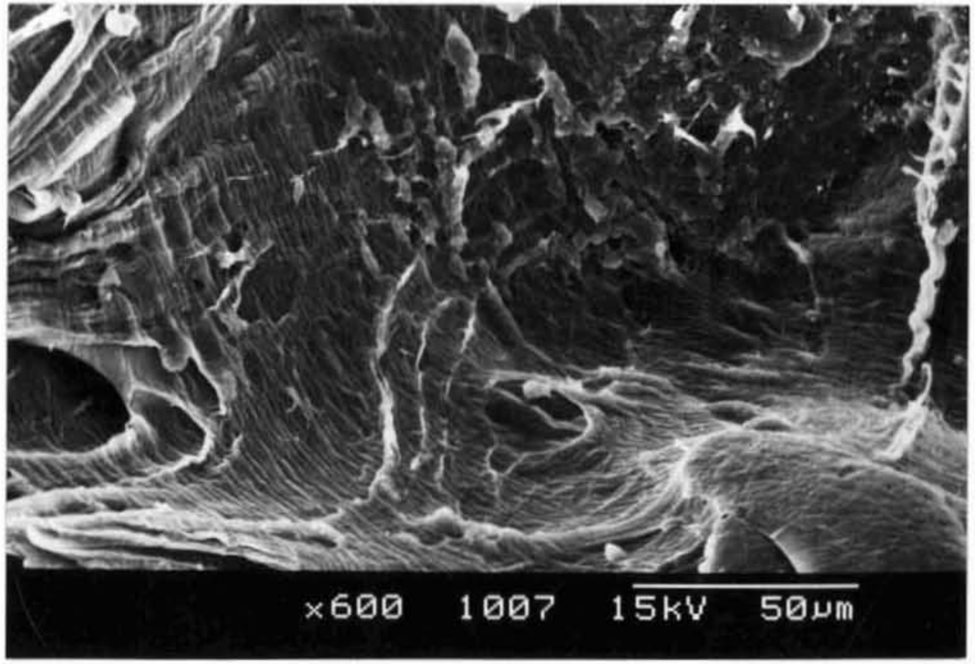


Fig IV(b) 2 Tensile fractograph of 80/20
LDPE / GW

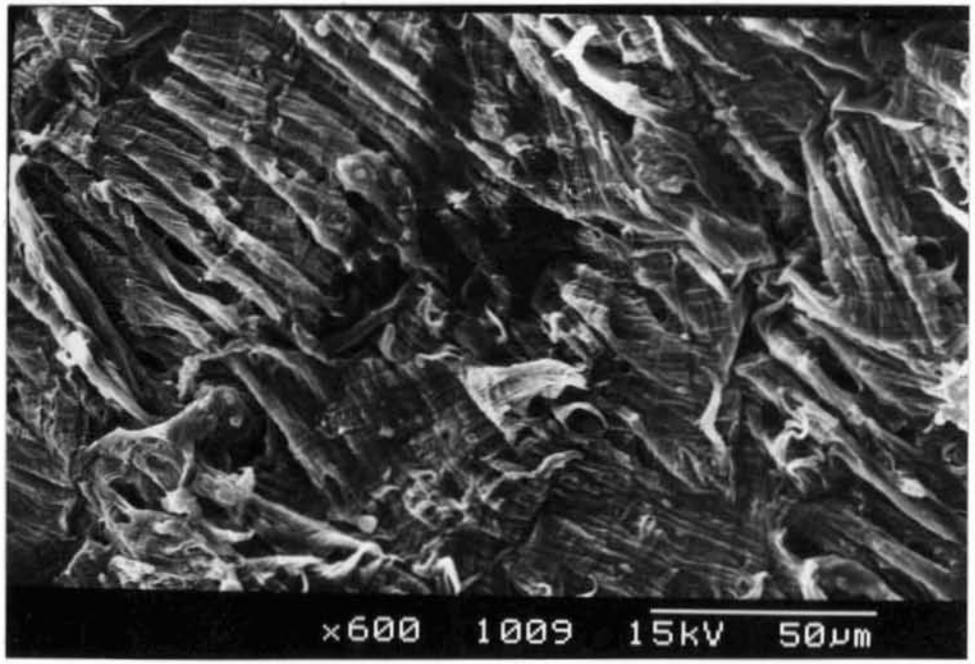
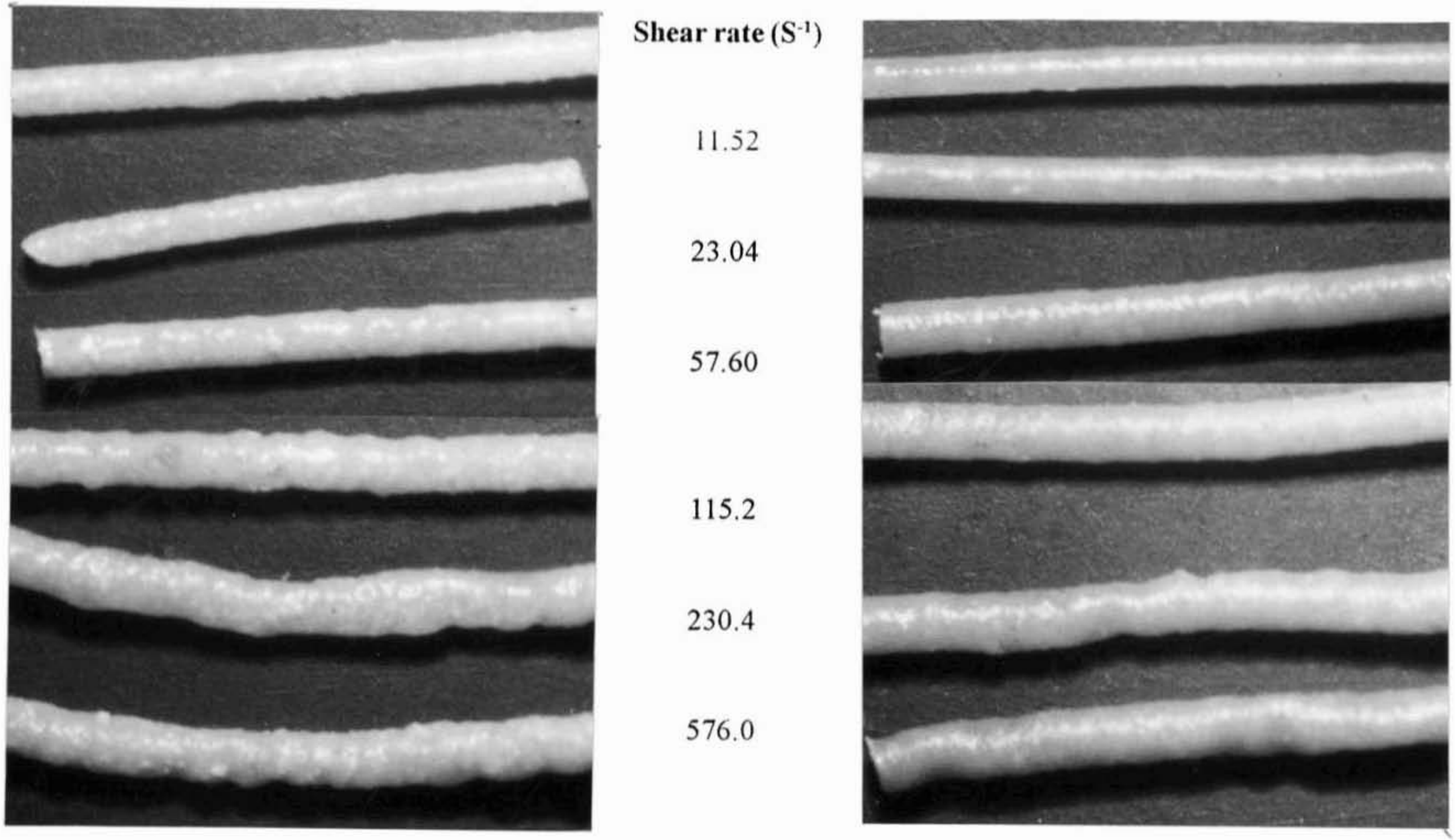


Fig IV(b) 9 Optical photographs of extrudates of 80/20 blends of



LDPE / TW

LDPE / GW

Fig IV(b) 9 Optical photographs of extrudates of 80/20 blends of
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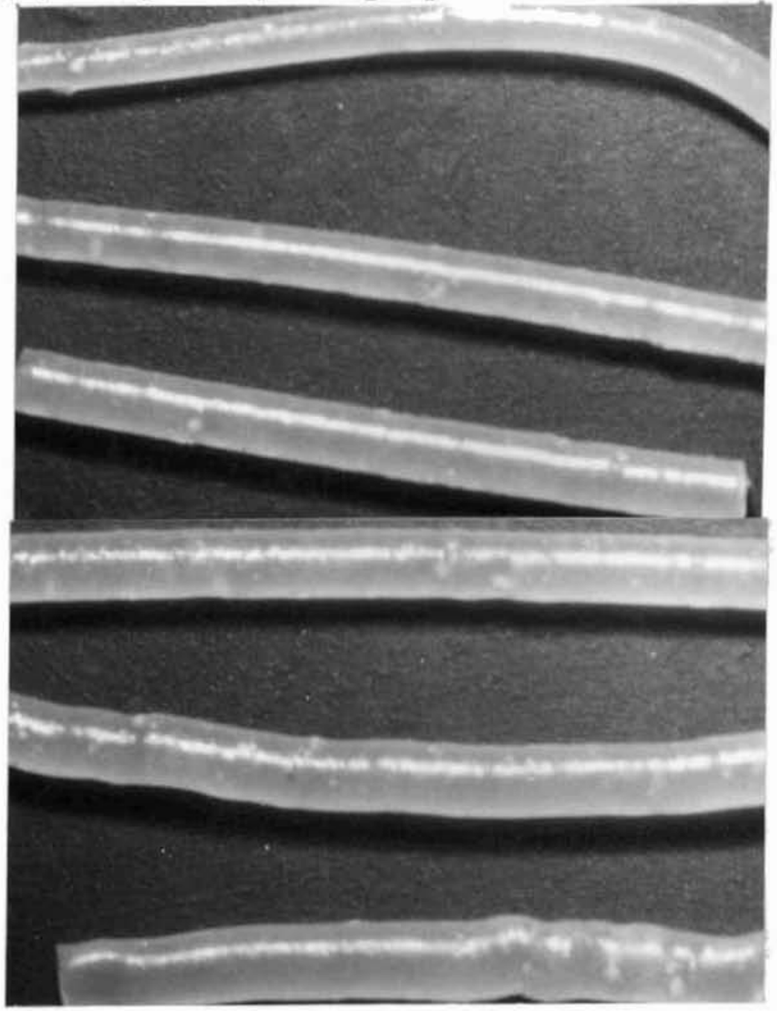
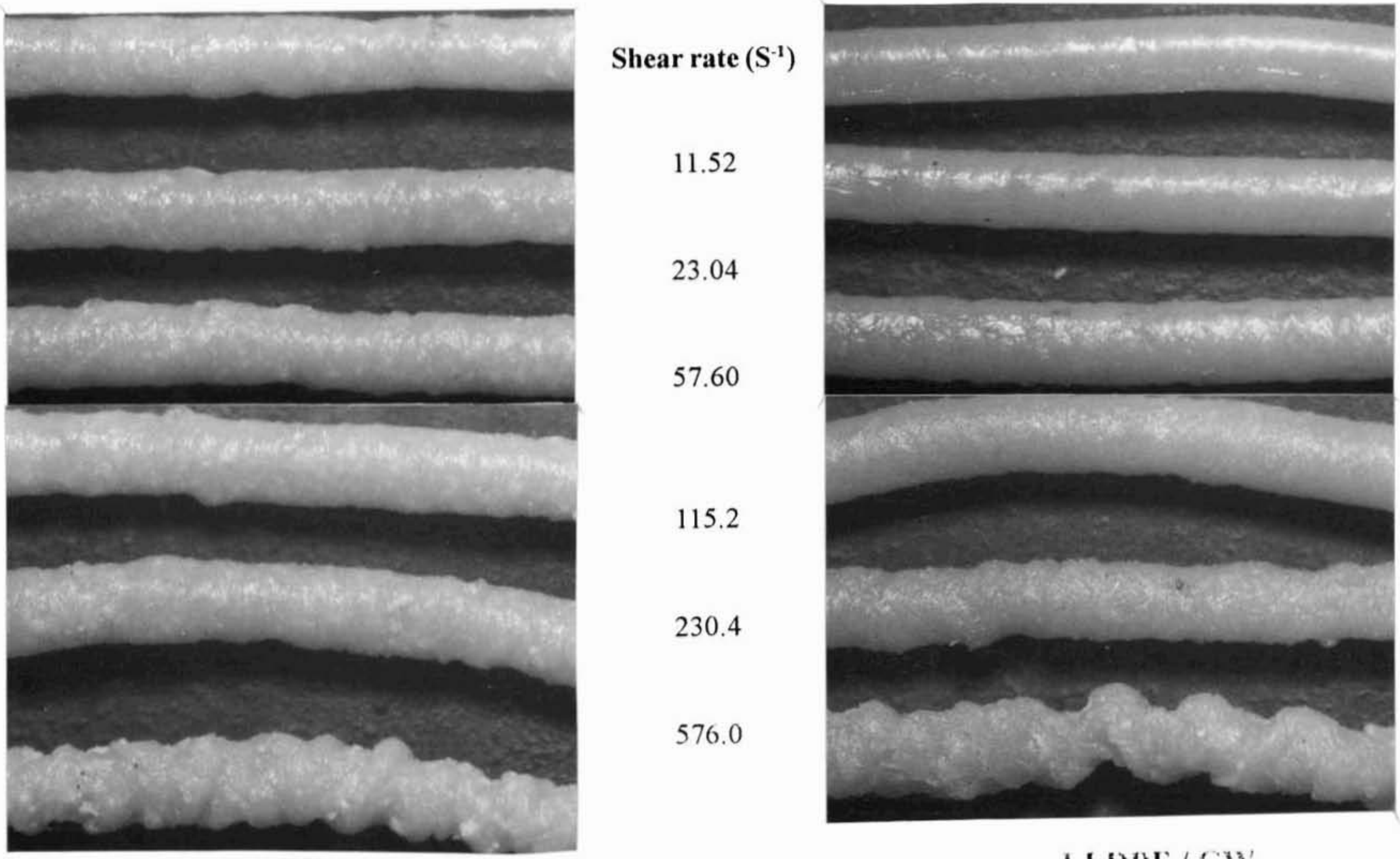


LDPE / NR

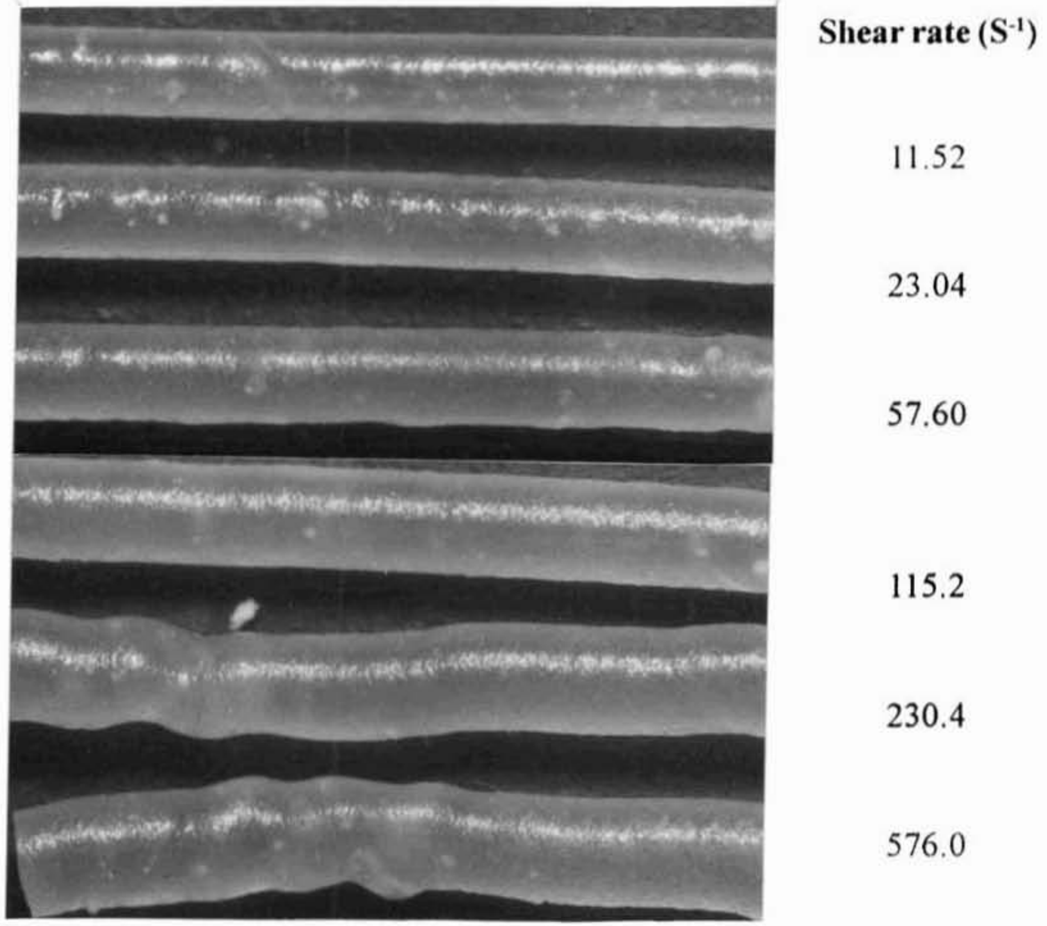
Fig IV(b) 10 Optical photographs of extrudates of 80/20 blends of



LLDPE / TW

LLDPE / GW

Fig IV(b) 10 Optical photographs of extrudates of 80/20 blends of



LLDPE / NR

CHAPTER IV (c)

THERMOPLASTIC ELASTOMER BASED ON HIGH DENSITY POLYETHYLENE AND LATEX PRODUCT WASTE MODIFIED WITH THIOCARBANILIDE

Experimental

In this part of the study, we have developed thermoplastic elastomers based on high density polyethylene and the latex waste modified with thiocarbanilide, both unvulcanized and dynamically vulcanized. Dynamic vulcanization has been defined by A.Y.Coran as the process of vulcanizing rubber during its intimate melt mixing with a non-vulcanizing thermoplastic polymer (21). The mechanical and morphological properties of the material were compared with those of the conventional polyethylene/natural rubber blends. The mechanical properties of the reprocessed and aged samples have also been evaluated.

Preparation of blends

Weight of the modified waste was adjusted according to the rubber hydrocarbon content so as to maintain the proportion of rubber in the blend. Blends were prepared according to the procedure in IV (a). Mechanical, rheological and morphological studies were also done.

Results and Discussion

Table IV (c) 1 shows the formulation for the preparation of GW (P). Dynamic vulcanization was given with 2.5 phr sulphur during the melt mixing of HDPE/GW (P).

Fig IV (c) 1 shows the variation of tensile strength with rubber content of unvulcanized and dynamically vulcanized HDPE/GW (P) and HDPE/NR blends. The values are higher for the unvulcanized blends with GW than those with NR and still higher for the dynamically vulcanized blends based on GW. The reasons may be the presence of residual crosslinks in GW (crosslink density 1.9 x 10^{-3} g mol/ cc) and the effect of dynamic crosslinking on improving the mechanical properties as expected (22).

Table IV (c) 1 Formulation for modified waste

Ingredients	Phr
Glove Waste	100.0
NR	20.0
ZnO	5.0
Stearic Acid	2.0
Thiocarbanilide	3.0
CBS	0.6
Naphthenic Oil	3.0
Hydroquinone	0.2

Fig IV (c) 1 Variation of Tensile strength with Rubber content of HDPE/GW (P), NR blends

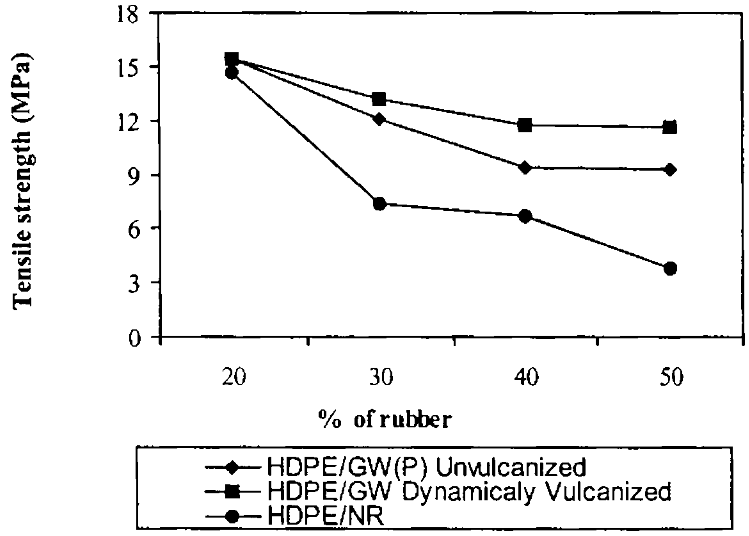
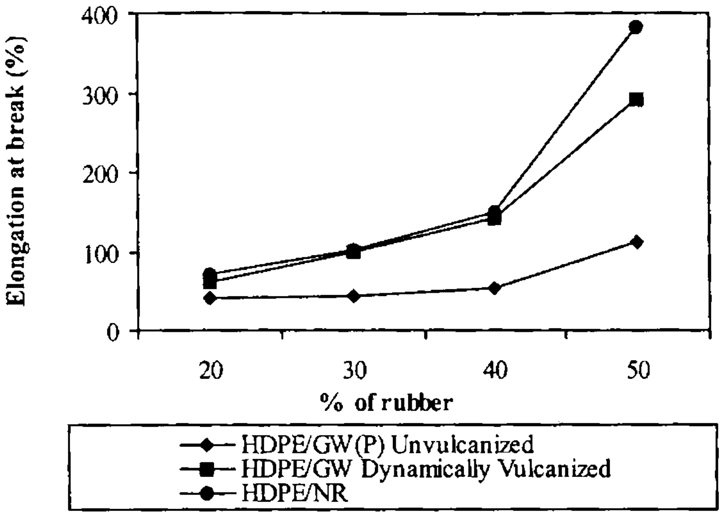


Fig IV (c) 2 shows the variation of elongation at break with rubber content. It can be seen that the elongation percentage is improved very much due to dynamic crosslinking. The lower elongation of the HDPE/GW (P) blends compared to the HDPE/NR blends is due to the slight crosslinking present in GW. The enhancing effect of dynamic crosslinking on mechanical properties may be the reason for the comparable values of dynamically vulcanized blends to those of the HDPE/NR blends.

Fig IV (c) 2 Variation of Elongation at break with Rubber content of HDPE/GW (P) blends



In Fig IV (c) 3, variation of tear strength with % of rubber is shown. The tear strength increases with increase in the plastic content and the values are higher for dynamically crosslinked blends. This may be due to the higher crosslink density in the dynamically vulcanised blend.

Fig IV (c) 3 Variation of Tear strength with Rubber content of HDPE/GW (P) blends

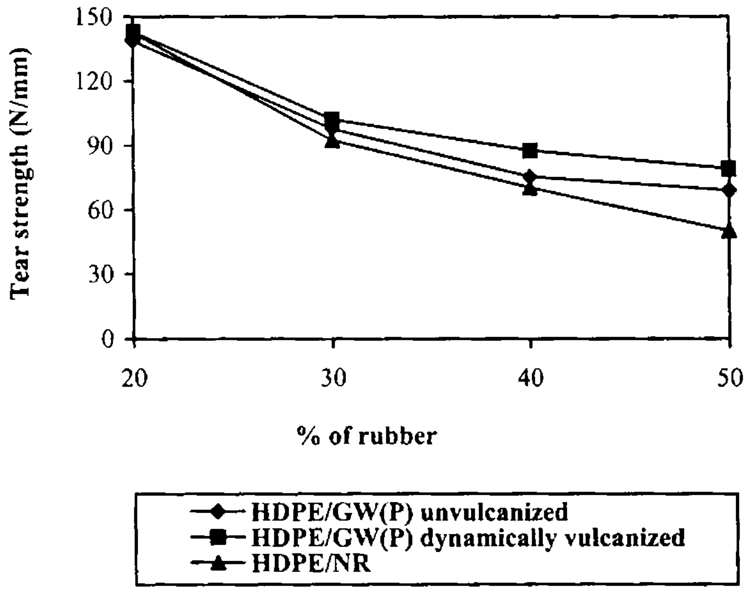


Fig IV (c) 4 Variation of Hardness with Rubber content of HDPE/GW (P) blends

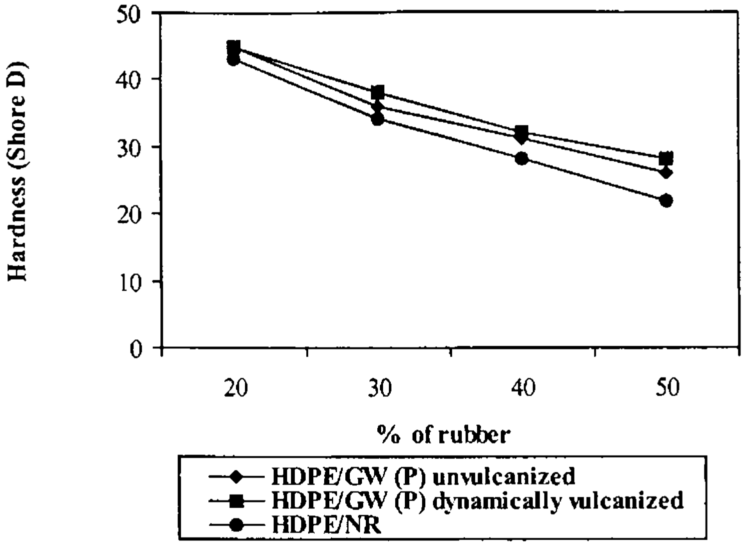


Fig IV (c) 4 gives the relationship between hardness and % of rubber. As the rubber content increases, values decreases. Higher values are observed again in the case of dynamically vulcanized samples.

Fig IV (c) 5 shows the variation of impact strength with rubber content. The impact strength increases with increase in rubber content as expected. The presence of soft and flexible rubber particles in polyethylene leads to absorption of more energy during fracture (21). The values are higher for dynamically vulcanized blends due to the

Fig IV (c) 5 Variation of Impact strength with Rubber content of HDPE/GW (P) blends

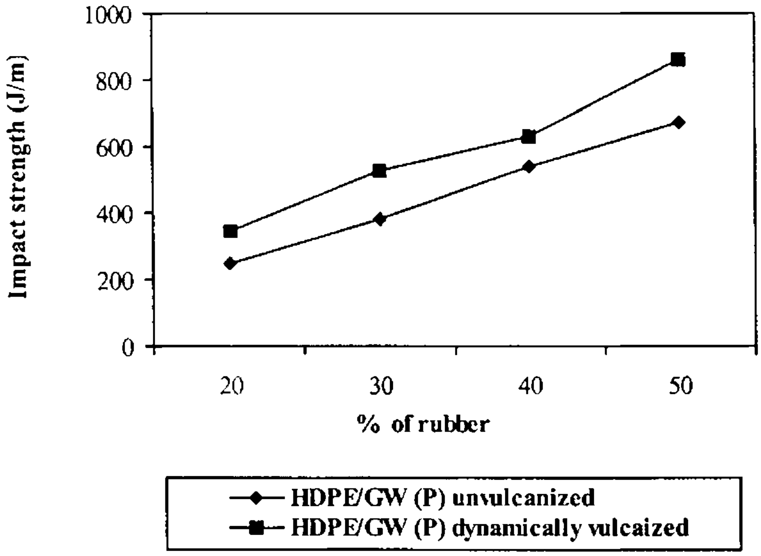
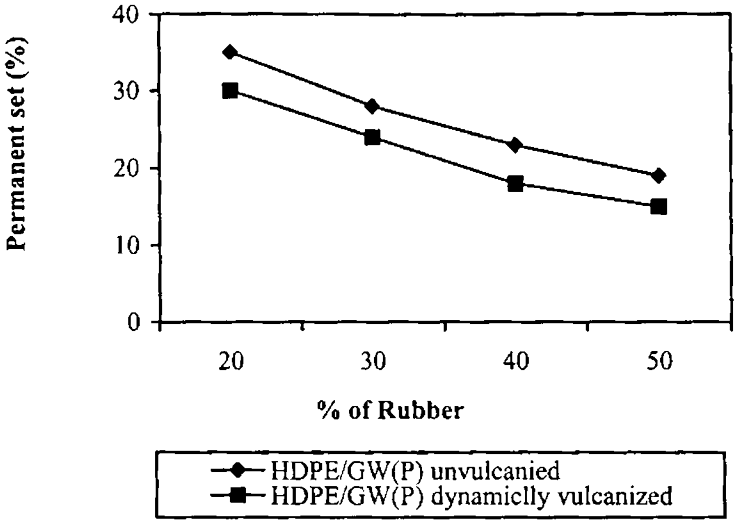


Fig IV (c) 6 Variation of Permanent set with Rubber content of HDPE/GW (P) blends



enhanced vulcanization effect.

Fig IV (c) 6 shows the relationship between permanent set and rubber content of HDPE/GW blends, both crosslinked and dynamically crosslinked. As the rubber content increases, permanent set decreases. On crosslinking the rubber phase dynamically, the permanent set values decreases significantly as expected.

This is due to the increased resistance of the blend towards the applied stress, on dynamic vulcanization.

Fig IV (c) 7 Variation of Tensile strength with Rubber content of aged HDPE/GW (P) blends

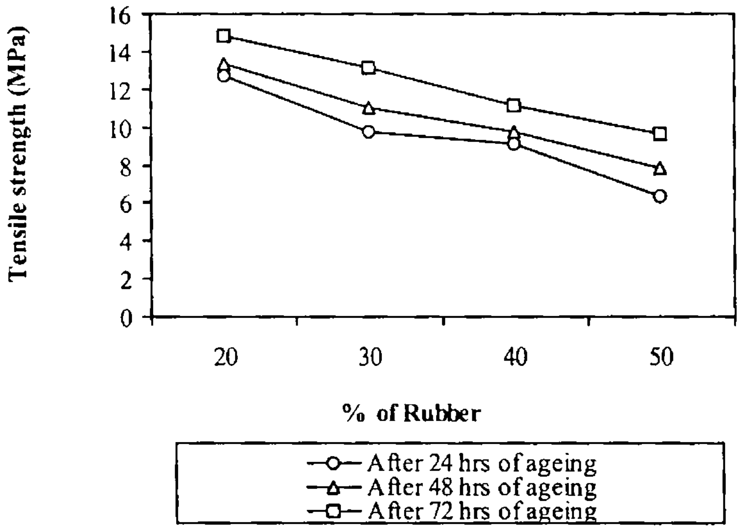


Fig IV (c) 7 shows the variation of tensile strength with rubber content of dynamically vulcanized HDPE/GW (P) blend after 24, 48 and 72 hrs of ageing. The values are found to increase as the time of ageing is increased. The reason may be the increase in the extent of crosslinking on prolonged ageing.

Fig IV (c) 8 Variation of Elongation at break with Rubber content of aged HDPE/GW (P) blends

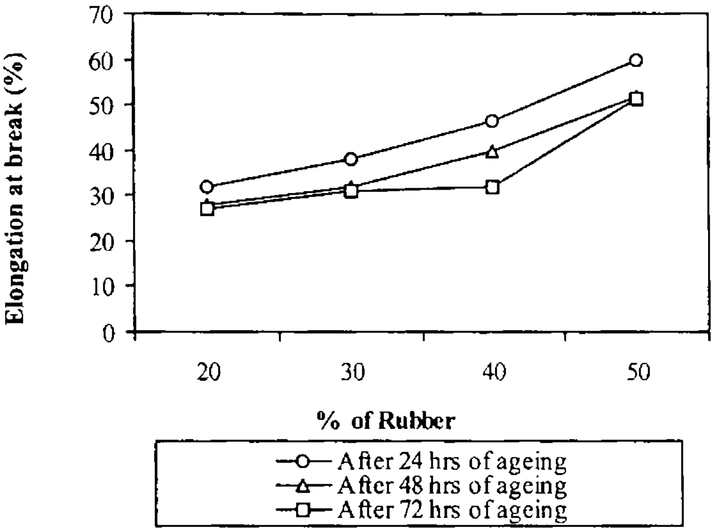
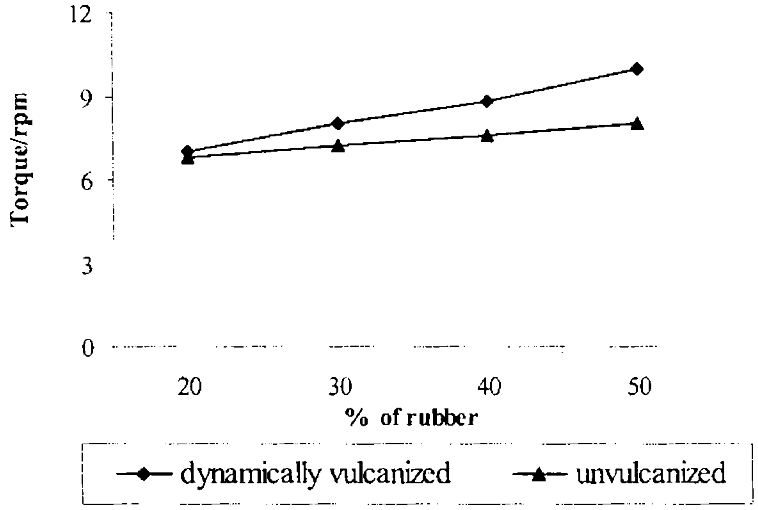


Fig IV (c) 9 Variation of Torque/rpm with rpm of HDPE/GW (P) blends



In Fig IV (c) 8, the variation of elongation at break with rubber content of the aged samples is shown. It is seen that as the duration of ageing is increased, the elongation at break decreases. The reason is again the increased extent of crosslinking as ageing period is increased. This shows that degradation of rubber is not taking place at this temperature (70^{0}C).

Fig IV(c) 10 Variation of Viscosity with Shear rate of 50/50 HDPE/GW (P) blend

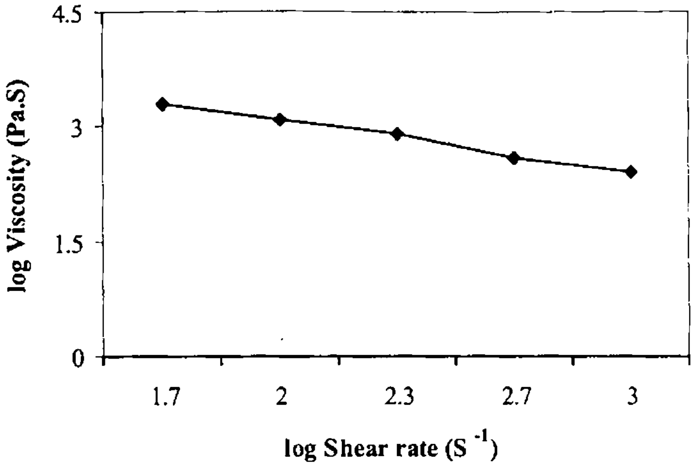
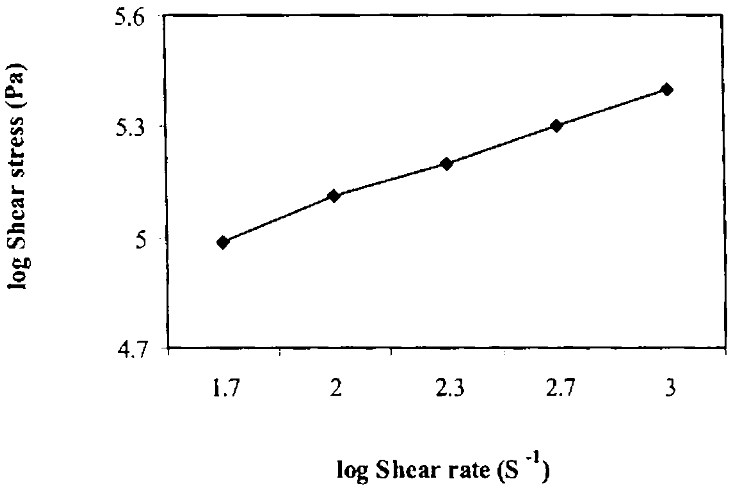


Fig IV (c) 9 shows the relationship between the rubber content and viscosity (torque/rpm) at 150^{0}C of both unvulcanized and dynamically vulcanized HDPE/GW (P) blends. It can be seen that as the rubber content increases, viscosity also increases. The viscosity values are found to be higher for the dynamically vulcanized blends as higher torque is developed during dynamic vulcanization.

Fig IV (c) 11 Variation of Shear stress with Shear rate of 50/50 HDPE/GW (P) blend



Above the melting temperature (150^{0}C) the plastic phase (HDPE) has a low viscosity compared to the rubber phase (GW (P).

Fig IV (c) 10 shows the variation of viscosity with shear rate of 50/50 HDPE/GW (P) blend studied on the capillary rheometer. It is clear that as the shear rate increases, viscosity decreases. This shows the pseudoplastic nature of the blend (19).

Fig IV (c) 11 shows the variation of shear stress with shear rate of 50/50 HDPE/GW (P) blend. As it is seen, with the increase in the shear rate, shear stress also increases as expected. It confirms the non-Newtonian behaviour of the blend.

Table IV (c) 2 shows the variation of die swell ratio with shear rate of 50/50 HDPE/GW (P) blend. It is seen that as the shear rate increases, the **d_e/ d_c** also increases, but the difference in the values is very small. This is due to the low deformation and quick elastic recovery of crosslinked particles of the modified waste. Also the pseudoplasticity index (n) has a low value ($n < 0.5$) which confirms the pseudoplastic nature of the blend.

Table IV (c) 2 die sell ratio and pseudoplasticity index of 50/50 HDPE/GW (P) blend

Shear rate	Die swell ratio (d_e/d_c)	Pseudoplasticity index (n)
50	1.127	
100	1.137	
200	1.157	0.268
500	1.192	
1000	1.202	

CHAPTER IV (d)

STUDIES ON THERMOPLASTIC ELASTOMER BASED ON LINEAR LOW DENSITY POLYETHYLENE AND LATEX PRODUCT WASTE MODIFIED WITH THIOCARBANILIDE

Experimental

In this study, we have developed a thermoplastic elastomer based on linear low density polyethylene and latex waste modified with thiocarbanilide, both unvulcanized and dynamically vulcanized. The mechanical, rheological and morphological properties of this material were studied and compared with those of polyethylene/natural rubber blends.

Preparation of blends

First, the latex product waste was modified as per the formulation given in Table IV (c) 1. Weight of the modified waste was adjusted according to the rubber hydrocarbon content so as to maintain the proportion of rubber in the blend. Blending was done as per the procedure in IV (a). Measurement of mechanical and rheological properties and morphological study were done as described earlier.

Results and Discussion

Fig IV (d) 1 shows the variation of tensile strength with rubber content of uncrosslinked and dynamically crosslinked LLDPE/GW (P) and uncrosslinked LLDPE/NR blends. In all the cases, tensile strength decreases with increase in the rubber content. LLDPE/GW (P) blends show higher tensile values than LLDPE/NR blends. Also the dynamically vulcanized LLDPE/GW (P) blends show the highest values when compared to unvulcanized blends. The reasons may be the presence of residual crosslinks in GW (P) (crosslink density 1.9 x 10^{-3} g mol/cc) and also the effect of dynamic vulcanization on mechanical properties. Advantage of dynamic vulcanization is more significant in the 50/50 LLDPE/GW (P) blend, as observed.

Fig IV (d) 1Variation of Tensile strength with Rubber content of LLDPE/GW (P) blends

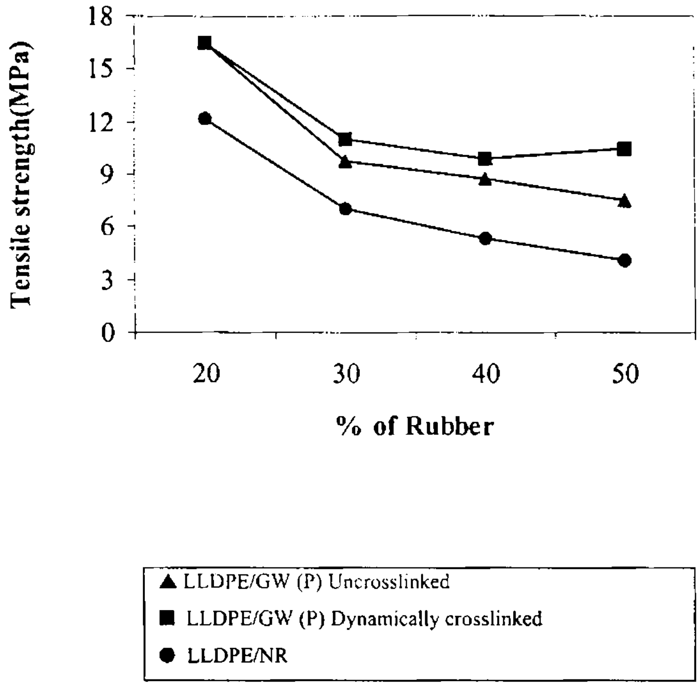


Fig IV (d) 2 shows the variation of elongation at break with plastic content. It can be seen that as the LLDPE content decreases, the elongation at break also decreases as expected (20). The elongation value decreases up to 60/40 plastic /rubber ratio. At 50/50 plastic/rubber ratio, a slight increase in the elongation at break is observed. This may be because of the higher proportion of rubber compared to other blends. On dynamic vulcanization of the LLDPE/GW (P) blends, the elongation at break still decreases due to the increase in the extent of crosslinking.

Fig IV (d) 3 shows the variation of tear strength with % of rubber. In all the cases, tear strength decreases with increase in % of rubber. Both the vulcanized and dynamically vulcanized LLDPE/GW (P) blends show higher tear strength than the LLDPE/NR blends. Again this may be due to the slight crosslinking which is already present in GW. The highest values are exhibited by the dynamically vulcanized blends.

Fig IV (d) 4 shows the relationship between hardness and % of rubber. As the rubber content increases, hardness decreases. The crosslinked blends show higher hardness as expected.

Fig IV (d) 2 Variation of Elongation at break with Plastic content of LLDPE/GW (P) blends

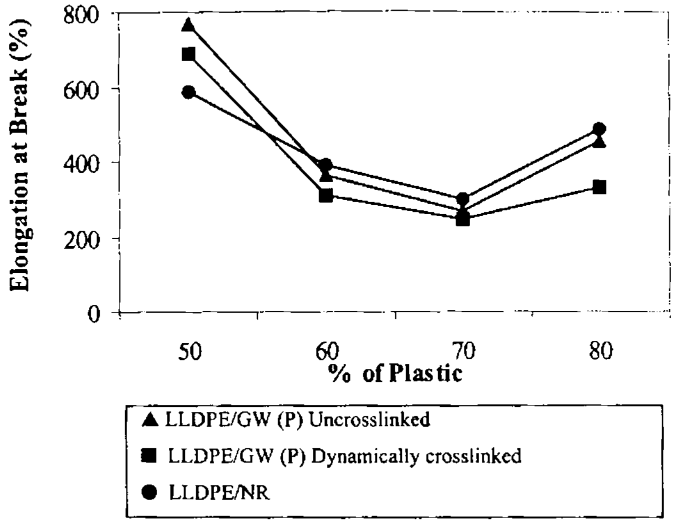
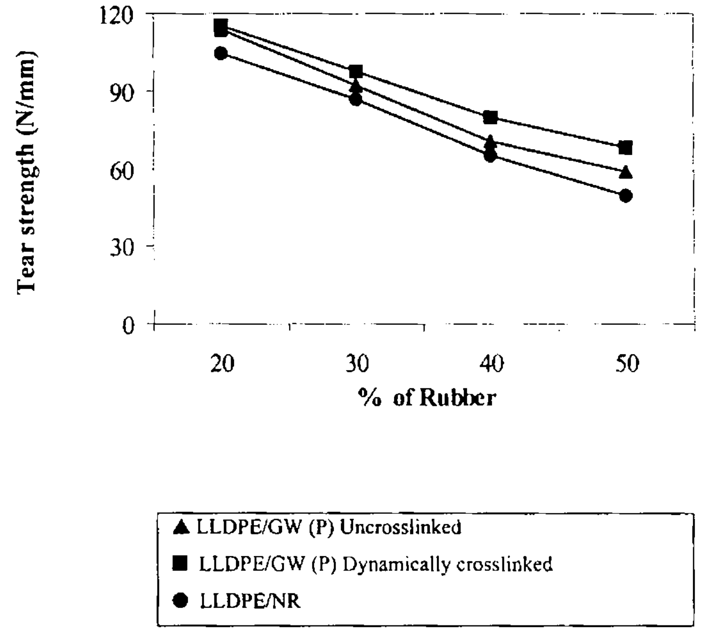


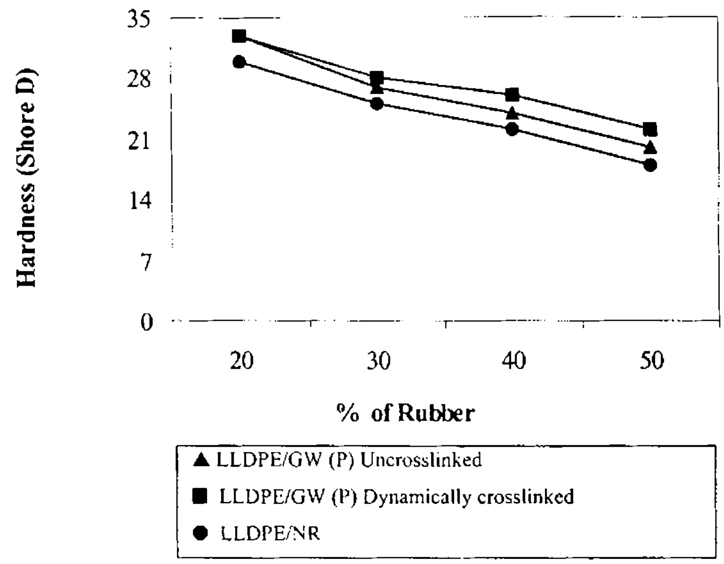
Fig IV (d) 3 Variation of Tear strength with Rubber content of LLDPE/GW (P) blends



In Fig IV (d) 5, the variation of modulus at 100 % elongation of uncrosslinked and dynamically crosslinked LLDPE/GW (P) blends with rubber content is shown. As the plastic content increases modulus also increases. Slightly higher values are observed for dynamically vulcanized blends.

Fig IV (d) 6 shows the relationship between permanent set and rubber content of

Fig IV (d) 4 Variation of Hardness with Rubber content of LLDPE/GW (P) blends



LLDPE/GW (P) blends, both crosslinked and uncrosslinked. As the rubber content increases, permanent set decreases. The permanent set values decrease significantly on dynamic vulcanization of the rubber phase. When the crosslinking increases, permanent set decreases as expected.

Fig IV (d) 5 Variation of Modulus with Rubber content of LLDPE/GW (P) blends

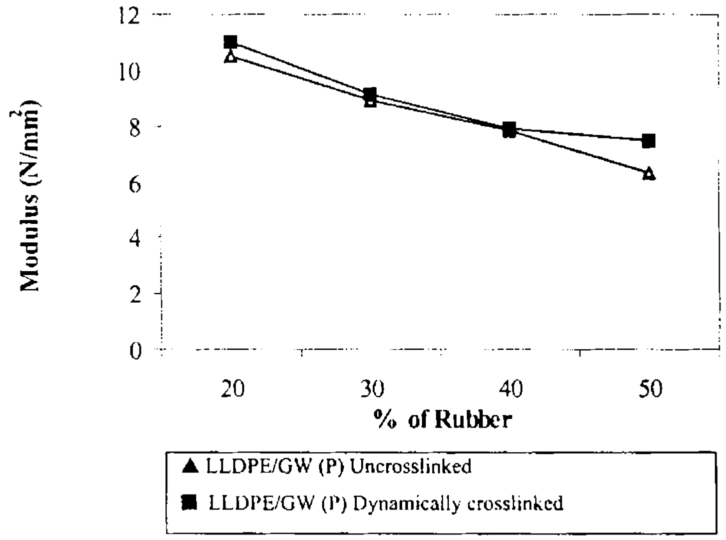
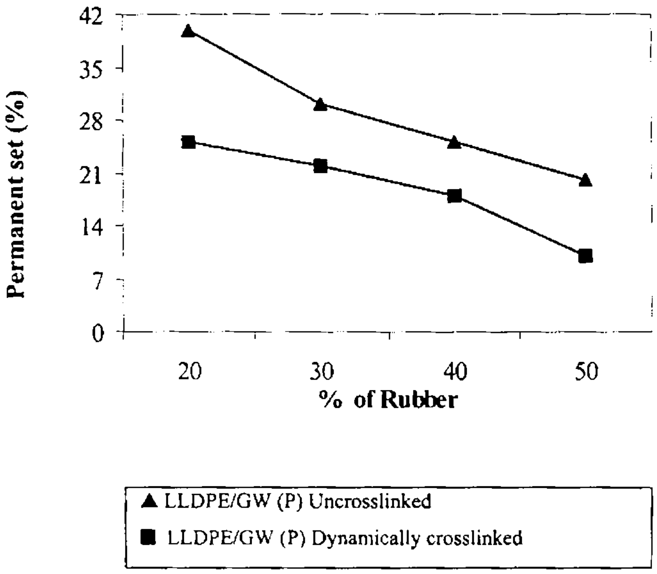


Fig IV (d) 7 gives the variation of tensile strength values of dynamically vulcanized, remelted and remoulded samples, with rubber content. The tensile strength is not much affected by remelting and the reason may be the dynamic vulcanization, which prevented the degradation of the rubber phase during remelting and remoulding.

Fig IV (d) 6 Variation of Permanent set with Rubber content of LLDPE/GW (P) blends



In Fig IV (d) 8, the elongation at break of remelted samples are plotted against plastic content. The values are very close to the original ones because the extent of crosslinking of rubber phase is retained even after remelting due to dynamic vulcanization.

Fig IV (d) 7 Variation of Tensile strength with Rubber content of reprocessed LLDPE/GW (P) blend

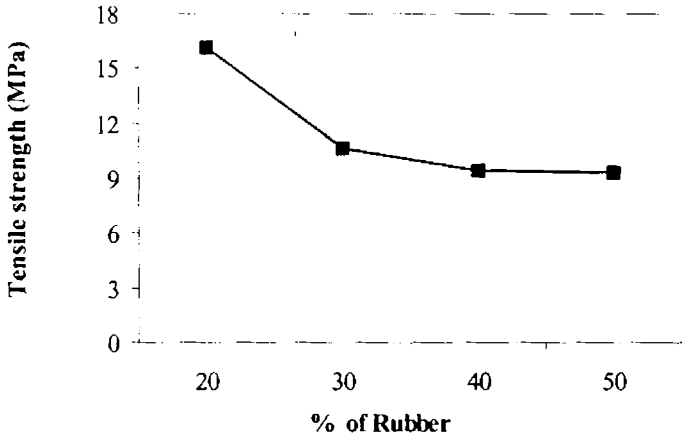


Fig IV (d) 9 shows the variation of tear strength with rubber content. Again the values are comparable with those of the original ones.

The impact strength values of all the LLDPE/GW (P) blends were found to be above 1 KJ/m. Presence of soft and elastomeric GW (P) along with highly flexible LLDPE leads to absorption of increased amount of energy during fracture, which resulted in high impact resistance.

Fig IV (d) 8 Variation of Elongation at break with Plastic content of reprocessed LLDPE/GW (P) blend

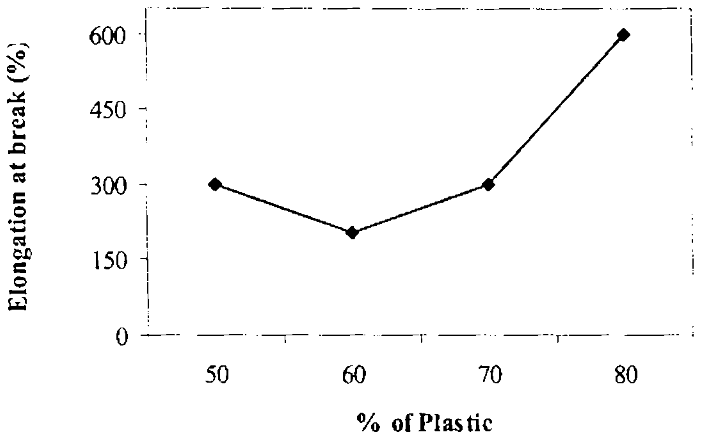


Fig IV (d) 9 Variation of Tear strength with Rubber content of reprocessed LLDPE/GW (P) blend

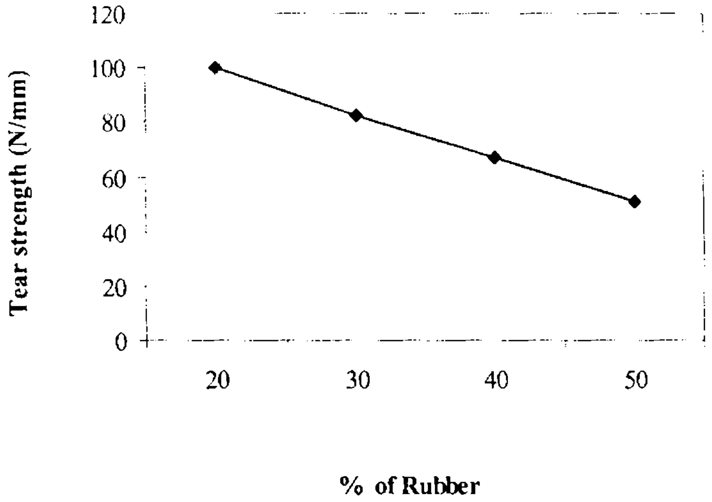


Fig IV (d) 10 shows the variation of viscosity (torque/rpm) with rubber of LLDPE/GW (P) blends, both uncrosslinked and dynamically crosslinked, measured on the Brabender Plasticorder at constant shear rate of 50 rpm. It is seen that as the rubber content increases, viscosity also increases in both the cases. Viscosity values of dynamically

Fig IV (d) 10 Variation of Torque/rpm with Rubber content of LLDPE/GW (P) blends

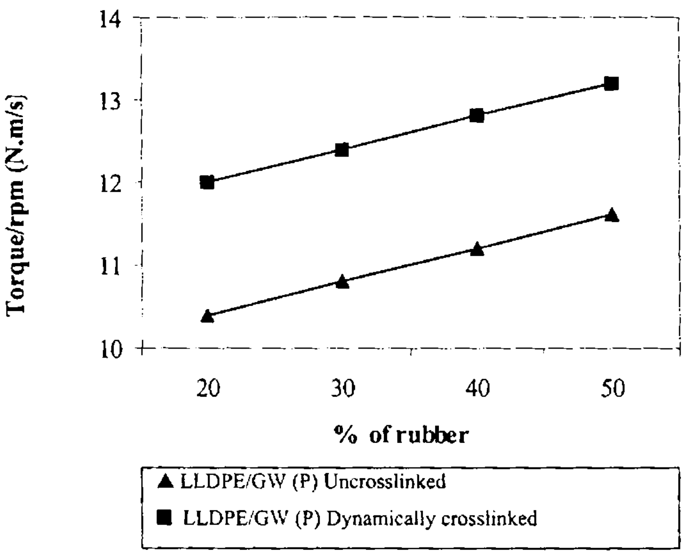
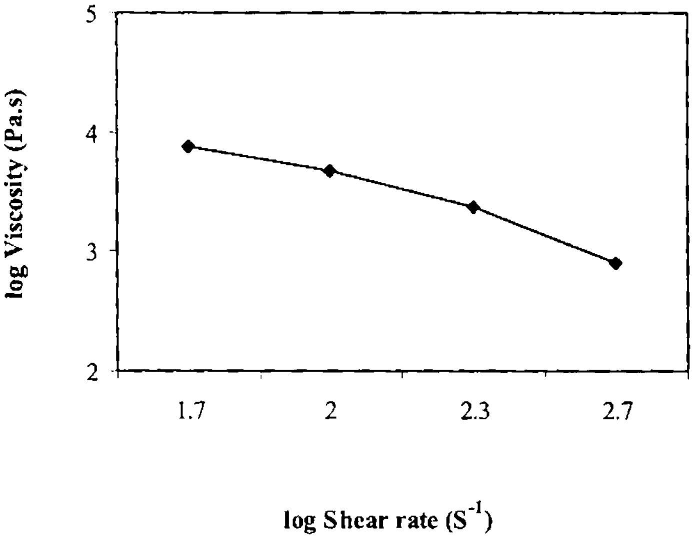


Fig IV (d) 11 Variation of Viscosity with Shear rate of 50/50 LLDPE/GW (P) blend



vulcanized blends are found to be higher than those of uncrosslinked blends. This is because of the higher torque developed during dynamic vulcanization.
Crosslinked rubber has higher viscosity compared to uncrosslinked rubber.

In Fig IV (d) 11, apparent viscosity is plotted against apparent shear rate of 50/50 LLDPE/GW (P) dynamically vulcanized blend, measured on HAAKE Rheoflixer V3.53. It is seen that as the shear rate increases viscosity decreases. This shows that the blend is pseudoplastic in nature (19).

Fig IV (d) 12 shows the variation of shear stress with shear rate of 50/50 LLDPE/GW (P) blend. As the shear rate increases, shear stress also increases as expected. This confirms the non-Newtonian behaviour of the blend.

Fig IV (d) 12 Variation of Shear stress with Shear rate of 50/50 LLDPE/GW (P) blend

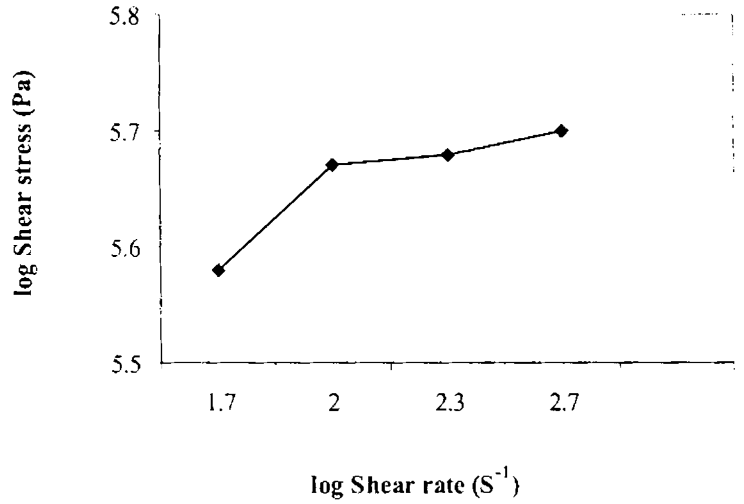


Table IV (d) 1 shows the value of pseudoplasticity index (n) and the variation of die swell ratio (d_e/d_c) with shear rate. As in the case of HDPE/GW (P), the increase in the die swell ratio with shear rate is very small that indicates the low deformation of the GW (P) phase. Again, the very low value of 'n' implies that the blend is pseudoplastic in nature.

Fig IV (d) 13 shows the variation of viscosity and shear stress with shear rate of 80/20 LLDPE/GW (P) dynamically vulcanized blend, measured on the Capillary Viscotester. The same trend as that of 50/50 blend is shown here also. i.e., as the shear rate increases, viscosity decreases and shear stress increases, indicating the non-Newtonian behaviour of the blend.

Table IV (d) 1 Variation of d_e/d_c with shear rate of LLDPE/GW (P) blend

Shear rate	Die swell ratio (d_e/d_c)	Pseudoplasticity index(n)
50	1.224	0.02
100	1.269	
200	1.277	
500	1.296	
1000	1.297	

Fig IV (d) 13 Variations of viscosity and Shear stress with Shear rate of 80/20 LLDPE/GW (P) blend

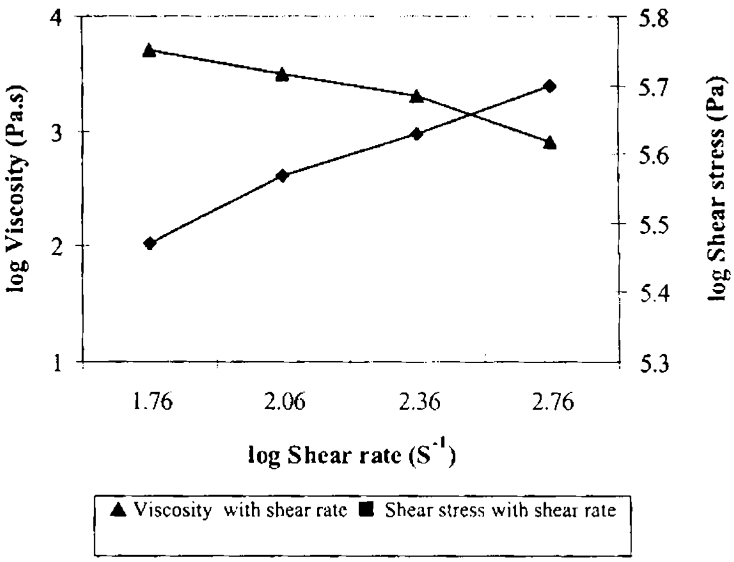


Fig IV (d) 14 shows the optical photographs of the extrudates of 80/20 LLDPE/GW (P) dynamically vulcanized blend, from the Capillary Viscotester. A rough surface is observed for extrudates at higher shear rates and smooth surface at lower shear rates. In this blend, at higher shear rates, the viscosity-shear rate profile resembles that of the plastic material as expected (23).

Elastomer/plastic blends are highly shear rate sensitive in respect to melt viscosity. Here, the difference in melt elasticities of the two phases [LLDPE and GW (P)] becomes higher at higher shear rates. Thus, the elastic recovery is difficult after the extrusion through the die. This difficulty is more for blends with dynamically crosslinked rubber phase.

Conclusions of studies on PE/modified waste blends

1. Blends of good mechanical properties and rheological behaviour can be developed from HDPE, LDPE and LLDPE and latex product waste modified with both MBT and Thiocarbanilide.

2. Among the blends, those from LLDPE and latex waste modified with thiocarbanilide show the best properties. Also, dynamic vulcanization of the rubber phase has enhanced the properties of the blends to a great extent. The peculiar elongation behaviour shown by LLDPE has very much influenced the elongation at break of the blends.

3. The best mechanical, rheological and remelt properties are given by the dynamically vulcanized 50/50 LLDPE/GW (P) blends. It is proposed as a novel thermoplastic elastomer that shows the properties of both thermoplastic and elastomer.

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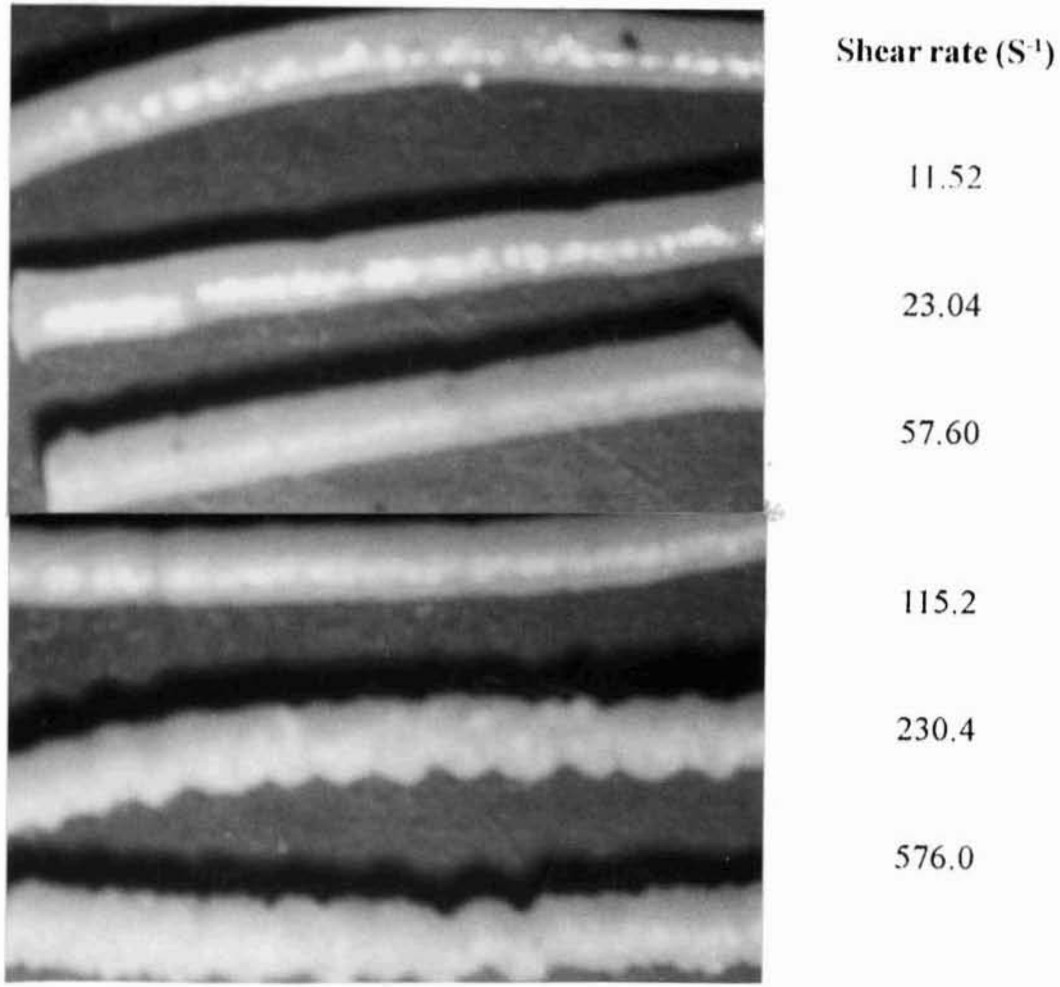
Fig IV(d) 14 Optical photographs of extrudates of 80/20 blends of



LLDPE / GW (P)

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CHAPTER V 000000000

CHAPTER V (a)

THERMOPLASTIC ELASTOMERS FROM HIGH DENSITY POLYETHYLENE AND BUTYL RUBBER

Introduction

Thermoplastic elastomers based on polyethylene and butyl rubber (IIR) have been reported by various investigators (1-6). Grafting of butyl rubber onto polyethylene was done by Hartman and coworkers (7) to develop a series of elastomeric thermoplastics called ET polymers. The Allied Chemical Corporation also has commercialized four compositions of thermoplastic elastomers based on grafted butyl rubber onto polyethylene. Blends of polyethylene and butyl rubber are becoming increasingly important because they can be processed like plastic but possess rubber-like properties.

In this study, we have developed a thermoplastic elastomer by blending high density polyethylene with butyl rubber. Both unvulcanized and vulcanized blends were prepared. Vulcanization to the butyl rubber phase was given dynamically with sulphur as the vulcanizing agent. Since the extent of unsaturation is very low in butyl rubber, only a small quantity of sulphur is required for the crosslinking of the butyl phase.
The mechanical, rheological and morphological properties of the blends were evaluated.

Experimental

Crosslinked and uncrosslinked blends of butyl rubber and high density polyethylene were prepared as per the formulation in Table V (a) 1. Mixing was done on a Brabender Plasticorder model PL 3S at 160^0C and 50 rpm rotor speed. HDPE was melted first in the mixer for 4 minutes and then butyl rubber was added and mixing was continued for 4 more minutes. Then the ingredients were added in regular intervals allowing thorough mixing of the whole materials for another 4 minutes. Then the mix was taken out and sheeted on a laboratory mixing mill at 20 mm nip-gap setting. This sheeted material was cut into small pieces and again mixed in the Plasticorder at 160^0C for 4 minutes so as to get uniform dispersion of the ingredients.

After mixing, the blends were compression moulded in an electrically heated hydraulic press at 180^{0}C for 6 minutes. Specially fabricated mould was used here also as in previous cases and cooling was done by circulating cold water.

Mechanical properties, rheological and morphological behaviours were studied as per the ASTM methods.

Results and Discussion

1. Mechanical properties

Fig V (a) 1 shows the variation of tensile strength with butyl rubber content of uncrosslinked and dynamically crosslinked HDPE/butyl blends. In both the cases, it is seen that, as the rubber content decreases, tensile strength increases. The tensile strength values of dynamically vulcanized blends are found to be higher than those of the unvulcanized blends. The reason may be that on dynamic vulcanization, the extent of crosslinking has been increased. The effect of dynamic vulcanization on mechanical properties has already been reported (8). On dynamic vulcanization, the size of the rubber particles decreases and the rubber phase gets uniformly dispersed in the plastic phase.

Fig V(a) 1 Variation of Tensile strength with Rubber content of HDPE/ Butyl blends

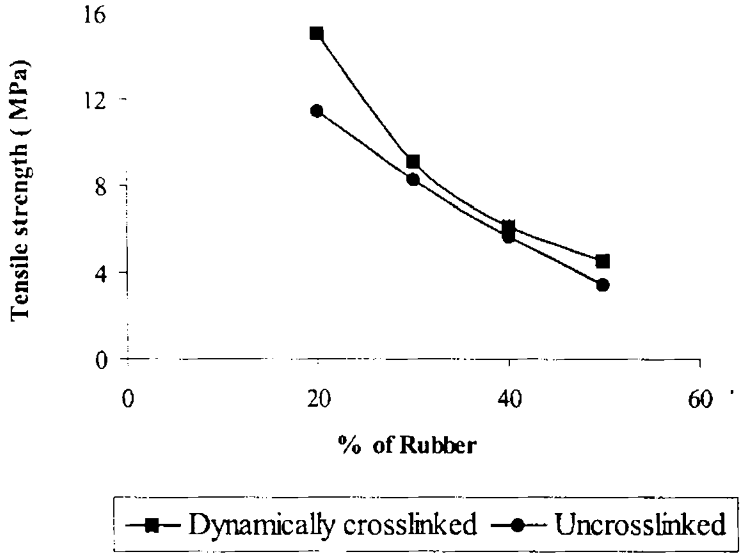


Fig V (a) 2 shows the elongation at break with rubber content of both vulcanized and unvulcanized HDPE/butyl blends. As the rubber content increases, elongation percentage also increases. A significant increment in elongation percentage is observed for dynamically vulcanized blends. The advantage of dynamic crosslinking is more prominent in this property. The amorphous nature of butyl rubber changes to a more rubbery nature on dynamic crosslinking, which results in higher elongation.

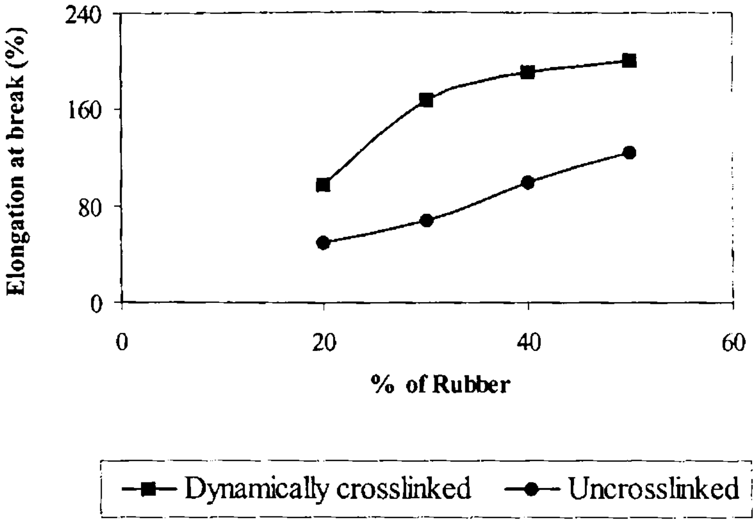


Fig V(a) 2 Variation of Elongation at break with rubber content of HDPE/ Butyl blends

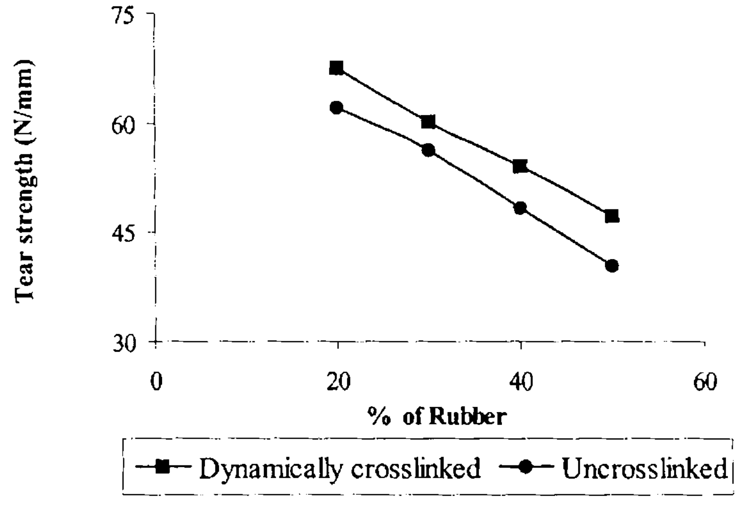


Fig V(a) 3 Variation of Tear strength with rubber content of HDPE/ Butyl blends

Fig V (a) 3 shows the relationship of tear strength with rubber content of the blends. The values are found to be decreasing with increase in rubber content. Again the dynamically vulcanized blends show higher values.

In Fig V (a) 4, Young's Modulus is plotted against rubber content. Modulus values are found to be decreasing with increase in rubber content. The plastic rich compositions have higher modulii and also dynamic crosslinking increases the modulii of all compositions as expected.

Fig V (a) 5 shows the variation of hardness with plastic content. As the plastic content increases, hardness also increases. The higher hardness of HDPE increases the hardness of the blend. Also, dynamic crosslinking imparts a higher degree of hardness to the rubber phase. So the dynamically vulcanized blends show higher values of hardness.

Fig V(a) 4 Variation of Young's modulus with rubber content of HDPE/ Butyl blends

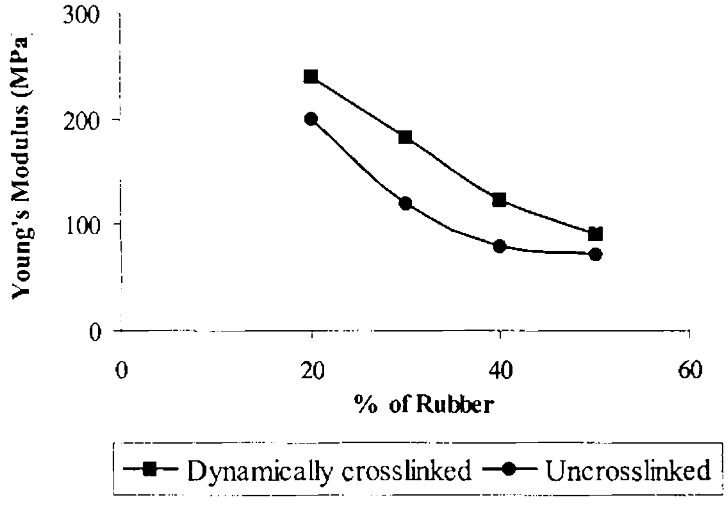


Fig V(a) 5 Variation of Hardness with rubber content of HDPE/ Butyl blends

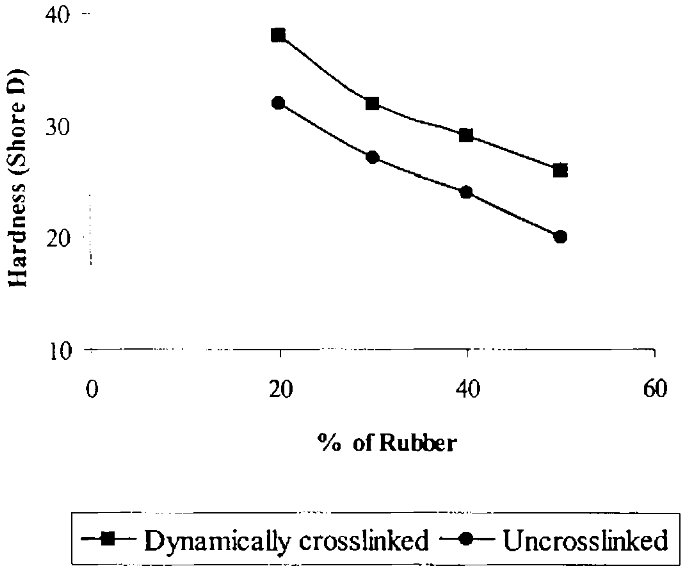


Fig V (a) 6 shows the variation of impact strength with % of rubber of the blends. The values increases with increase in rubber content. Dynamic vulcanization has enhanced the impact strength values very much. The 50/50 dynamically crosslinked blend shows an impact strength of nearly 1 KJ/ m.

In Fig V (a) 7, the melt flow indices of the blends are plotted against plastic content. In both the cases, as the plastic content increases, MFI also increases. Dynamic vulcanization decreases the MFI values significantly. This due to the increased extent of crosslinking on dynamic vulcanization, which results in decreased flexibility and flow of the rubber phase.

Fig(a) 6 Variation of Impact strength with rubber content of HDPE/ Butyl blends

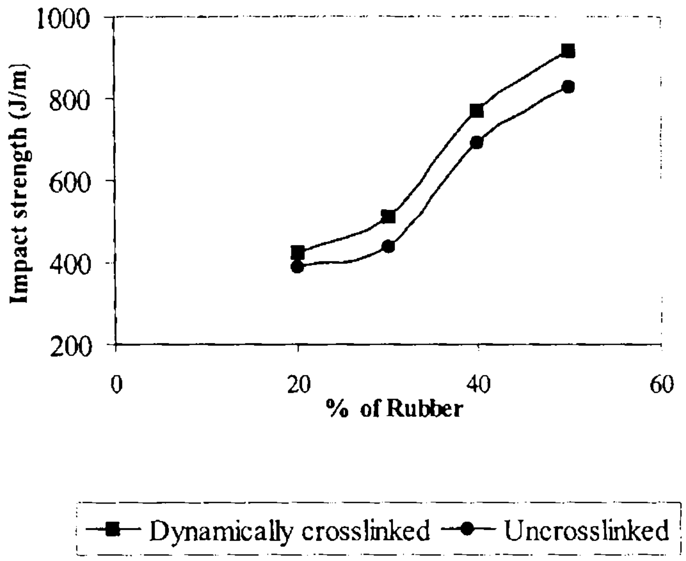


Fig V(a) 7 Variation of Melt Flow Index with plastic content of HDPE/ Butyl blends

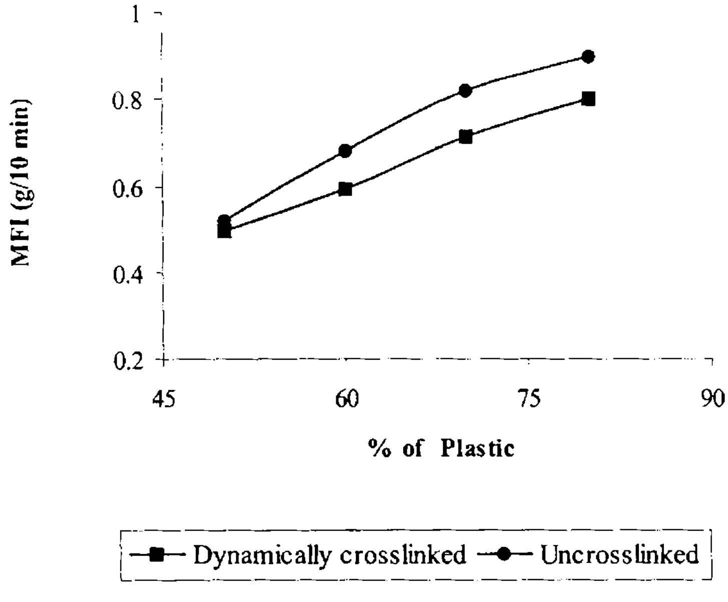


Fig V (a) 8 shows the permanent set values plotted against rubber content. Set values decrease with increase in rubber content. Dynamic vulcanization significantly decreases the permanent set values. This is also attributed to the increased extent of crosslinking on dynamic vulcanization that prevents the rubber phase from deformation after the removal of applied stress.

Fig V(a) 8 Variation of Permanent set with rubber content of HDPE/ Butyl blends

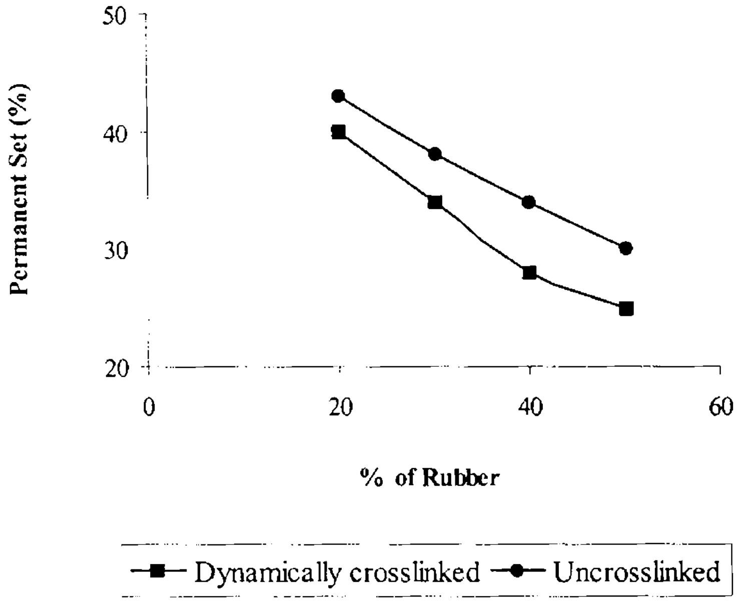


Fig V(a) 9 Variation of tensile strength and elongation at break with rubber content of aged HDPE/ Butyl blends

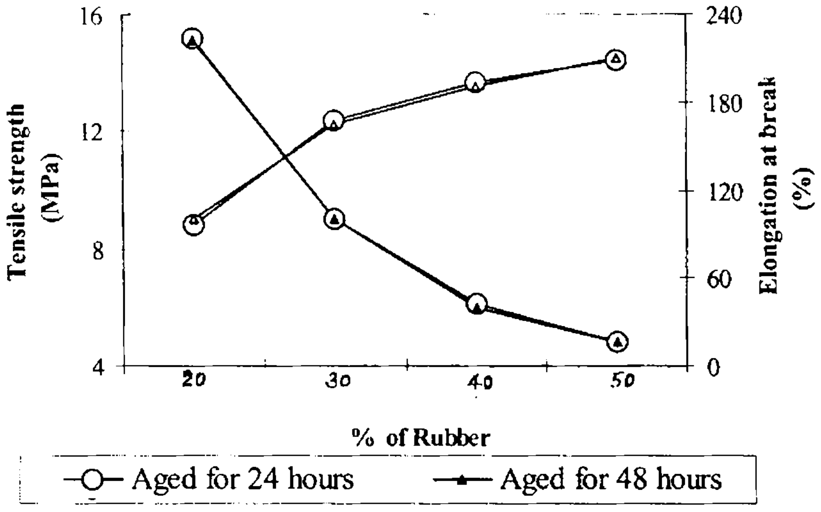


Fig V (a) 9 shows the variation of tensile strength and elongation at break with rubber content of dynamically vulcanized HDPE/butyl blends after 24 and 48 hours of ageing at 100^0C. It can be seen that ageing has not affected the properties even after 48 hrs at 100^0C.

Fig V (a) 10 shows the tensile fractographs of 80/20 HDPE/butyl, crosslinked and uncrosslinked blends. For the crosslinked HDPE/ butyl blend, the initiation of fracture is propagated as short-curved lines as the shear advances. As a result of dynamic vulcanization, the size of the rubber particles is reduced and the dispersion of the rubber phase in the blend is improved. These crosslinked particles resist to high deformation and thus restrict the flow under stress. This results in many short-curved shear lines on the fracture surface of the dynamically vulcanized blend. The deformation of the uncrosslinked blend is higher resulting in multidirectional shear lines.

Table V (a) 2 shows the physical properties of the remelted samples of dynamically crosslinked HDPE/butyl blends. It is observed that remelting and remoulding has not affected the mechanical properties, as the values are more or less unchanged. The reason may be that the dynamic vulcanization has enabled the butyl rubber phase to retain its extent of crosslinking and hence the properties.

Table V (a) 1 Formulation for PE/IIR blends

Blend proportion	PE	IIR	ZnO	Stearic acid	MBTS	ZDC	S
50/50	20	20	1	0.5	0.1	0.2	0.1
60/40	24	16	0.8	0.4	0.08	0.16	0.08
70/30	28	12	0.6	0.3	0.06	0.12	0.06
80/20	32	8	0.4	0.2	0.04	0.08	0.04

Table V (a) 2 Physical properties of remelted, dynamically vulcanized HDPE/IIR blends

Blend proportion	Tensile strength (MPa)	Tear strength (N/mm)	Elongation at break (%)	Young's modulus (MPa)	Hardness (Shore D)	Impact strength (J/m)
50/50	4.50	45.5	198	89	25	910
60/40	6.05	53.1	190	120	28	765
70/30	9.10	59.2	167	182	32	508
80/20	15.10	67.1	97	238	38	422

2. Rheological behaviour of the blends

Fig V (a) 11 shows the variation of torque/rpm, which represents viscosity with rubber content of crosslinked and uncrosslinked blends measured on the Brabender Plasticorder. As the rubber content increases, viscosity also increases as expected. Higher viscosity values are observed for the dynamically crosslinked blends. This is because of the higher torque developed during dynamic vulcanization. It implies that the proportion of the elastomer phase in the blend and the extent of dynamic crosslinking have a profound influence on the viscosity of the blends.

Fig V (a) 12 shows the variation of torque/rpm with rpm of 50/50 HDPE/butyl, crosslinked and uncrosslinked blends. The torque that represents the viscosity decreases with the increase in rpm, which represents the shear rate. This shows that the blend is non-Newtonian in behaviour. Viscosity values of the crosslinked blends are higher, resulting from higher torque values.
Viscosity is related to molecular size. The crosslinked rubber will have a higher molecular size compared to the uncrosslinked rubber.

Fig V(a) 12 Variation of torque/ rpm with rpm of 50/50 HDPE/ Butyl blneds

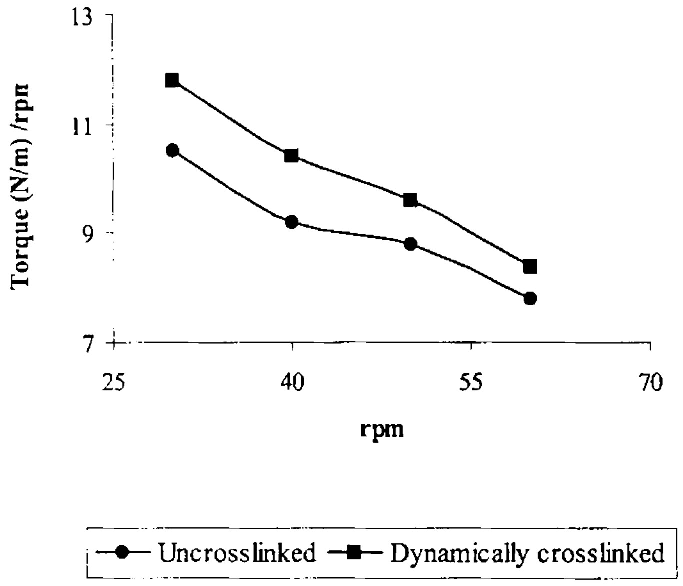
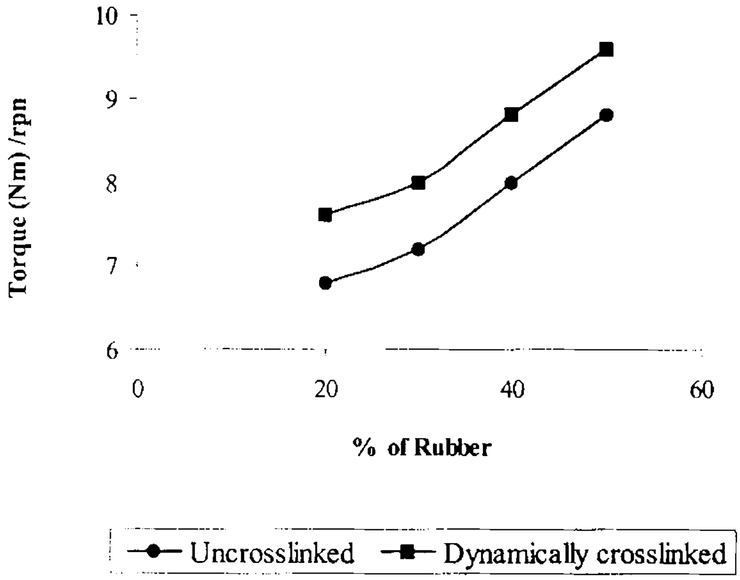
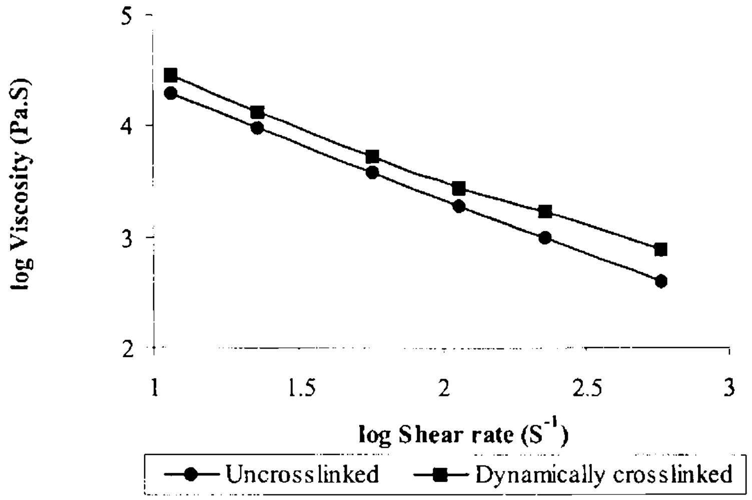


Fig V(a) 11 Variation of torque/ rpm with rubber content of HDPE/ Butyl blends



In Fig V (a) 13, the relationship between shear rate and viscosity of 80/20 HDPE/butyl blends is shown. As the shear rate increases, viscosity decreases, which proves the non-Newtonian behaviour of the blends. The crosslinked blend shows higher values due to the increased shear stress. The reason is same as that for Fig. V (a) 12.

Fig V(a) 13 Variation of Viscosity with Shear rate of 80/20 HDPE/ Butyl blends



In Fig V (a) 14, shear stress is plotted against shear rate of 80/20 HDPE/butyl blends. As the shear rate increases, shear stress also increases. This confirms the pseudoplastic behaviour of the blends (9). Again, higher values are exhibited by the dynamically vulcanized blends.

Fig V(a) 14 Variation of Shear stress with Shear rate of 80/20 HDPE/ Btuyl blends

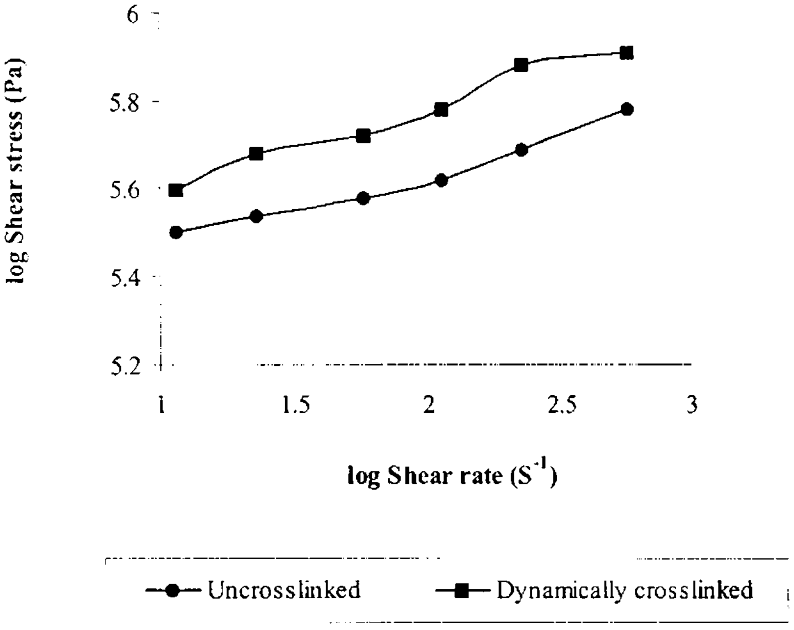


Fig V (a) 15 and V (a) 16 show the optical photographs of the extrudates of 80/20 HDPE/butyl uncrosslinked and crosslinked blends respectively. As the shear rate increases, a slight deformation of the extrudate surface is observed in both the cases.

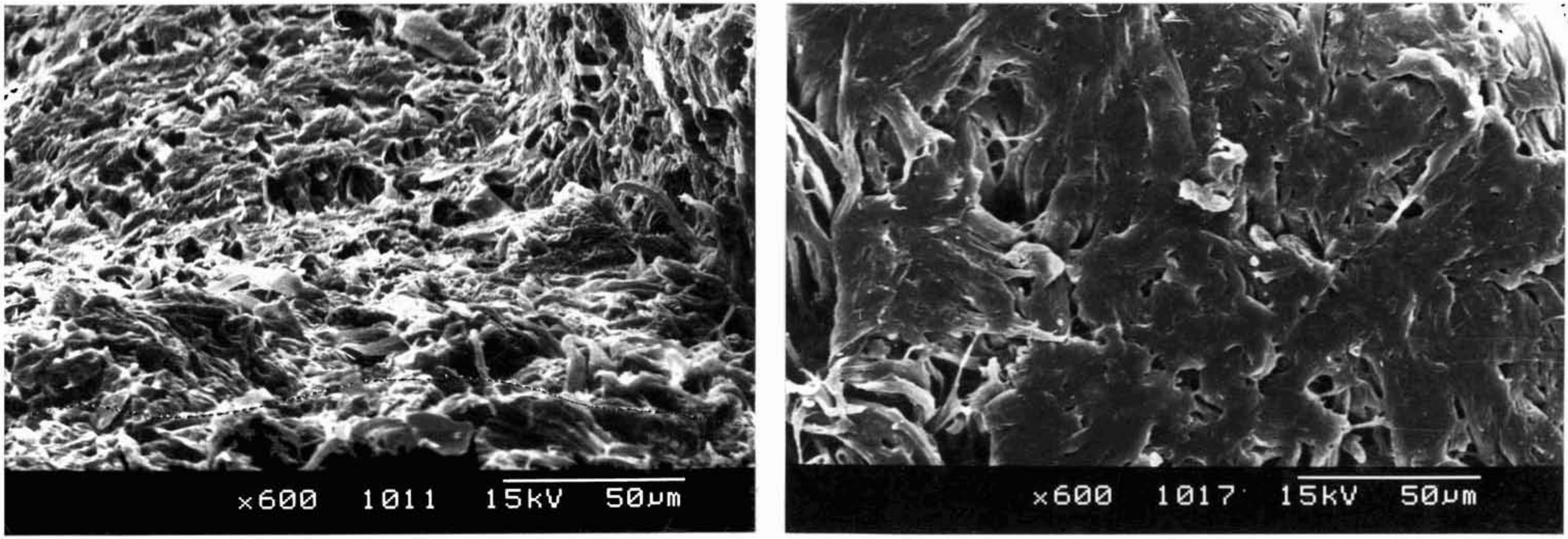
At lower shear rates, the surfaces of the extrudates appear smoother. Generally, the melt rheology of an elastomer-plastic blend composition with higher plastic content is related to that of the plastic material. At higher shear rates, the viscosity-shear rate profile of the blend resembles that of the plastic material (10). In this case, there is a difference in the rate of flow of the rubber and plastic phases at various shear rates. At higher shear rates, this difference increases a little, resulting in the deformation of the extrudates surface. The flow rate difference between the rubber- plastic phases is still higher for the dynamically vulcanized blend and hence deformation increases further.

Table V (3) d_e/d_c and n of HDPE/ Butyl blends

Shear rate (S^{-1})	**Die swell ratio (HDPE/IIR)**		**Pseudoplasticity Index, n**
	Uncrosslinked	**Crosslinked**	
11.52	2.11	1.86	0.313
23.04	2.18	1.89	
57.60	2.25	1.91	
115.2	2.29	1.95	
230.4	2.36	1.96	
576	2.41	1.98	

Table V (a) 3 shows the die swell ratios of 80/20 HDPE/ Butyl blends at various shear rates. The swell ratio increases slightly with shear rate due to the greater orientation of the particles at higher shear rates. Dynamically vulcanized blend has lower die swell ratios than the unvulcanized blend, which may attributed to its better elastic recovery. The lower value of n indicates the pseudoplastic nature of the blend.

Fig V(a) 10 Tensile fractographs of 80/20 blends of

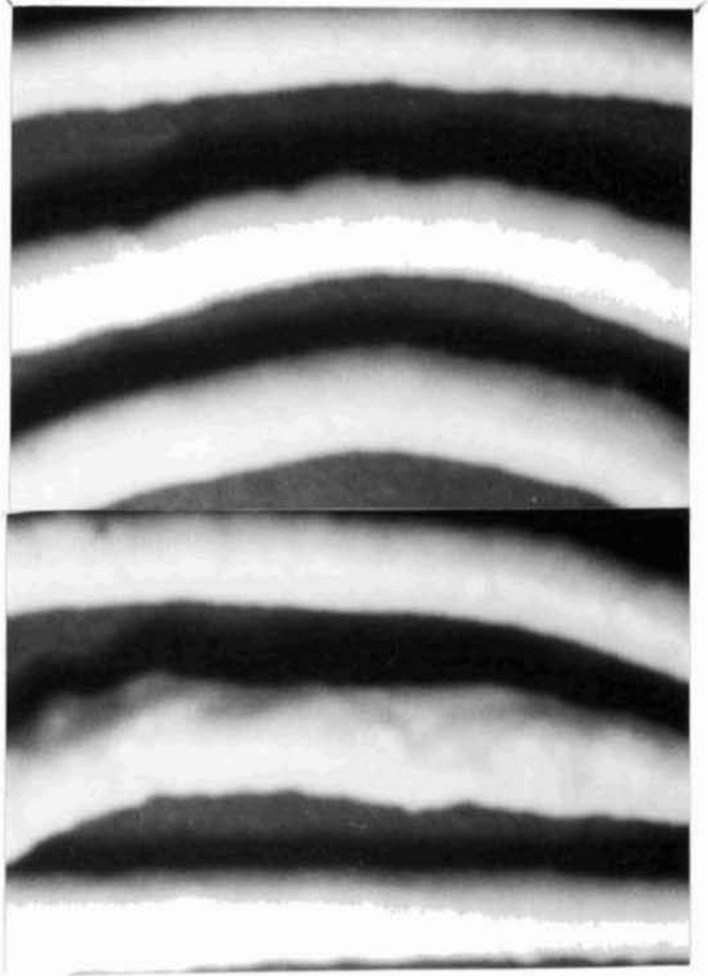


HDPE / IIR (Dynamically crosslinked)

HDPE / IIR (Uncrosslinked)

Optical photographs of extrudates of 80/20 blends of

Fig V(a) 15



HDPE / IIR (Dynamically crosslinked)

Shear rate (S^{-1})

115.2

230.4

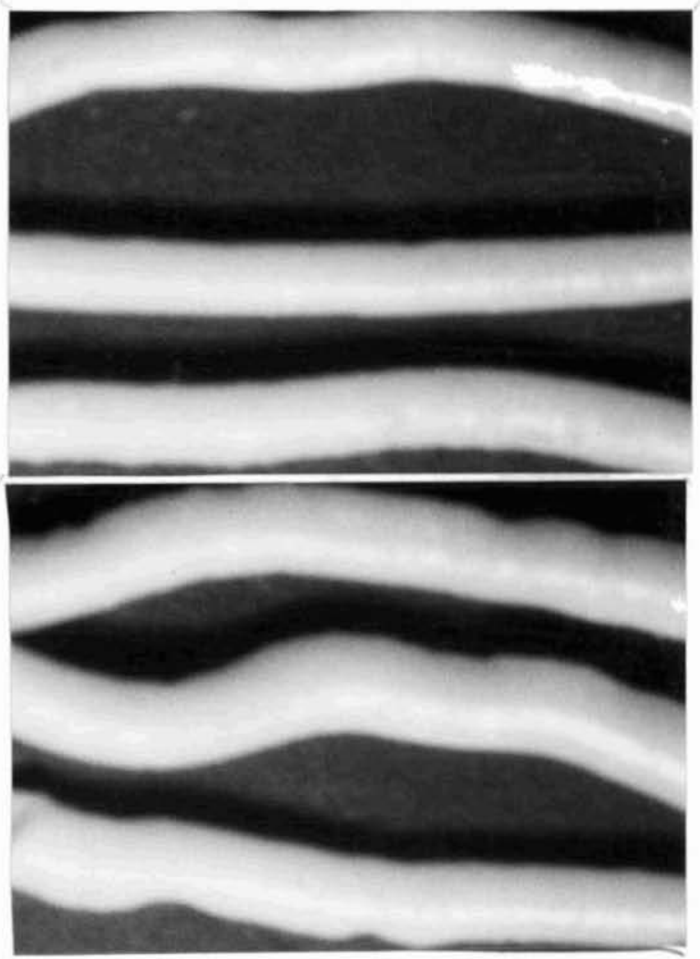
576.0

1153.0

1728.0

2304.0

Fig V(a) 16



HDPE / IIR (Uncrosslinked)

CHAPTER V (b)

BLENDS OF LOW DENSITY POLYETHYLENE WITH BUTYL RUBBER

Experimental

LDPE was blended with butyl rubber in the Brabender Plasticorder model PL 3S. Both crosslinked and uncrosslinked blends were prepared. The formulation and procedure was same as in V (a). Mechanical, rheological and morphological properties were studied according to the ASTM standard procedure.

Results and Discussion

1. Mechanical properties

Fig V(b) 1 Variation of Tensile strength with rubber content of LDPE/ Butyl blends

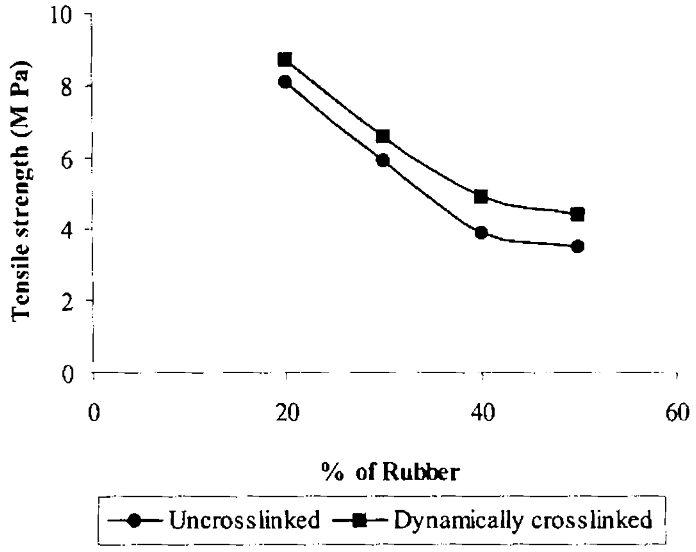


Fig V (b) 1 shows the variation of tensile strength with rubber content of both crosslinked and uncrosslinked LDPE/butyl blends. Tensile strength values are found to decrease as the rubber content increases. On dynamic vulcanization, the values increase (8) and the increment is higher for blends with higher rubber contents. Since, only a little amount of sulphur is accepted owing to the low extent of unsaturation in butyl rubber, and also due to the comparatively lower crystallinity of LDPE than HDPE, high values for tensile strength are not exhibited by the dynamically vulcanized blends.

Fig V(b) 2 Variation of elongation at break with % of Rubber of LDPE/ Butyl blends

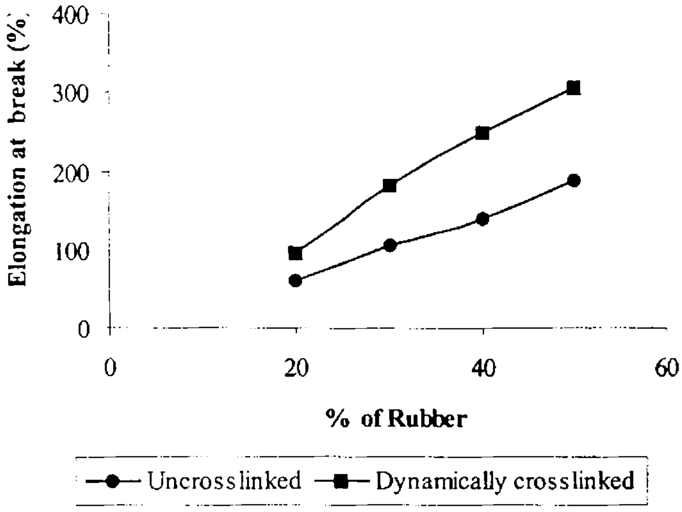


Fig V (b) 2 shows the plot of elongation at break against rubber content of the blends. As the rubber content increases, elongation percentage also increases. The values still increase on dynamic vulcanization. Again the advantage of dynamic crosslinking is more in blends with higher rubber content. The elongation values are found to be higher than those of the HDPE/butyl blends. This may be attributed to the lower crystallinity of LDPE compared to that of HDPE.

Fig V(b) 3 Variation of Tear strength with % of rubberof LDPE/ Butyl blends

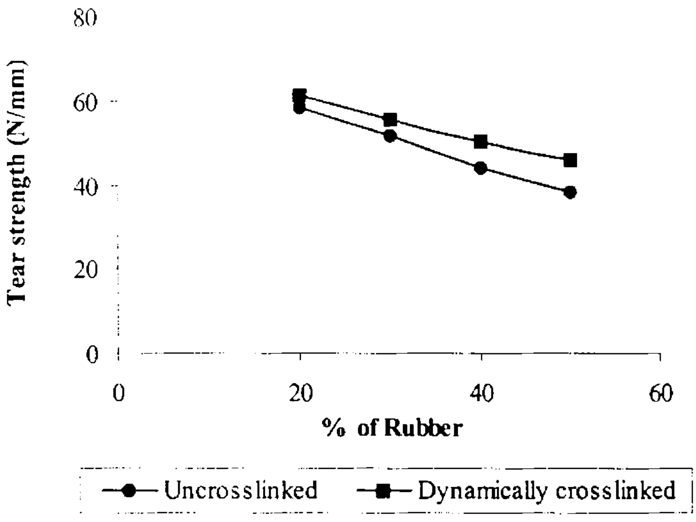


Fig V (b) 3 is the plot of tear strength against rubber content of the blends. With the increase in rubber content, tear strength decreases in both the cases and the crosslinked blends exhibit higher values here also.

Fig V(b) 4 Variation of Young's Modulus with % of Rubber of LDPE/ Butyl blends

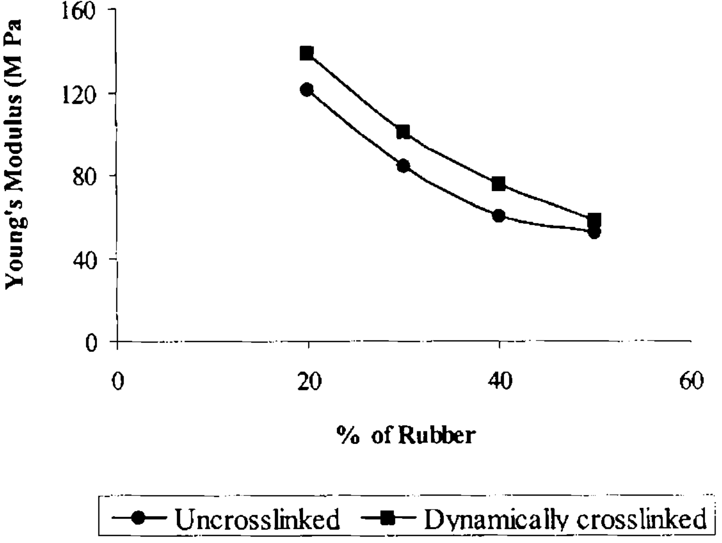


Fig V (b) 4 shows the relationship between Young's modulus and rubber content of the LDPE/butyl blends and Fig V (b) 5 gives the relationship between hardness and rubber content. As the rubber content increases, the corresponding Y-axis value decreases. When the plastic content is increased in the blend, the crystallinity of the blend is also increased. This causes higher modulus and hardness values of blends with higher plastic content. Dynamic vulcanization of the blends imparts some extent of crosslinking to the butyl phases, which in turn enhances the modulus and hardness values.

Fig V(b) 5 Variation of Hardness with % of Rubber of LDPE/Butyl blends

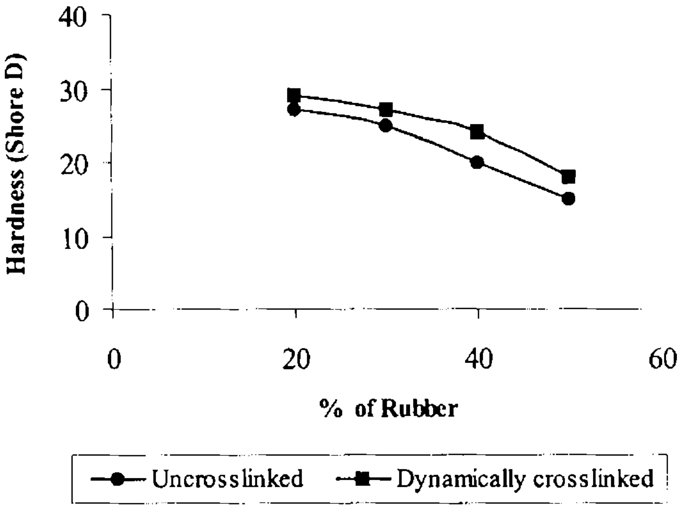
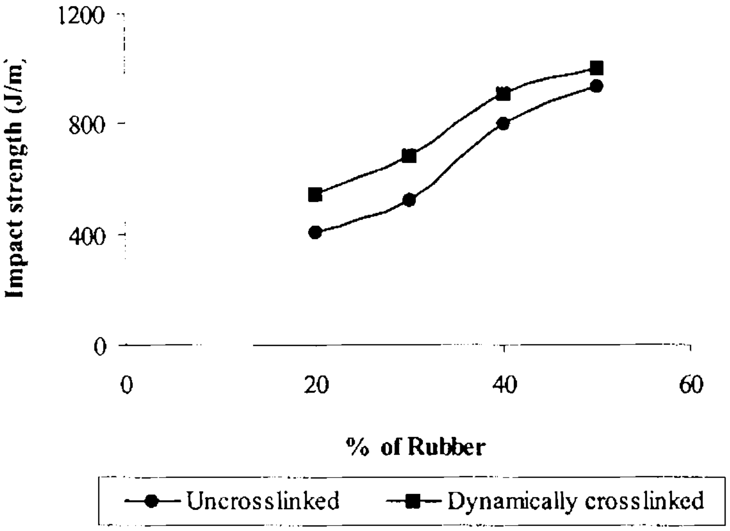


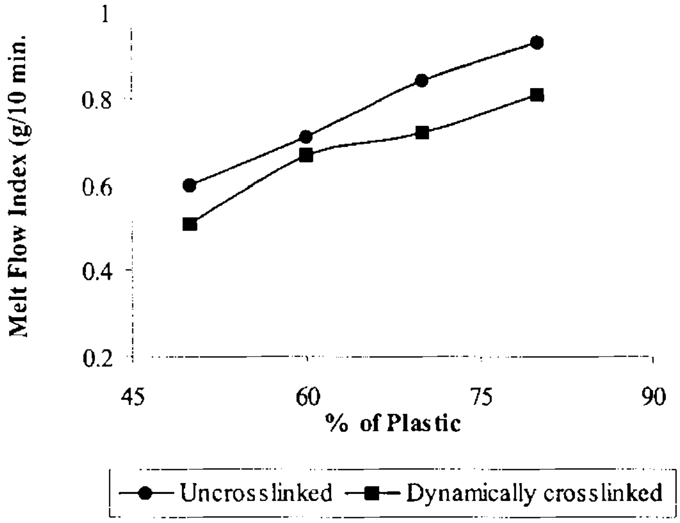
Fig V (b) 6 shows the variation of impact strength with rubber content of both the types of blends. It is seen that at higher rubber contents, impact strength also is higher. Dynamically vulcanized 50/50 LDPE/butyl blend shows a value greater than 1 KJ/m.

Fig V(b) 6 Variation of Impact strength with % of Rubber of LDPE/ Butyl blends



The impact strength values of LDPE/butyl blends are found to be higher than those of the HDPE/butyl blends and the reason may be the lower crystallinity of LDPE compared to that of HDPE.

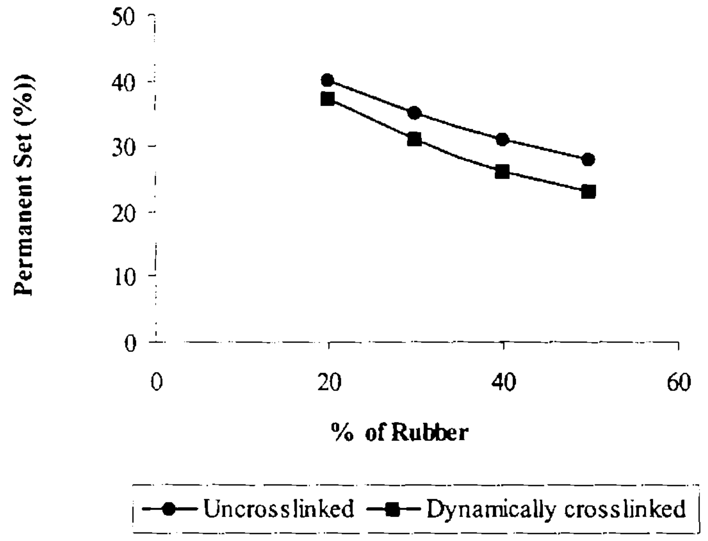
Fig V (b) 7 Variation of MFI with % of Plastic content of LDPE/Butyl blends



In Fig V (b) 7, melt flow indices of the blends are plotted against plastic content. As the plastic content increases, MFI also increases significantly. Dynamic vulcanization decreases the melt flow, due to the crosslinked rubber phase.

Fig V (b) 8 gives the relationship between permanent set and rubber content of the LDPE/butyl blends. As the rubber content increases, permanent set values decrease.

Fig V (b) 8 Variation of Permanent Set with % of Rubber of LDPE/Butyl blends



The advantage of dynamic crosslinking is very significant here. On dynamic crosslinking, the set values decrease considerably. The elastomeric property of the butyl rubber phase must have been enhanced through dynamic vulcanization.

Fig V (b) 9 Variation of Tensile strength with % of Rubber of aged LDPE/Butyl blends

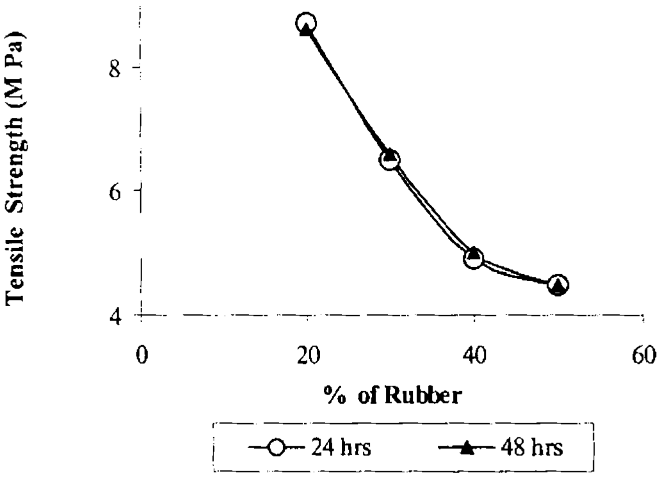


Fig V (b) 9 shows the variation of tensile strength with rubber content of the aged samples of dynamically crosslinked LDPE/butyl blends, after 24 and 48 hours of ageing at 100^{0}C. It is clear that the values are more or less the same as those of the unaged samples. In some cases, a slight increase in the values is observed. This may be due to the completion of vulcanization on prolonged heating, as in the case of HDPE/butyl blends.

Fig V (b) 10 Variation of Elongation at Break with % of Rubber of aged LDPE/Butyl blends

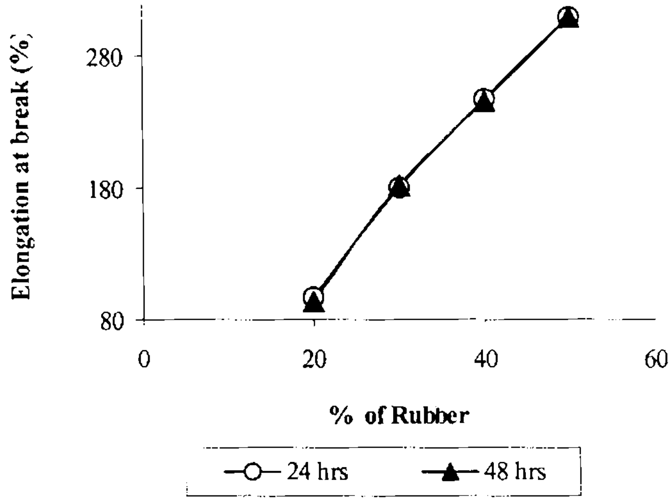


Fig V (b) 10 gives the plot of elongation at break with rubber content of the aged samples. Again the values are found to be same as of the original ones.

Table V (b) 1 shows the mechanical properties of the reprocessed blends of dynamically vulcanized LDPE/butyl blends. It is found that the properties of the blends are not much affected by reprocessing. This is the characteristic property of thermoplastic elastomers, as they can be reprocessed without change in properties.

Table V (b) 1 Mechanical Properties of remelted and remoulded blends of dynamically vulcanized LDPE/IIR

Blend ratio	Tensile strength (MPa)	Elongation at break (%)	Tear strength (N/mm)	Young's Modulus (MPa)	Hardness (Shore D)	Impact strength (J/m)
50/50	4.1	292	44.9	56	17	>1000
60/40	4.8	239	48.8	74	23	904
70/30	6.6	162	55.0	102	27	670
80/20	8.7	95	62.0	138	29	543

2. Rheological properties

Fig V (b) 11 shows the variation of torque/rpm which denotes viscosity, with rubber content of the crosslinked and uncrosslinked blends of LDPE/butyl, done on the Brabender Plasticorder. With the increase in rubber content, viscosity also increases, as expected. Higher viscosity values are exhibited by the dynamically crosslinked blends because of the higher torque developed during dynamic vulcanization. The influence of elastomer proportion and dynamic crosslinking on viscosity is evidenced here also as in HDPE/butyl blends.

Fig V (b) 11 Variation of torque/ rpm with % of Rubber of 80/20 LDPE/Butyl blends

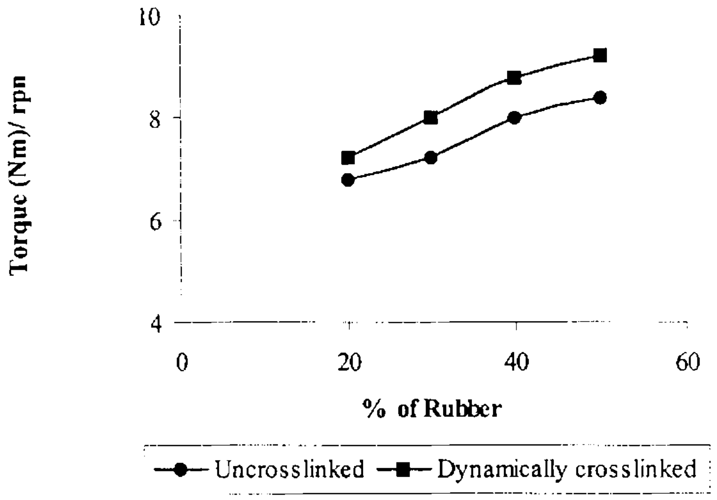


Fig V (b) 12 Variation of Torque/rpm with rpm of 50/50 LDPE/Butyl blends

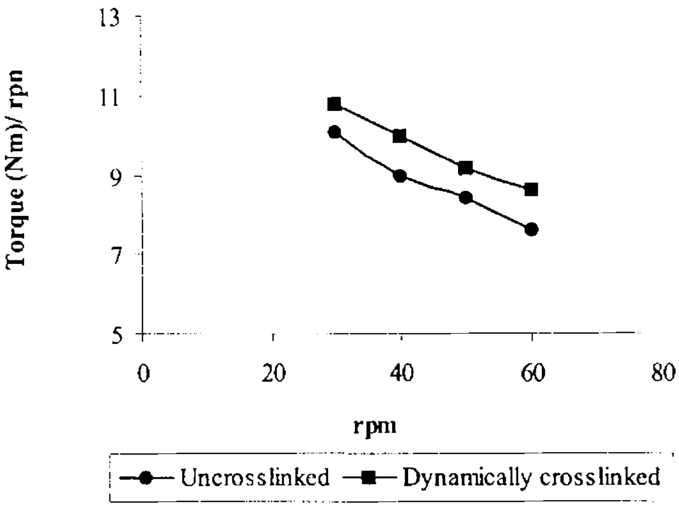


Fig V (b) 12 shows the variation of torque/rpm with rpm of 50/50 LDPE/butyl blends. The torque/rpm that represents the viscosity decreases with increase in rpm that represents the shear rate. This implies that the blend is non-Newtonian in behaviour (9). Also, the dynamically crosslinked blend shows higher viscosity values. But the viscosity values are found to be lower than those of HDPE/butyl blends. This is attributed to the high crystallinity of HDPE.

Fig V (b) 13 Variation of Viscosity with Shear rate of 80/20 LDPE/Butyl blends

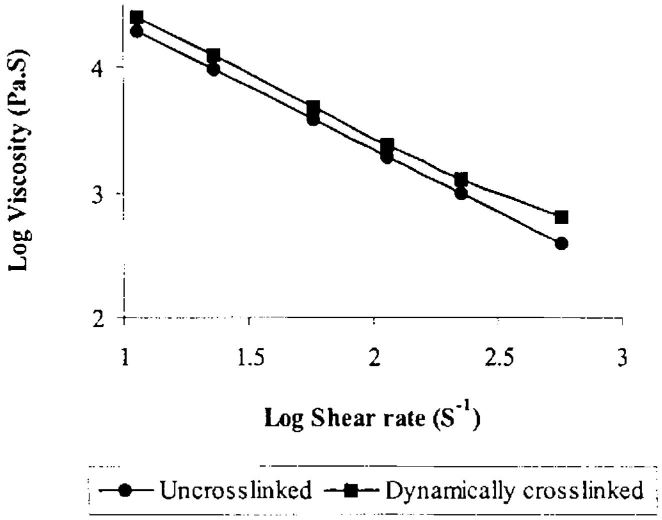
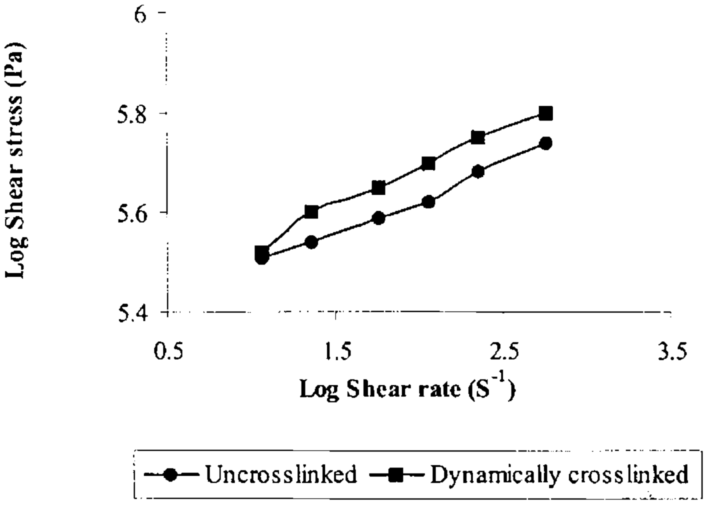


Fig V (b) 13 shows the variation of viscosity with shear rate of both crosslinked and uncrosslinked blends of 80/20 LDPE/butyl, measured on a capillary torque rheometer.

Fig V (b) 14 Variation of Shear stress with Shear rate of 80/20 LDPE/Butyl blends



It is found that as the shear rate increases, viscosity decreases. This again indicates the non-Newtonian behaviour of the blends. Due to the crosslinked nature of the rubber phase, higher shear stress is developed and that results in higher viscosity values.

Fig V (b) 14 gives the relationship between shear stress and shear rate, with the increase in shear rate, shear stress also increases but not proportionally. This confirms the pseudoplastic nature of the blends.

Figs V (b) 15 and V (b) 16 show the optical photographs of the extrudates of 80/20 LDPE/butyl, crosslinked and uncrosslinked blends respectively. As the shear rate increases, a slight deformation of the extrudate surface is observed in both the cases. At lower shear rates the surfaces of the extrudates appear more uniform. Generally, the melt rheology of an elastomer-plastic blend composition with higher plastic content is related to that of the plastic material. A difference in the rate of flow of the rubber and plastic phases occurs at various shear rates. As the shear rates increases, this difference still increases and this results in the deformation or non- uniformity of the extrudate surface. Owing to the lower crystallinity of LDPE compared to that of HDPE, the difference in the flow rates of LDPE and butyl phases will be higher. This results in more deformation of the extrudate surfaces of the LDPE/butyl blends. Dynamic crosslinking further increases the flow rate difference, which results in enhanced non- uniformity.

Fig V (b) 17 shows the tensile fractographs of LDPE/butyl blends. The nature of fracture in the dynamically crosslinked blend is such that as the shear increases, the fracture propagates unidirectional, where as in the uncrosslinked blend, it is multidirectional. Also the dynamically vulcanized blend is found to have a more uniform distribution of rubber phase in the plastic phase. Thus it may be assumed that upon dynamic crosslinking, the rubber particles become more resistant to high deformation which restricted their flow under stress.

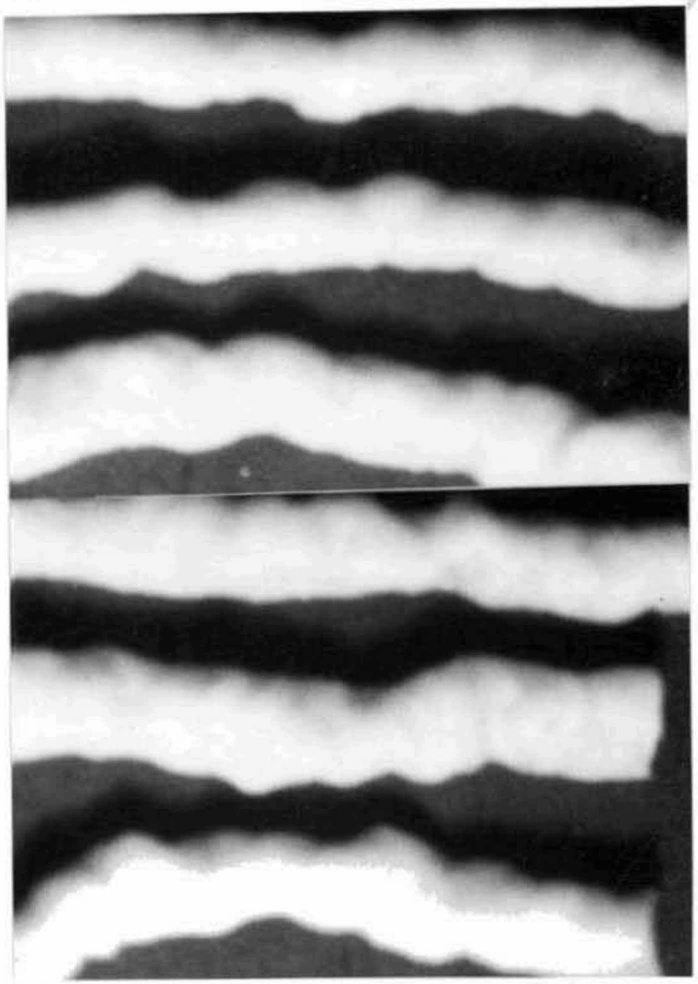
Table V (b) 2 shows the variation of die swell ratio with shear rate and the value of pseudoplasticity index of LDPE/butyl blends. The swell ratios of these blends are found to be lower than those of the HDPE/butyl blend due to the lower crystallinity of LDPE. Again, the value of n implies the pseudoplastic nature of the blends.

Table V (b) 2 Die swell ratio and pseudoplasticity index of LDPE/IIR blends

Shear rate (S^{-1})	Die swell ratio (LDPE/IIR) Crosslinked	 Uncrosslinked	n
11.52	1.75	1.83	0.278
23.04	1.79	1.86	
57.60	1.83	1.90	
115.2	1.85	1.92	
230.4	1.86	1.95	
576	1.88	1.96	

Optical photographs of extrudates of 80/20 blends of

Fig V(b) 15



LDPE / IIR (Dynamically crosslinked)

Shear rate (S^{-1})

115.2

230.4

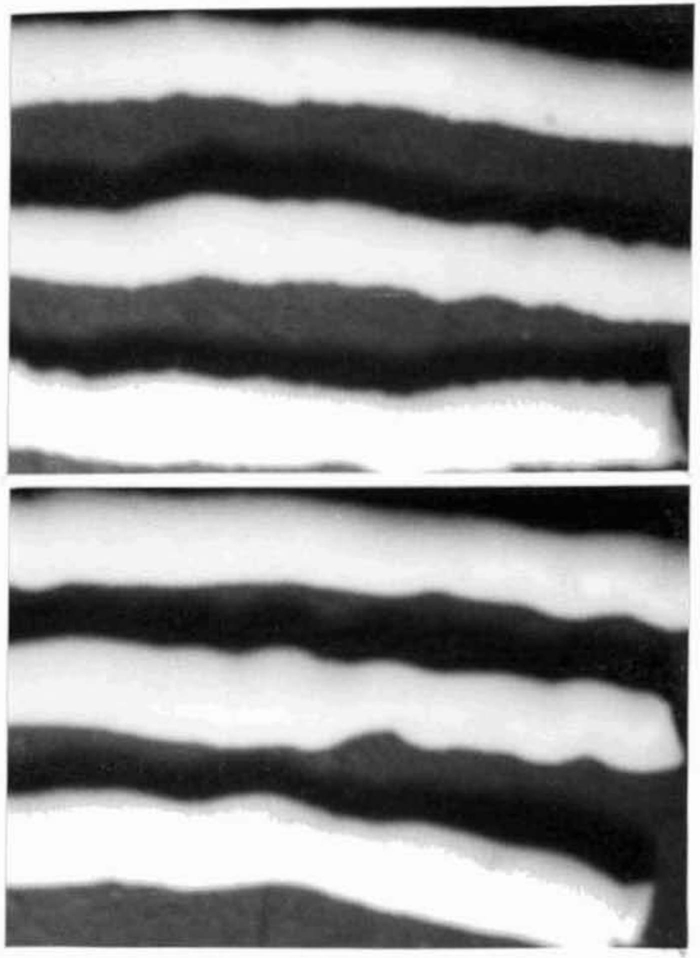
576.0

1153.0

1728.0

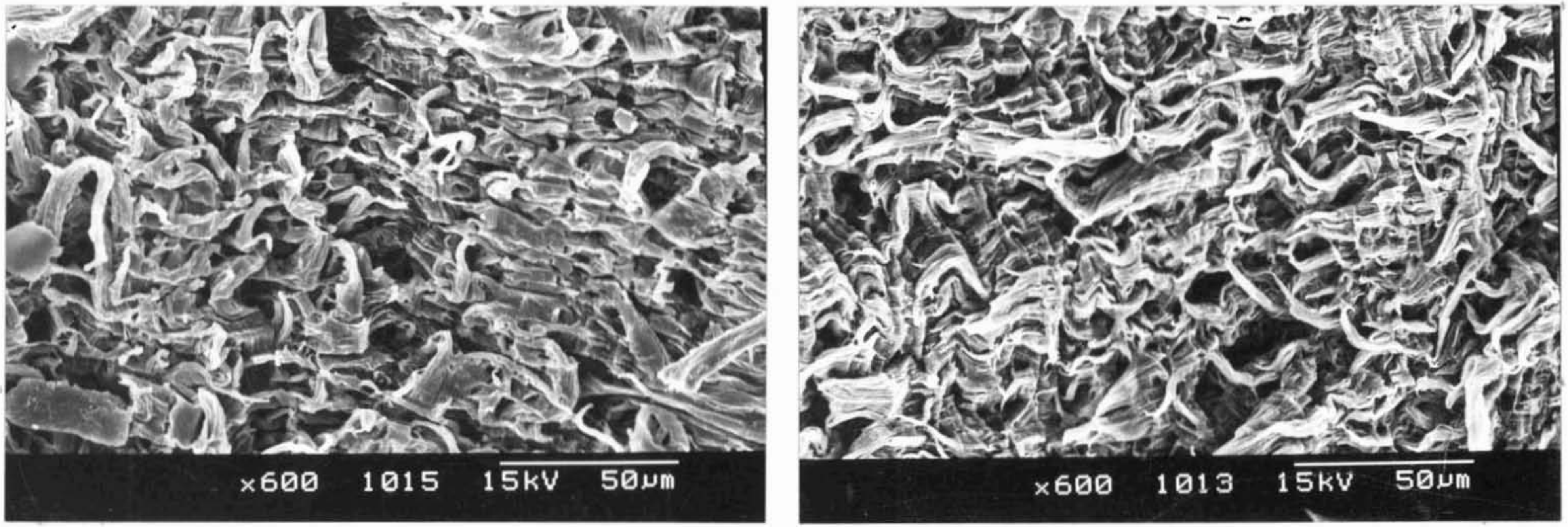
2304.0

Fig V(b) 16



LDPE / IIR (Uncrosslinked)

Fig V(b) 17 Tensile fractographs of 80/20 blends of



LDPE / IIR(Dynamically Crosslinked)

LDPE / IIR (Uncrosslinked)

CHAPTER V (c)

STUDIES ON LINEAR LOW DENSITY POLYETHYLENE/BUTYL RUBBER BLENDS

Introduction

The positive features of linear low density polyethylene (LLDPE) can be combined with the elastomeric properties of butyl rubber (IIR) to develop a novel thermoplastic elastomer. The excellent stretchability, high crystallinity [illegible] and LDPE, higher and better balanced impact resistance etc. of LLDPE can be effectively linked up with the high heat resistance, permanent set etc. of butyl rubber. Though the melt viscosity of LLDPE, associated with its long, regular molecular chains, is higher compared to that of HDPE and LDPE, comparable processability is observed when blended with butyl rubber.

In the present study, a set of thermoplastic elastomers have been developed based on different blend proportions of LLDPE and butyl rubber. Dynamic vulcanization was given to the rubber phase to prepare vulcanized blends. Mechanical, rheological and morphological properties of both vulcanized and unvulcanized blends were measured.

Experimental

Blends were prepared as per the formulation in Table V (a) 1 with LLDPE and butyl rubber. Sample sheets were molded on the hydraulic press at 150^{0}C for 5 minutes. Mechanical properties were measured as per ASTM methods. Rheological and morphological studies were also done.

Results and Discussion

1. Mechanical properties

Fig V (c) 1 shows the variation of tensile strength with rubber content of LLDPE/butyl blends, both vulcanized and unvulcanized. In both cases, as the rubber content increases, tensile strength decreases. On dynamic vulcanization, tensile strength values are found to increase significantly. This is attributed to the increased extent of crosslinking on dynamic vulcanization as expected (8). Due to the [illegible] better adhesion of the LLDPE and the butyl phases on dynamic vulcanization, higher tensile strength values are exhibited by the LLDPE/ butyl blends.

Fig V (c) 1 Variation of Tensile strength with rubber content of LLDPE/ Butyl blends

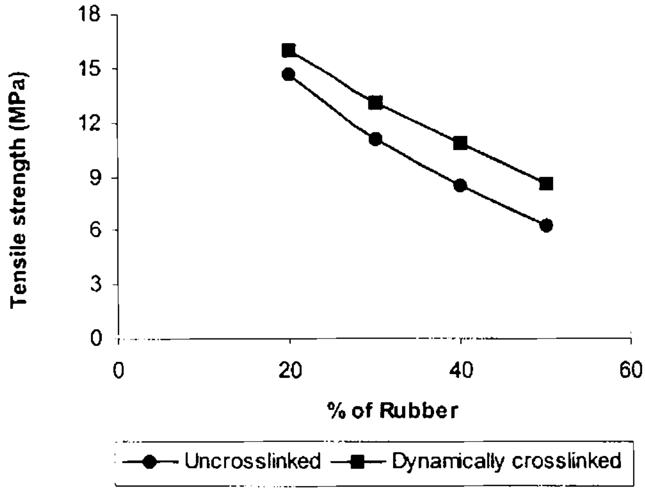
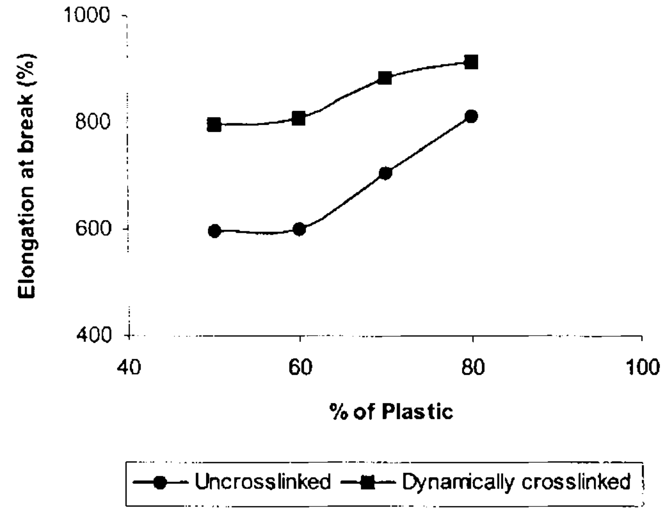


Fig. V (c) 2 shows the variation of elongation at break with plastic content of the blends. As the plastic content increases, elongation percentage also increases. This is due to the peculiar elongation behaviour exhibited by LLDPE, which is attributed to its linear configuration with many short, side chains, all of uniform length (11). The comparatively higher values of 50/50 blend than expected may be due to the higher amount of rubber in it. Dynamic vulcanization enhances the elongation values to a great extent, as the butyl phase becomes more elastomeric on crosslinking.

Fig V (c) 2 Variation of Elongation at break with % of rubber of LLDPE/ Butyl blends



In Fig. V (c) 3, variation of tear strength with rubber content of the blends is shown. As the rubber content increases, tear strength decreases. Here also dynamically vulcanized blends show higher values due to the increased extent of crosslinking.

In Fig. V (c) 4, Young's Modulus is plotted against rubber content. Modulus values are found to decrease with increase in rubber content. Due to the higher crystallinity of LLDPE, the plastic rich compositions exhibit higher modulii. The modulus values of all the blends with LLDPE are higher than those of the blends with HDPE and LDPE. This is also due to the greater amount of crystallinity of LLDPE when compared to that of HDPE and LDPE.

Fig V (c) 3 Variation of Tear strength with rubber content of LLDPE/Butyl blends

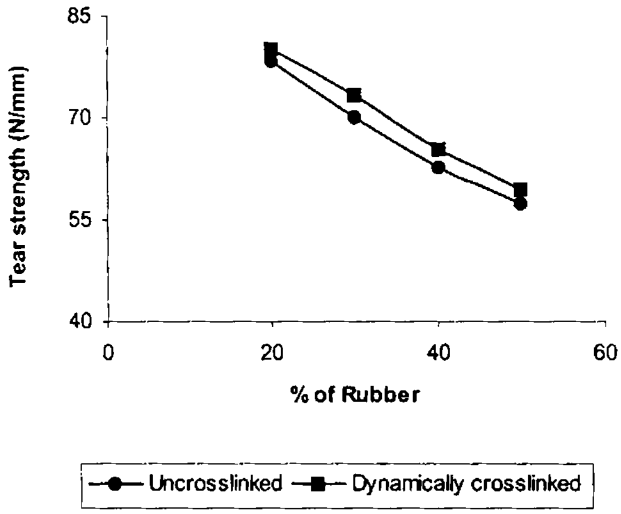


Fig V (c) 4 Variation of Young's Modulus with Rubber content of LLDPE/Butyl blends

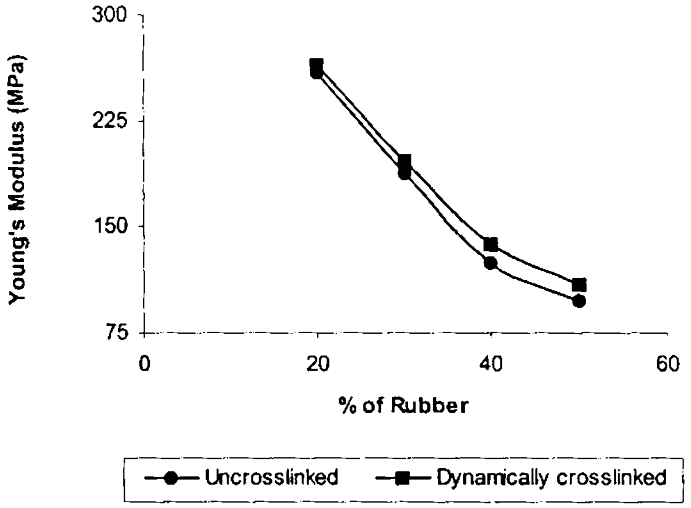
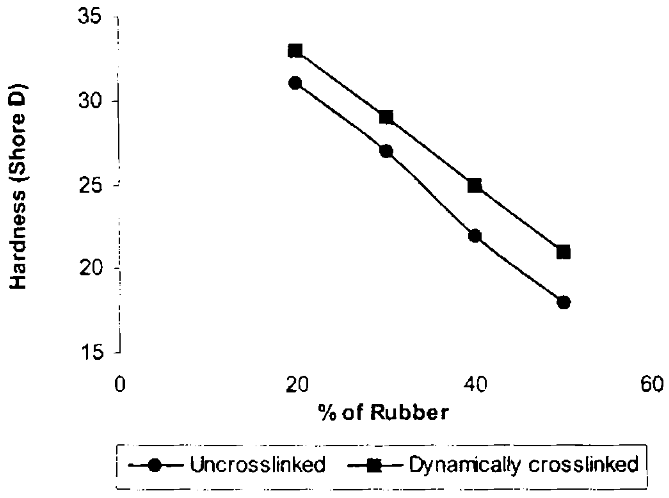


Fig. V (c) 5 gives the relationship between hardness and rubber content. As the rubber content increases, hardness values decrease. Again, owing to the higher crystallinity of LLDPE, blends with more plastic content exhibit higher hardness values. Dynamically vulcanized blends show better hardness than the unvulcanized blends.

The impact strength values of all the LLDPE/ butyl blends were found to be greater than 1 KJ/m.

Fig V (c) 5 Variation of Hardness with Rubber content of LLDPE/ Butyl blends



In Fig V (c) 6, melt flow indices (MFI) of the blends are plotted against plastic content. As the plastic content increases, MFI also increases. High melt viscosity of LLDPE due to betterr crystallinity, makes its blends show low

Dynamic crosslinking still decreases the MFI due to greater extent of crosslinking in the rubber phase.

Fig V (c) 6 Variation of Melt Flow Index with Plastic content of LLDPE/ Butyl blends

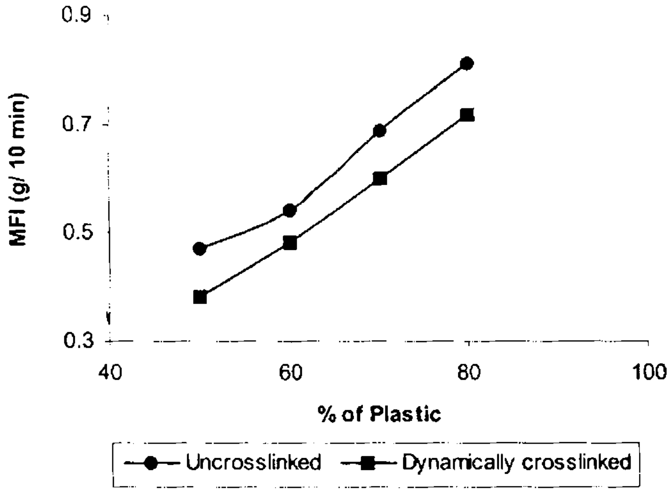
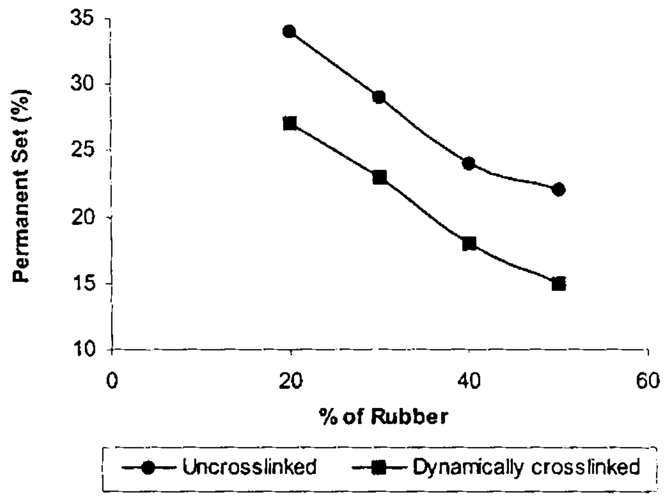


Fig. V (c) 7 shows the relationship between permanent set and rubber content of the blends. It is seen that as the rubber content increases, set values decrease. On dynamic vulcanization, set values decrease significantly. One of the best effects of dynamic vulcanization can be observed in this case. The ability of the butyl phase to resist the deformation due to an applied stress improves on crosslinking.

Fig. V (c) 8 shows the variation of tensile strength with rubber content of aged samples of dynamically vulcanized LLDPE/IIR blends at 100^{0}C for 24 hrs and 48 hrs.

Fig V (c) 7 Variation of Permanent Set with Rubber content of LLDPE/ blends



It is clear that the values are unaffected by ageing. In some cases a slight increase in strength is observed and this may be due to the completion of vulcanization on heating.

Fig V (c) 8 Variation of Tensile strength with Rubber content of aged, dynamically vulcanized LLDPE/ Butyl blends

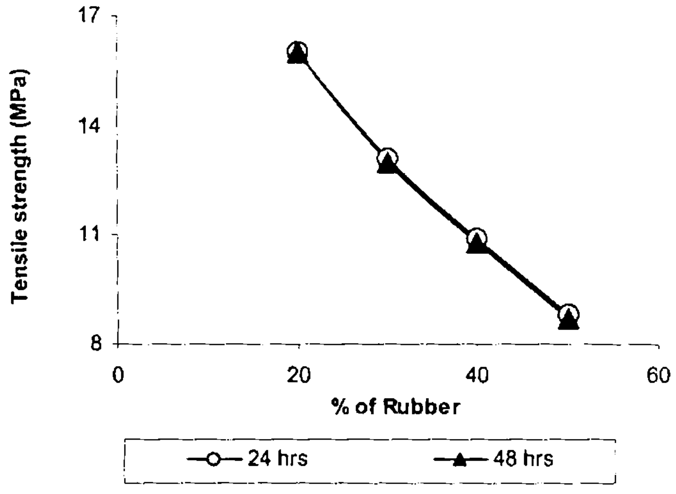


Fig. V (c) 9 shows the variation of elongation at break with plastic content of aged samples. Here also values are more or less the same as those of the unaged blends. So it is assumed that ageing does not affect the mechanical properties of dynamically vulcanized LLDPE/ butyl blends.

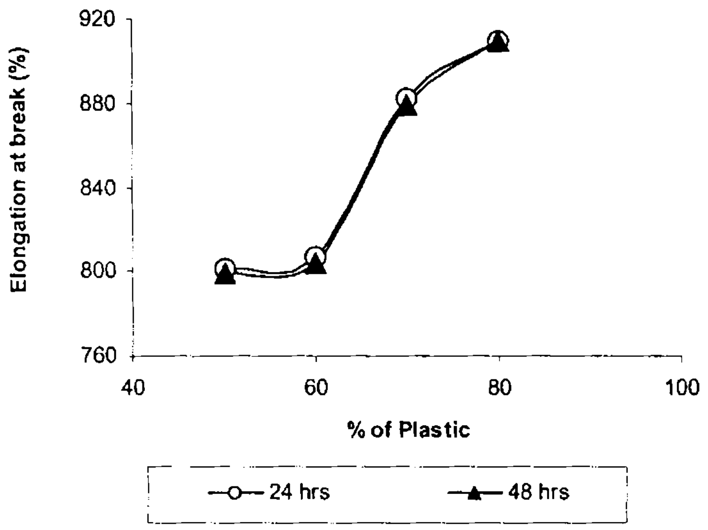


Fig V (c) 9 Variation of Elongation at break with Plastic content of aged, dynamically vulcanized LLDPE/ Butyl blends

Table V (c) 1 shows the mechanical properties of the reprocessed samples of dynamically vulcanized LLDPE/butyl blends. It is seen that remelting and remoulding have not affected the mechanical properties of the blends, since the values are more or less unchanged. This may be due to the retention of the extent of crosslinking due to dynamic vulcanization.

Table V(c) 1 Mechanical properties of reprocessed samples of dynamically vulcanized LLDPE/IIR blends (160°c)

Blend Ratio	Tensile strength (MPa)	Elongation at break (%)	Tear strength (N/mm)	Young's Modulus (MPa)	Hardness (Shore D)
50/50	8.5	795	59.38	107	20
60/40	10.8	803	64.97	136	24
70/30	13.1	883	72.85	195	29
80/20	16.0	911	79.18	263	33

2. Rheological evaluation of LLDPE/IIR blends

Fig V (c) 10 shows the variation of torque/rpm, which represents the viscosity, with rubber content of LLDPE/IIR blends. As the rubber content increases, viscosity also increases as expected. On dynamic vulcanization, viscosity increases which may be due to the higher torque developed during dynamic crosslinking. Higher torque values are exhibited by LLDPE blends when compared to HDPE and LDPE blends. This may be attributed to the high melt viscosity of LLDPE, associated with its long, regular molecular chains. This makes the LLDPE blends more difficult to be processed than HDPE and LDPE blends.

Fig V (c) 10 Variation of Torque/ rpm with Rubber content of LLDPE/ Butyl blends

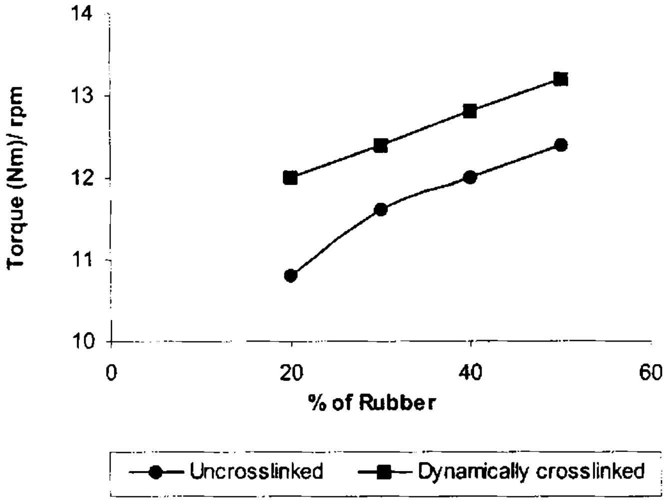
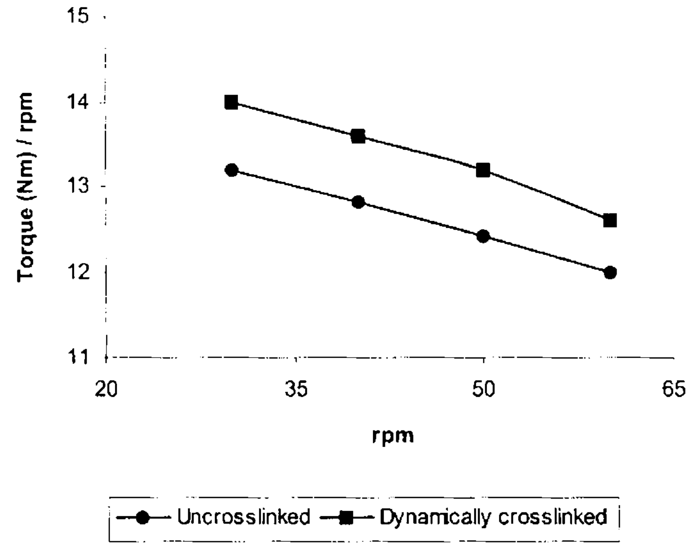


Fig V (c) 11 Variation of Torque/ rpm with rpm of 50/50 LLDPE/ Butyl blends



In addition, MFI of LLDPE is more than that of HDPE and LDPE.

Fig V (c) 11 shows the relationship between viscosity (torque/rpm) and shear rate (rpm) of 50/50 LLDPE/IIR blends. As the shear rate increases, viscosity decreases but not proportionally. This implies that the blends are pseudoplastic in nature (9). The high viscosity value is due to the higher rubber content, which makes the processing difficult, along with the highly crystalline nature of LLDPE. These together restrict the flow.

Fig V (c) 12 Variation of Viscosity with Shear rate of 80/20 LLDPE/ Butyl blends

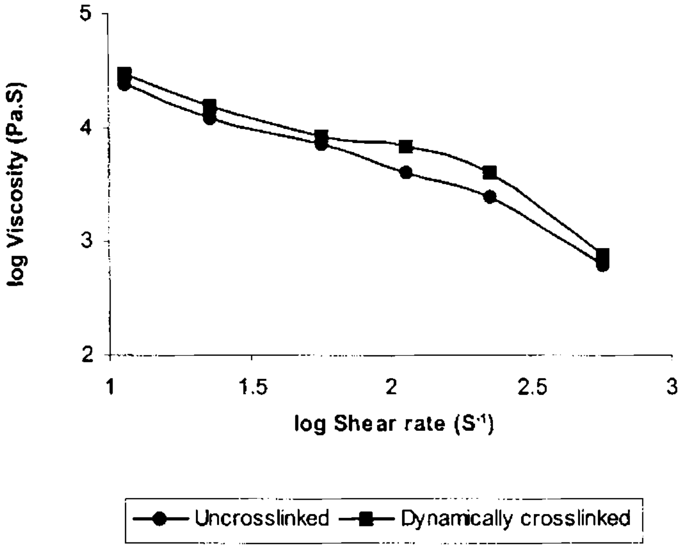


Fig V (c) 13 Variation of Shear stress with Shear rate of 80/20 LLDPE/ Butyl blends

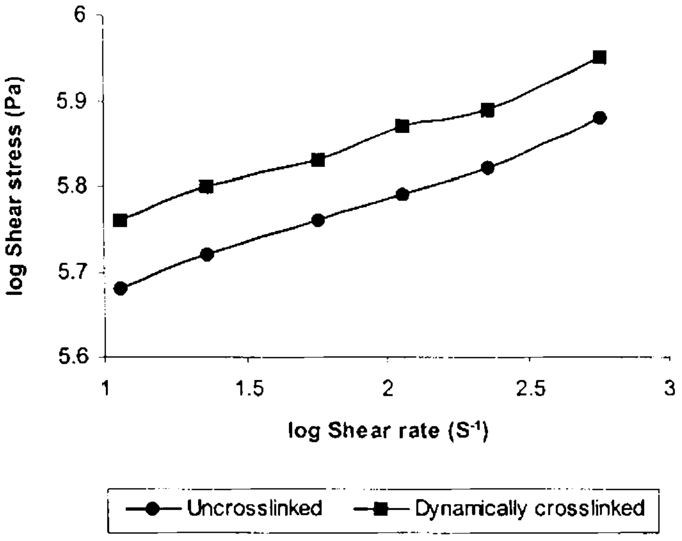


Fig V (c) 12 gives the relationship between viscosity and shear rate of 80/20 LLDPE/IIR blends, measured on Capillary Rheometer. With the increase in the shear rate, viscosity decreases but not linearly. This again indicates the pseudoplastic nature of the blends. Here also the viscosity values of crosslinked blends are higher than those of the uncrosslinked ones, due to the decreased flexibility of the rubber phase that produces higher stress.

In Fig V (c) 13, shear stress of the blends is plotted against shear rate. As the shear rate increases shear stress also increases. This confirms the non-Newtonian behavior of the blend.

Fig V (c) 14 is the optical photographs of the extrudates of uncrosslinked 80/20 LLDPE/IIR blend and Fig V (c) 15 is that of crosslinked 80/20 LLDPE/IIR blend. As the shear rate increases, the surfaces of the extrudates become more and more rough and deformed. Generally for elastomer-plastic blends with higher plastic content, the melt rheology resembles with that of the plastic material (10). Here the plastic phase, viz., LLDPE, exhibits high melt viscosity owing to its long, regular molecular chains. This in turn makes it difficult to get extruded. The blend contains butyl rubber phase also and its melt viscosity is higher than that of LLDPE phase. The higher viscosity values and the difference in viscosities of the two phases together cause the deformation of the extrudates. For crosslinked blends, the difference in melt viscosities of the two phases will be still higher resulting in more deformation.

Table V (c) 2 gives the die swell ratios and pseudoplasticity index of the LLDPE/IIR blends. It can be seen that the swell ratios are higher than those of the HDPE and LDPE blends. The reason is the higher crystallinity of LLDPE compared to HDPE and LDPE. As the shear rate increases, the swell ratio also increases though the increment is not marginal.

Table V (c) 2 Variation of Die swell ratio with shear rate of LLDPE/ IIR blends

Shear rate (S^{-1})	Die swell ratio (LLDPE/IIR)		Pseudoplasticity index, n
	Crosslinked	Uncrosslinked	
11.52	2.32	2.48	0.324
23.04	2.38	2.56	
57.60	2.43	2.61	
115.20	2.45	2.63	
230.40	2.49	2.67	
576.00	2.51	2.69	

Conclusions of studies on PE/IIR blends

1. Blends of HDPE, LDPE and LLDPE with IIR exhibit good mechanical, rheological and morphological properties.
2. 50/50 dynamically vulcanized PE/IIR blend proportion of all the three types of blends can be considered as thermoplastic elastomers.
3. Compared to HDPE blends, LDPE and LLDPE blends with IIR are found to be more soft and flexible.
4. Of the three types of blends, dynamically vulcanized LLDPE/ IIR blends exhibit the best properties and they are proposed as competing thermoplastic elastomers for various industrial applications.

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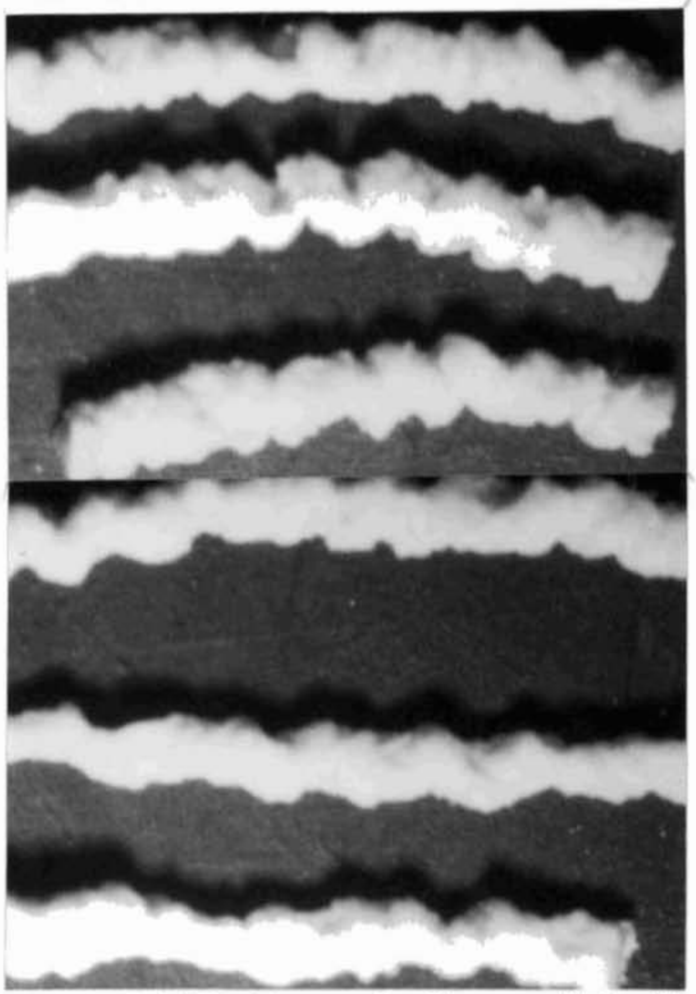
Optical photographs of extrudates of 80/20 blends of

Fig V(c) 14



LLDPE / IIR (Dynamically crosslinked)

Shear rate (S^{-1})

115.2

230.4

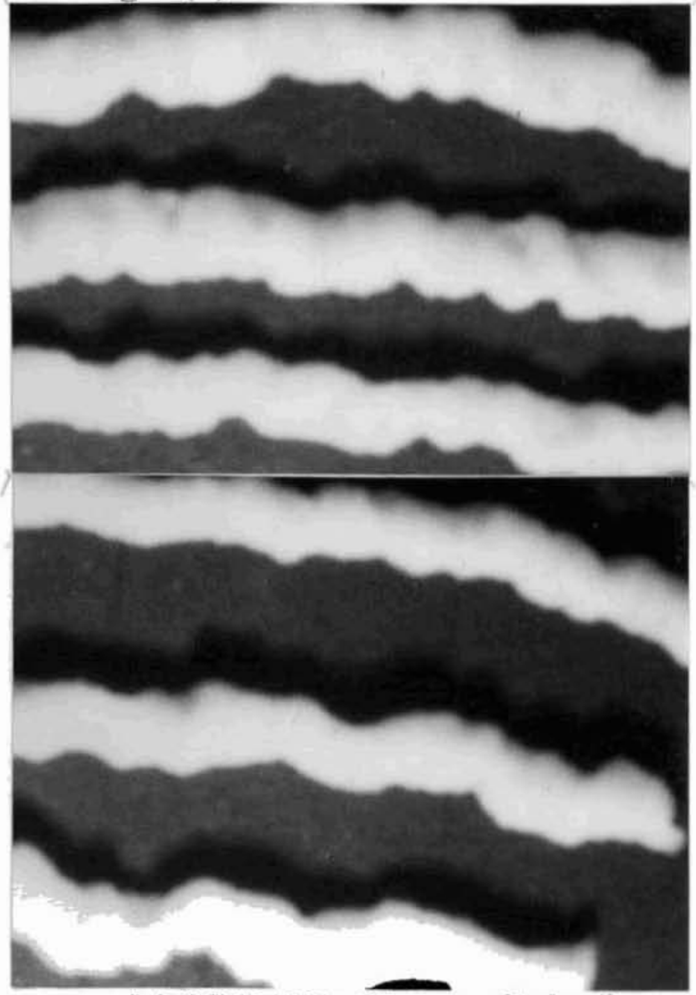
576.0

1153.0

1728.0

2304.0

Fig V(c) 15



LLDPE / IIR (Uncrosslinked)

CHAPTER VI

CHAPTER VI (a)

EFFECT OF COMPATIBILIZERS ON THE MECHANICAL PROPERTIES OF POLYETHYLENE / ELASTOMER BLENDS

Introduction

The practical utility of a polymer blend is determined by the compatibility of the component polymers, which is considered as the fundamental property (1-3). But it has been observed that majority of thermoplastic elastomeric systems are incompatible (4-7), though most of their useful properties arise from their incompatibility. If these properties can be improved by making the blends compatible, they can be very successfully utilized in the academic and industrial fields. Physical or chemical modifiers can be used as compatibilizers for polymer blends (8-9).

In this chapter, Chlorinated Polyisobutylene (Chl.PIB), Chlorobutyl rubber (CIIR) and Liquid Natural Rubber (LNR) have been utilized as compatibilizers for PE/Butyl rubber and PE/modified NR waste blends.

Experimental

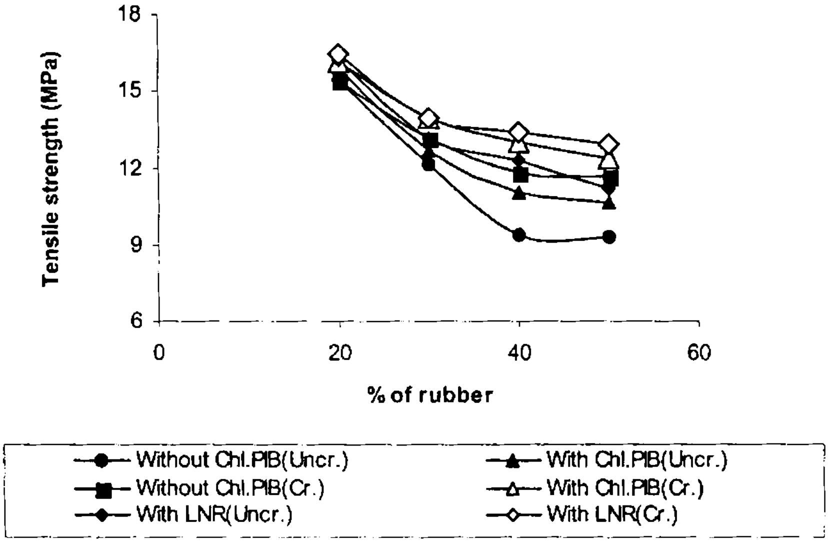
(i) LNR and Chl.PIB as compatibilizers in PE/modified NR waste blends

Blends were prepared according to the formulation given in Table VI (a) 1. The waste utilized was the one modified with thiocarbanilide [GW (P)]. Blending was done as in Chapter IV (a) and samples were moulded. The mechanical properties of these samples were tested as per the ASTM methods.

Results and Discussion

Fig VI (a) 1 shows the variation of tensile strength with rubber content of HDPE/GW (P) blends compatibilised with chlorinated polyisobutylene and liquid natural rubber. It is clear that on adding 5 phr of the compatibilizers, the tensile strength values increase for all the blends. Dynamic vulcanization of the elastomer phase still increases the strength in

Fig VI (a) 1 Variation of Tensile strength with rubber content of HDPE/GW (P) blends with compatibilizers



both the cases. Of the two compatibilizers, LNR gives better result. This may be explained as follows. The LNR used contains an amino group in it, which has a lone pair of electrons. This lone pair may have an interaction with the π electrons of NR. Thus a low level of polar- polar interaction may be occuring between NR and LNR. It may be assumed that the above mentioned interaction results in a little similarity in the structures of NR and PE, by the influence of LNR on NR. This causes a decrease in the surface energy difference between the plastic and the rubber phases, which in turn results in mutual wetting and increased interaction between the phases. Also, relatively small particles of cured elastomer dispersed in HDPE might have enhanced the mutual wetting between the two phases (10-11). A similar but lesser effect may be occuring in the case of Chl.PIB modified blends also. Here the chlorine atom induces the polar- polar interaction on the double bonds of isoprene units. But this effect is not strong enough to bring about a marginal increase in properties.

Table VI (a) 1 Formulation for PE/GW (P) blends with compatibilizers

Ingredient	Phr							
PE (HDPE, LLDPE)	80	70	60	50	80	70	60	50
GW (P)	20	30	40	50	20	30	40	50
Chl.PIB	5.0	5.0	5.0	5.0	-	-	-	-
CIIR	-	-	-	-	-	-	-	-
LNR	-	-	-	-	5.0	5.0	5.0	5.0
Sulphur	0.50	0.75	0.10	1.25	0.50	0.75	0.10	1.25

Fig VI (a) 2 shows the variation of percentage of elongation at break with rubber content of the blends with the two compatibilizers. The elongation values are found to be higher for the blends with compatibilizers. Highest values are shown by the dynamically vulcanized blends with LNR as compatibilizer. The reason may again be the decreased surface energy and mutual wetting of the two phases of the polymer blend, due to the presence of reactive sites in LNR.

Fig VI (a) 2. Variation of elongation at break with % of rubber of HDPE/ GW(P) blends with compatibilizers

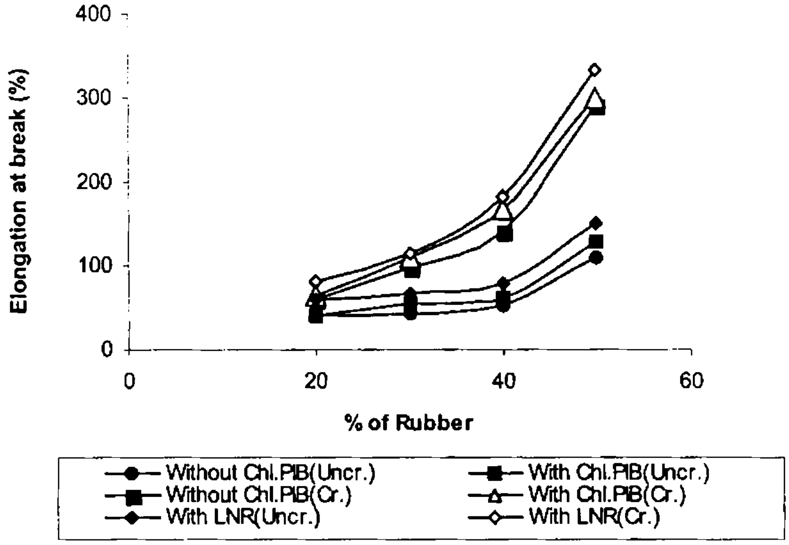


Fig VI (a) 3. Variation of Tear strength with rubber content of HDPE/ GW(P) blends with compatibilizers

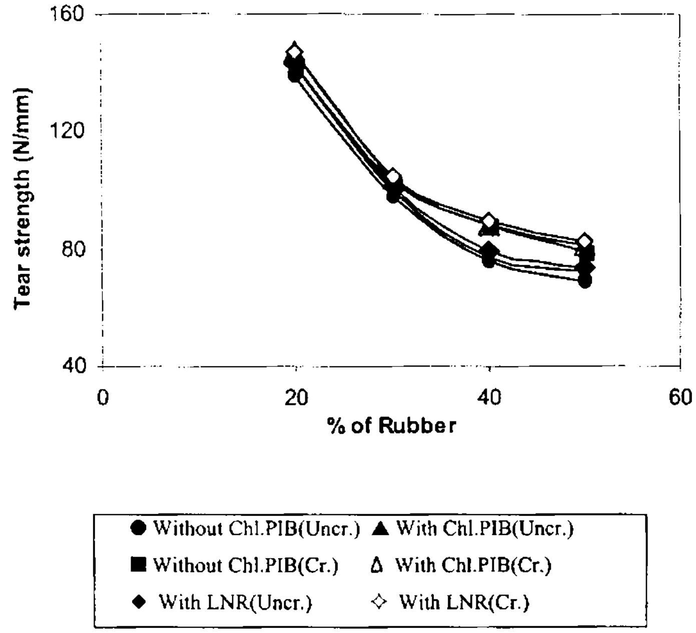


Fig VI (a) 3 gives the variation of tear strength with rubber content of the blends. Here also compatibilization has enhanced the values to a great extent. The reasons may be the same as in the case of tensile strength and elongation at break.

Fig VI (a) 4. Variation of Permanent set with % of Rubber of HDPE/ GW(P) blends with compatibilizers

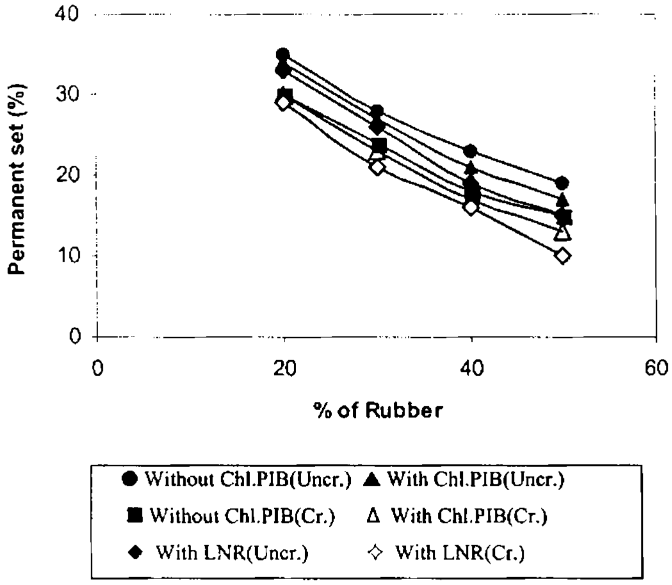


Fig VI (a) 4 is the plot of permanent set with rubber content. The advantage of the compatibilizers is more prominent in this property. A significant drop in the permanent set percentage is observed in the case of dynamically vulcanized, LNR compatibilized blends. This indicates the higher extent of vulcanized elastomeric behaviour of the blends.

Fig VI (a) 5. Variation of Hardness with % of rubber of HDPE/ GW (P) blends with compatibilizers

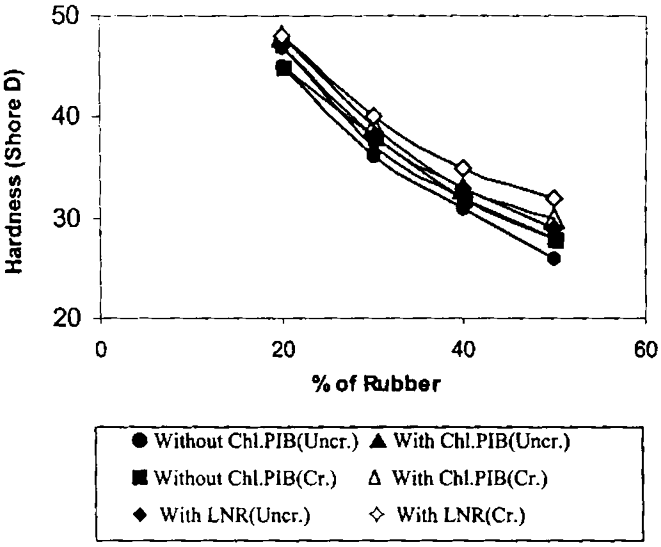


Fig VI (a) 5 shows the variation of hardness with rubber content of the blends. Hardness values are also found to increase on adding compatibilizers, especially LNR. Again, this may be attributed to the decrease in the surface energy difference between the two phases, which in turn increased the interaction between them.

Fig VI (a) 6 is the plot of tensile strength with rubber content of LLDPE/GW (P) blends, compatibilized with LNR. The values are found to be enhanced considerably on adding the compatibilizer as expected (12-13). The values of dynamically vulcanized blends are still higher. Dynamically vulcanized 50/50 blends with LNR produced the most significant improvement in strength. The LNR modified vulcanized NR phase has greater adhesion with LLDPE, which resulted in increased interaction between the two phases.

Fig VI (a) 6. Variation of tensile strength with rubber content of LLDPE/ GW (P) blends with LNR

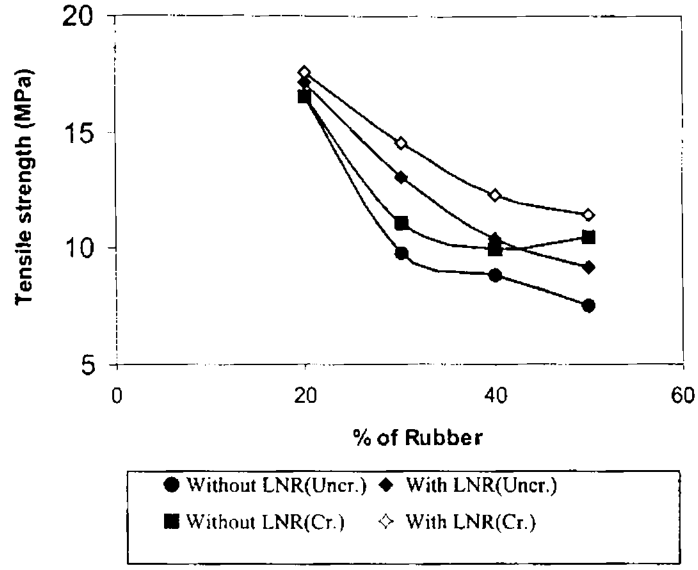


Fig. VI (a) 7 gives the relationship between elongation at break and plastic content of the LLDPE/GW (P), LNR compatibilized blends. Both the crosslinked and uncrosslinked blends show higher * elongation on adding LNR, .. On dynamic vulcanization, the elongation at break decreases slightly, which may be attributed to the higher extent of crosslinking (14).

* compared to uncompatibilized blend.

Fig VI (a) 7 Variation of elongation at break with plastic content of LLDPE/ GW(P) blends with LNR

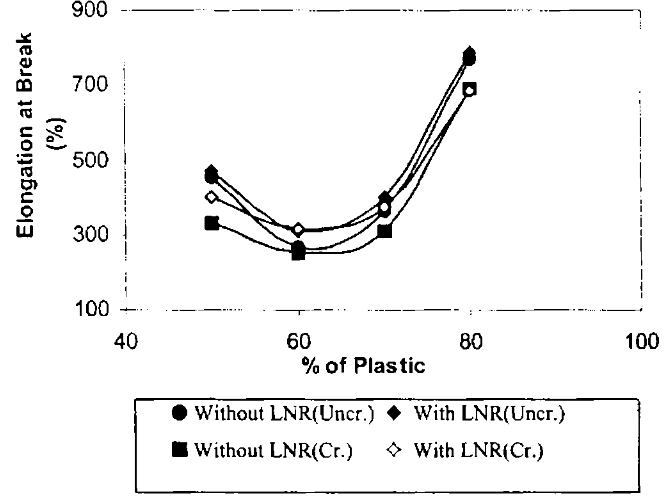


Fig VI (a) 8 shows the variation of tear strength with rubber content of the blends. Here also enhancement of values is observed on compatibilization.

Fig VI (a) 8 Variation of Tear strength with rubber content of LLDPE/ GW (P) blends with LNR

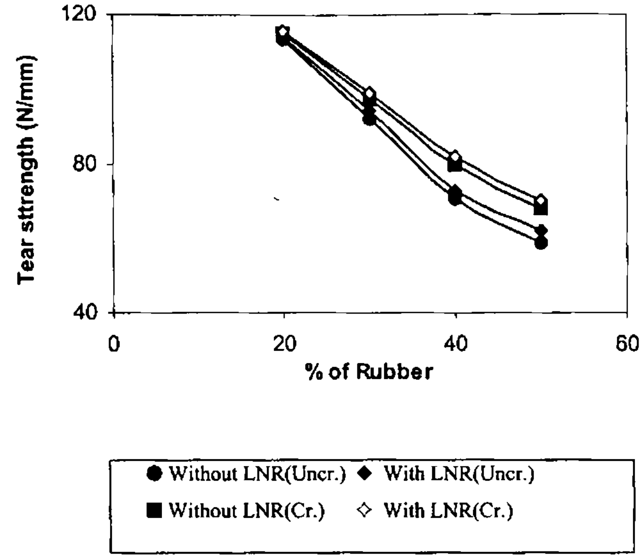


Fig VI (a) 9 is the variation of permanent set percentage with rubber content of the blends. A significant decrease in set values is observed here on the addition of LNR to the blends. Dynamically vulcanized blends with higher rubber content show very low set values. The elastomeric property is very much enhanced on modifying the crosslinked rubber phase with LNR. This enabled the blend to resist the deformation caused by stress.

Fig VI (a) 9 Variation of Permanent set with % of rubberof LLDPE/ GW(P) blends with LNR

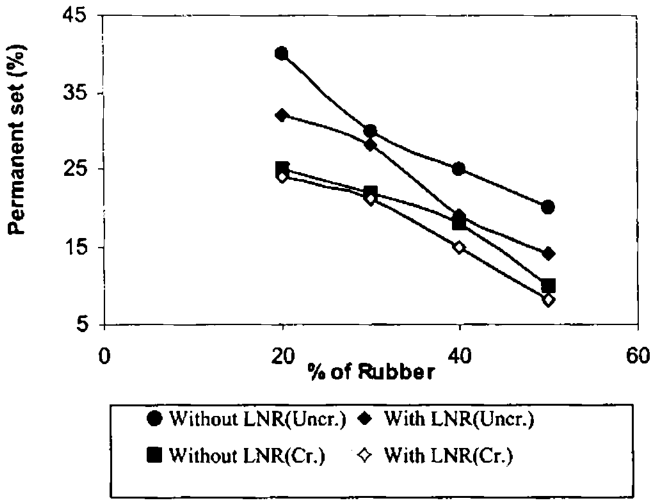
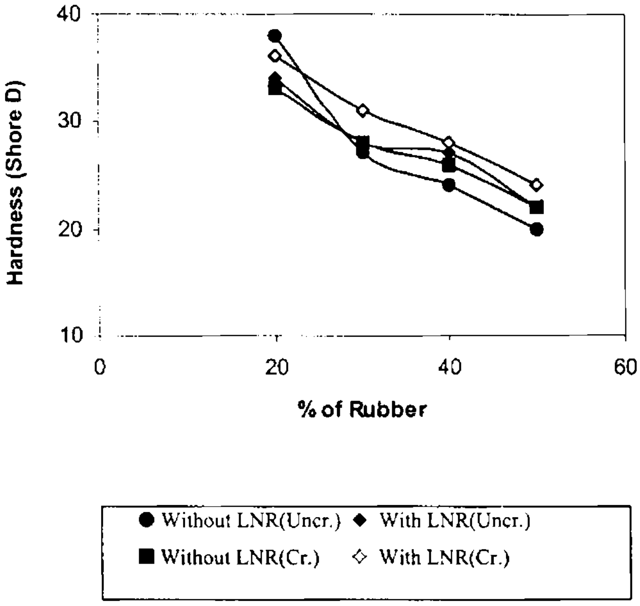


Fig VI (a) 10 shows the relationship between hardness and rubber content. Better values are obtained for the compatibilized blends, especially the dynamically vulcanized ones.

This may be due to the increased extent of crosslinking together with the crystallinity of LLDPE.

Fig VI (a) 10 Variation of hardness with rubber content of LLDPE/ GW(P) blends with LNR



(ii) Chl.PIB and CIIR as compatibilizers in PE/Butyl rubber blends

Blends were prepared according to the formulation given in Table VI (a) 2. Blending was done as above and samples were moulded. The mechanical properties of these samples were tested as per the ASTM methods.

Table VI (a) 2 Formulation for dynamically vulcanized PE/Butyl rubber blends with Compatibilizers

Ingredient	Phr							
HDPE/LDPE/LLDPE	80	70	60	50	80	70	60	50
Butyl	20	30	40	50	20	30	40	50
Chl.PIB	2.0	3.0	4.0	5.0	-	-	-	-
Chl.butyl	-	-	-	-	2.0	3.0	4.0	5.0
Sulphur	0.04	0.06	0.08	0.10	0.04	0.06	0.08	0.10

Fig VI (a) 11 Variation of tensile strength with rubber content of HDPE/ Butyl blends with compatibilizers

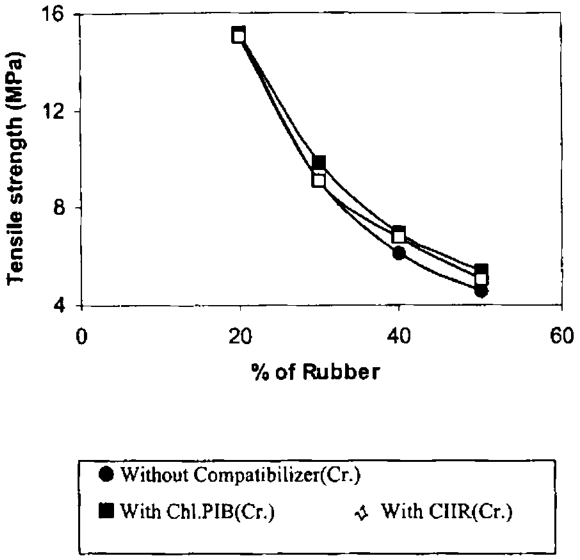
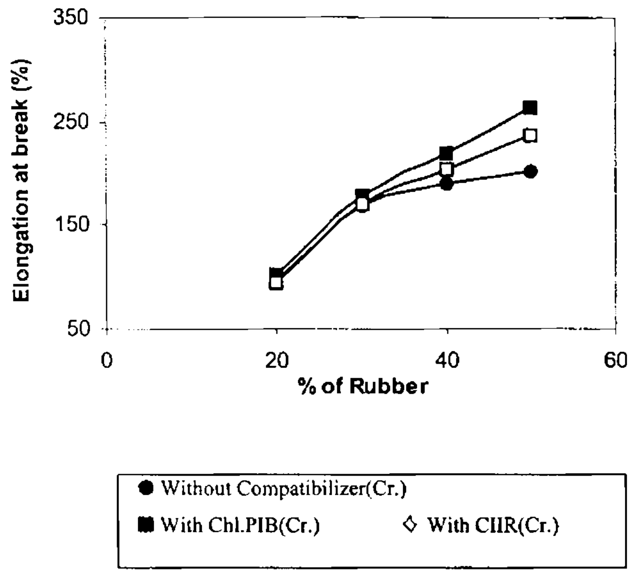


Fig VI (a) 11 is the plot of tensile strength with rubber content of dynamically vulcanized HDPE/butyl blends with Chl.PIB and CIIR as compatibilizers. It is seen that a slight improvement in the property is observed when compatibilizers are used. Better result is obtained from Chl.PIB. This may be due to the better interaction of the two phases, which may be explained as follows. Chlorination takes place at the double bond in polyisobutylene. Since the extent of chlorination is low (7.6%),

This chlorine atom is the active group on Chl.PIB, which causes the interfacial linking between the polyethylene phase and the butyl rubber phase (12). Thus, the mutual wetting of the two phases may be enhanced, which in turn gave better properties.

In the case of CIIR, the chlorine atom is present on the allylic carbon atom. It is resonance stabilized within the molecule and may not have as much effect on butyl phase as the chlorine atom on Chl.PIB has. This causes the decreased properties of the blends with CIIR compared to those with Chl.PIB. Also, the chlorine content of CIIR is comparatively lower (1.3%) than that of Chl.PIB. This may also account for the lower adhesion of CIIR modified IIR with the PE phase.

Fig VI (a) 12. Variation of elongation at break with % of rubber of HDPE/ Butyl blends with compatibilizres



In Fig VI (a) 12, variation of elongation at break with rubber content is shown. Comparatively better values are obtained for the blends with compatibilizers. Chl.PIB gives slightly higher values here also.

Fig VI (a) 13. Variation of tear strength with rubber content of HDPE/ Butyl blends with compatibilizers

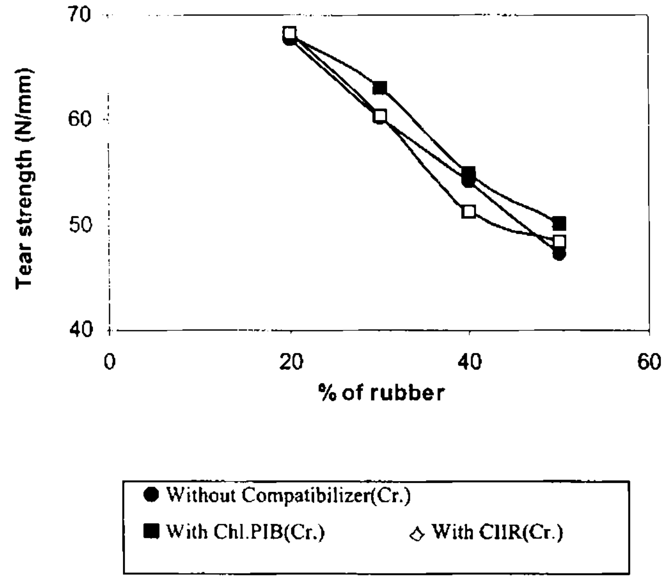


Fig VI (a) 13 is the plot of tear strength against rubber content of the blends. Here also improvement in property is observed, though minimal.

Fig VI (a) 14. Variation of permanent set with % of rubber of HDPE/ GW(P) blends with compatibilizers

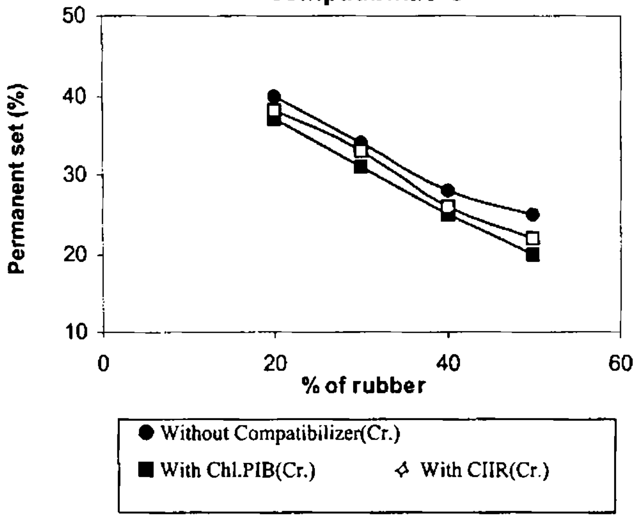


Fig VI (a) 14 shows the variation of permanent set with % of rubber of the blends. Significant improvement is observed in this property, especially for the 50/50 blends. This may be because of the decreased interfacial tension, which resulted in smaller, vulcanized elastomer particles with improved elastic recovery.

Fig VI (a) 15. Variation of hardness with rubber content of HDPE/ Butyl blends with compatibilizers

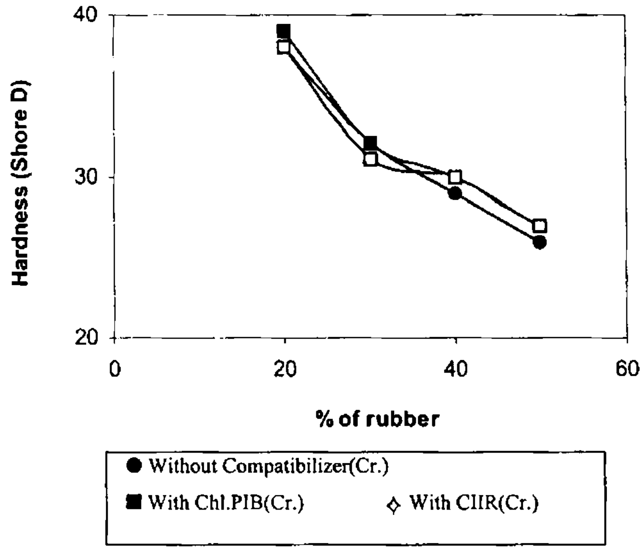


Fig VI (a) 15 shows the relationship between hardness and % of rubber. Though the variations in the values are not remarkable, slight increment can be observed in some cases.

Fig VI (a) 16. Variation of tensile strength with rubber content of LDPE/ Butyl blends with compatibilizers

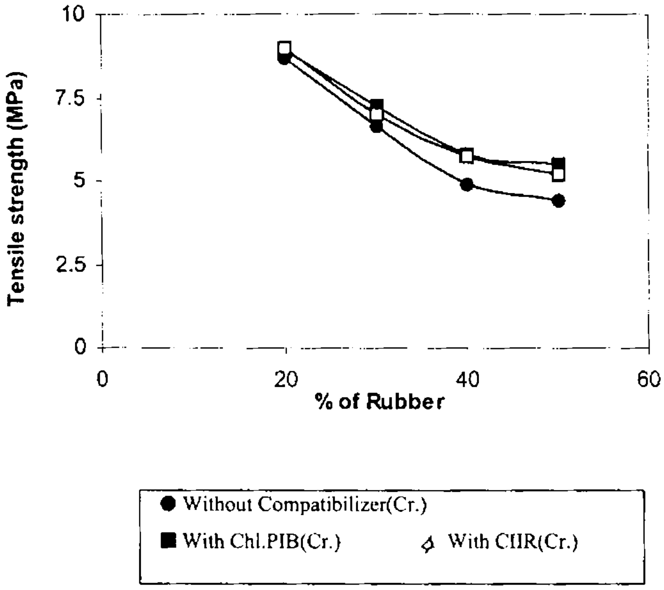
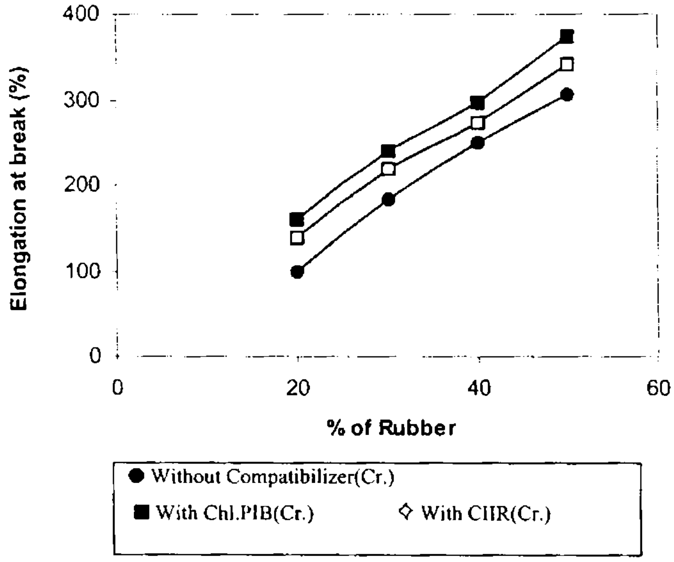


Fig VI (a) 16 shows the variation of tensile strength with rubber content of dynamically vulcanized LDPE/butyl blends, compatibilized with Chl.PIB and CIIR. Improvement in

Fig VI (a) 17 Variation of elongation at break with rubber content of LDPE/ Butyl blends with compatibilizers



tensile strength is seen for the blends with compatibilizers. Of the two compatibilizers, Chl.PIB produced better results.

Fig VI (a) 17 gives the relationship between elongation at break with % of rubber of LDPE/butyl, compatibilized blends. Better elongation is obtained on using the compatibilizers. Addition of the compatibilizers produces significant improvement in elongation at break in the case of 50/50 blends.

Fig VI (a) 18. Variation of tear strength with rubber content of LDPE/ Butyl blends with compatibilizers

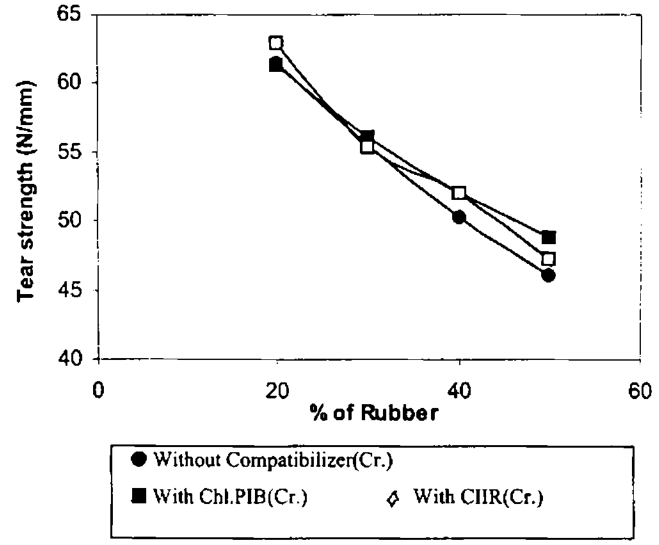
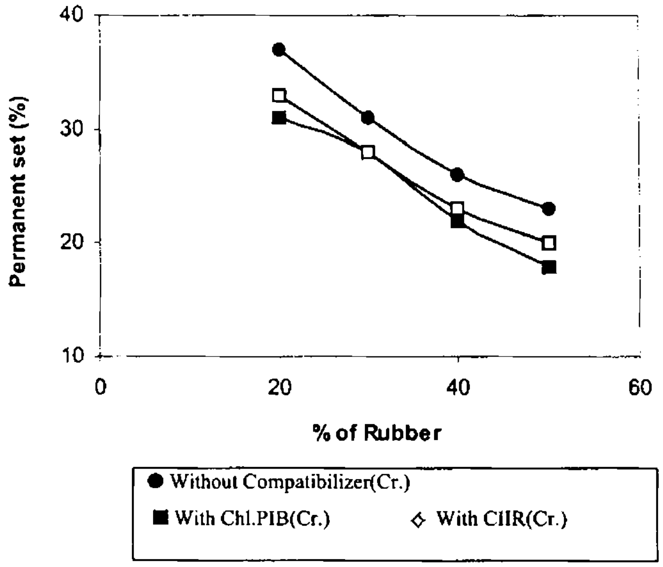


Fig VI (a) 18 shows the variation of tear strength with rubber content of the blends. Only

Fig VI (a) 19 Variation permanent set with rubber content of LDPE/ Butyl blends with compatibilizers



nominal variations can be observed in the property.

Fig VI (a) 19 is the plot of permanent set percentage with increase in rubber content of the blends. Set values show marked reduction on adding the compatibilizers, especially Chl.PIB.

Fig VI (a) 20 gives the variation of hardness with rubber content. Slight improvement in the hardness values is observed for blends with compatibilizers.

Fig VI (a) 20 Variation of hardness wtih rubber content of LDPE/ Butyl blends with compatibilizers

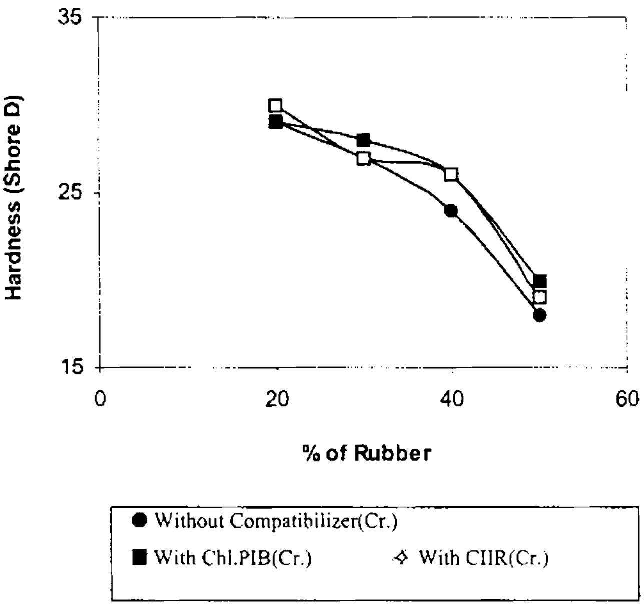


Fig VI (a) 21 shows the variation of tensile strength with rubber content of dynamically vulcanized LLDPE/butyl blends with both the types of compatibilizers. The values exhibited by the blends with compatibilizers are found to be higher than those without compatibilizers. Chl.PIB produces better results in this case also. Of the three types of blends, LLDPE/butyl blends seem to be compatibilized more with Chl.PIB and CIIR, as they show better results than HDPE/butyl and LDPE/butyl blends.

Fig VI (a) 22 is the plot of elongation at break with % of plastic of LLDPE/butyl blends. Better results are obtained when compatibilizers are used.

Fig VI (a) 23 shows the variation of tear strength with % of rubber. Again, improvement of tear strength is observed for blends with Chl.PIB and CIIR.

Fig VI (a) 21. Variation of tensile strength with rubber content of LLDPE/ Butyl blends with compatibilizers

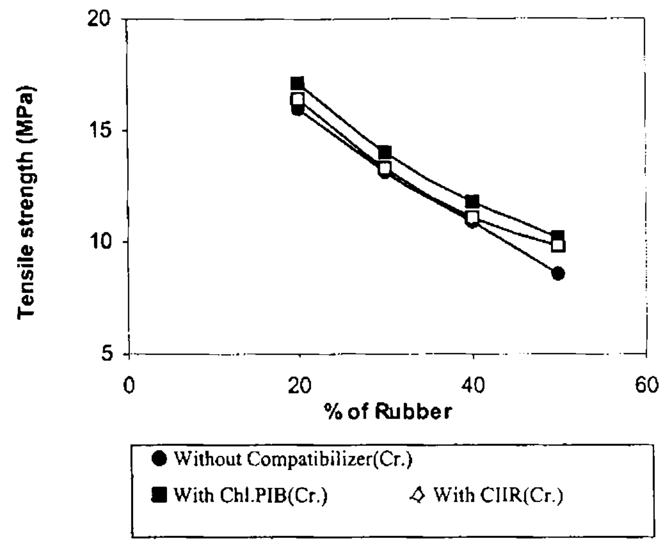


Fig VI (a) 22 Variation of elongation at break with plastic content of LLDPE/ Butyl blends with compatibilizers

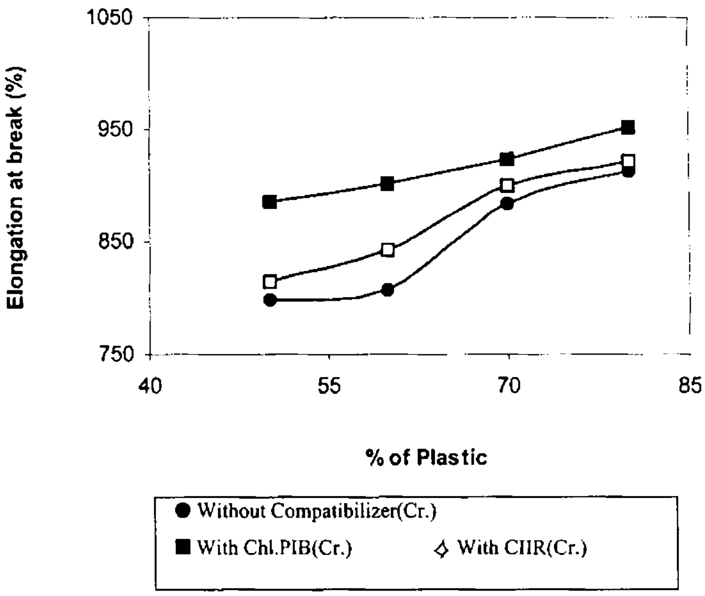


Fig VI (a) 24 shows the relationship between permanent set and % of rubber. A significant improvement is observed here. Much reduced set values are obtained for the compatibilized blends, especially for those with higher rubber content. This indicates the improved elastic recovery on compatibilization.

Fig VI (a) 23. Variation of tear stength with rubber content of LLDPE/ Butyl blends with compatibilizers

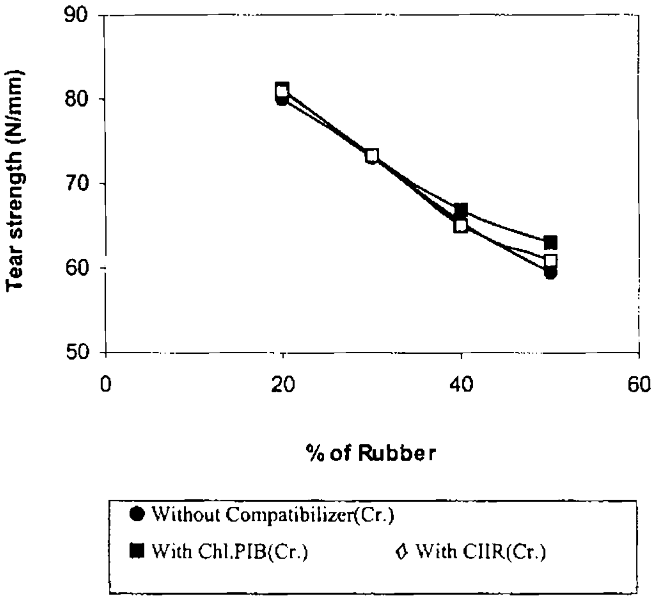


Fig VI (a) 24 Variation permanent set with rubber content of LLDPE/ Butyl blends with compatibilizers

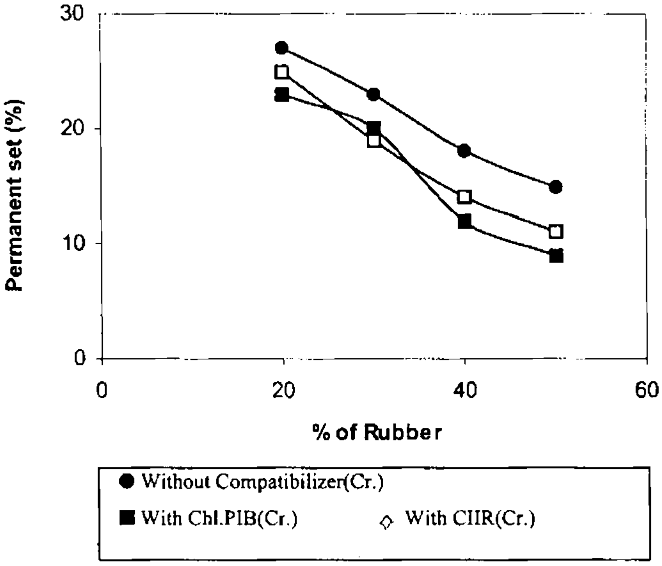
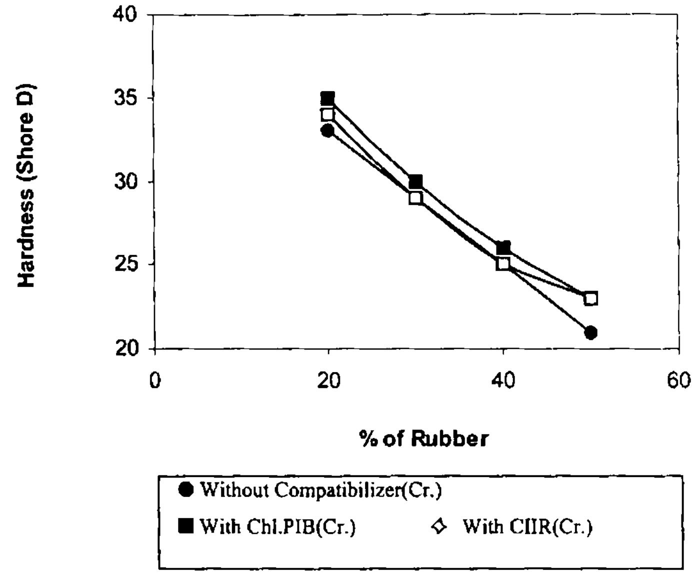


Fig VI (a) 25 shows the variation of hardness with % of rubber. Slight improvement is exhibited by the compatibilized blends here also.

Fig VI (a) 25 Variation of hardness with rubber content of LLDPE/ Butyl blends with compatibilizers



Conclusions

1. LNR and Chl.PIB can act as compatibilizers in modified PE/NR waste blends. LNR is found to be a better compatibilizer, especially for LLDPE/NR waste blends.

2. Chl.PIB and CIIR can be used as compatibilizers for PE/butyl blends. Of the two, Chl.PIB is found to produce better results, markedly for LLDPE/butyl blends.

THERMAL ANALYSIS OF 80/20 POLYETHYLENE/BUTYL RUBBER BLENDS

Experimental

Dynamic mechanical analysis of the 80/20 blends of HDPE/IIR blends with and without Chlorinated polyisobutylene (Chl.PIB) and LDPE/ IIR blends with Chl.PIB have been done. The influence of blending on the T_g of butyl rubber was evaluated. The effect of Chl.PIB on HDPE/butyl and LDPE/butyl blends was also examined.

Results and Discussion

Fig VI (b) 1 is the plot of tan δ vs. temperature of 80/20 HDPE/butyl (uncrosslinked) blend. The T_g of only the butyl phase could be detected from this thermogram. Pure butyl rubber exhibits a T_g of -65°C. But on blending with HDPE, the butyl phase shows a T_g around -52°C to -43°C. It indicates that blending with HDPE influences the T_g of butyl rubber.

Fig. VI (b) 1. Plot of tan(dlt) with temperature of 80/20 HDPE/Butyl blend

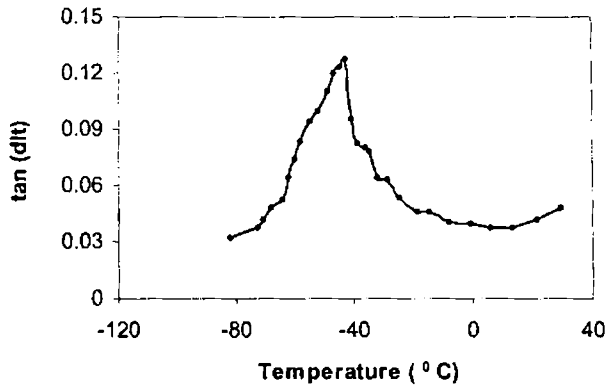
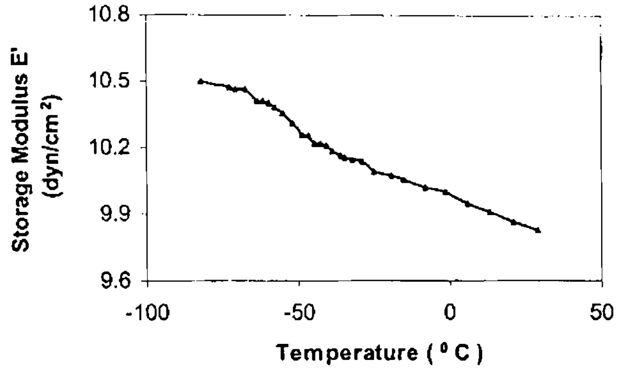


Fig VI (b) 2 is the plot of storage modulus (E') of HDPE/butyl (uncrosslinked) blend with temperature. As the temperature increases, E' value decreases as expected and a broadened rubbery plateau is obtained.

Fig. VI (b) 2 Plot of Storage Modulus with temperature of 80/20 HDPE/Butyl blend



In fig VI (b) 3, tan δ of dynamically vulcanized 80/20 HDPE/butyl blend is plotted against temperature. The T_g is found to be within the range -55^{0}C to -42^{0}C as in the case of the uncrosslinked blend since the crosslink density is low.

Fig VI (b) 3 Plot of tan (dlt) with temperature of dynamically vulcanized 80/20 HDPE/Butyl blend

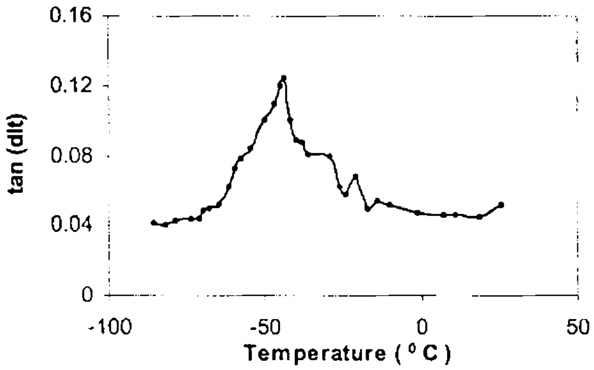


Fig VI (b) 4 shows the plot of storage modulus with temperature of dynamically vulcanized 80/20 HDPE/butyl blend. Here, a more broadened plastic plateau extending into the -50^{0}C region can be observed, when compared to the uncrosslinked blend. This may be due to the presence of crosslinks in the rubber phase.

Fig VI (b) 5 is the plot of tan δ vs. temperature of dynamically vulcanized 80/20 HDPE/butyl blend with Chl.PIB as compatibilizer. A peak around -50^{0}C to -41^{0}C region shows the T_g of butyl rubber. This implies that the addition of Chl.PIB has some influence on the T_g of butyl rubber, though the blend still exists as a binary, incompatible system. A small peak observed very near to the T_g of butyl rubber may be the T_g of Chl.PIB.

Fig VI (b) 4 Plot of Storage Modulus with temperature of dynamically vulcanized 80/20 HDPE/Butyl blend

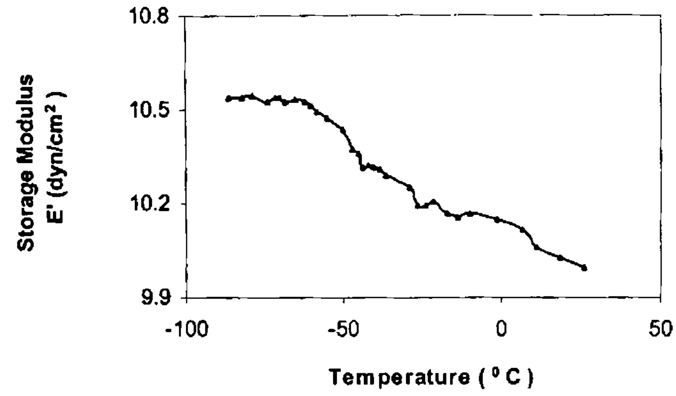


Fig VI (b) 5 Plot of tan (dlt) with temperature of dynamically vulcanized 80/20 HDPE/Butyl with Chl.PIB

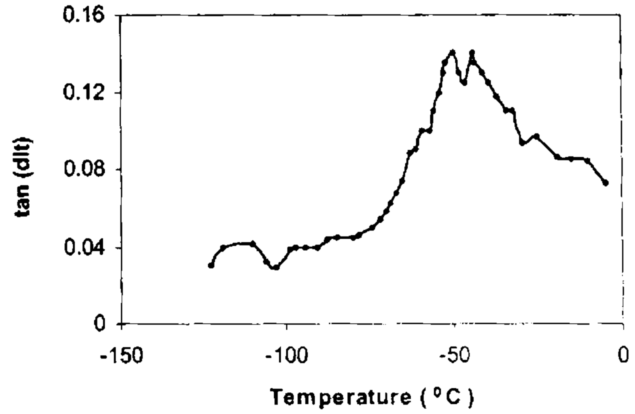


Fig VI (b) 6 shows the plot of storage modulus with temperature of dynamically vulcanized 80/20 HDPE/butyl blend with Chl.PIB. A well-defined plastic plateau can be seen here, in comparison with the blend without Chl.PIB as compatibilizer. Thus, it can be assumed that Chl.PIB enhances the interaction between the plastic and rubber phases to an extent.

Fig VI (b) 7 is the plot of tan δ vs. temperature of dynamically vulcanized 80/20 LDPE/butyl blend with Chl.PIB. The T_g corresponding to butyl rubber is around -54°C to

-46^{0}C. Though there is a slight variation in the T_g from that of the pure component, the blend still exists as a binary, incompatible system even after the addition of Chl.PIB.

Fig VI (b) 8 shows the plot of storage modulus vs. temperature of dynamically vulcanized LDPE/butyl blend with Chl.PIB. A more or less distinct plastic plateau can be

Fig VI (b) 6 Plot of Storage Modulus with temperature of dynamically vulcanized 80/20 HDPE/Butyl with Chl.PIB

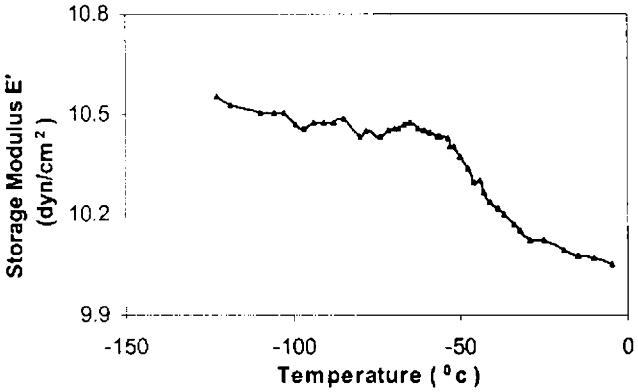


Fig VI (b) 7 Plot of tan (dlt) with temperature of dynamically vulcanized 80/20 LDPE/Butyl with Chl.PIB

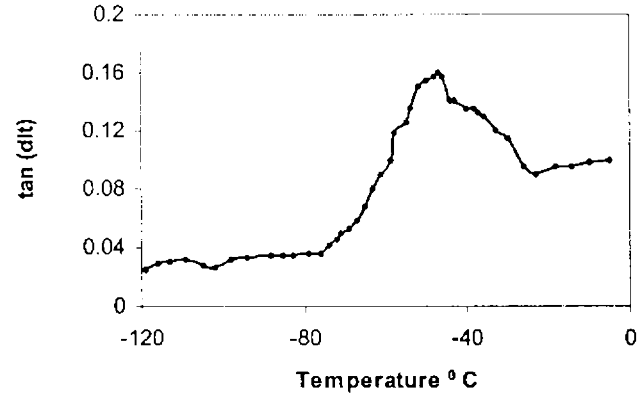
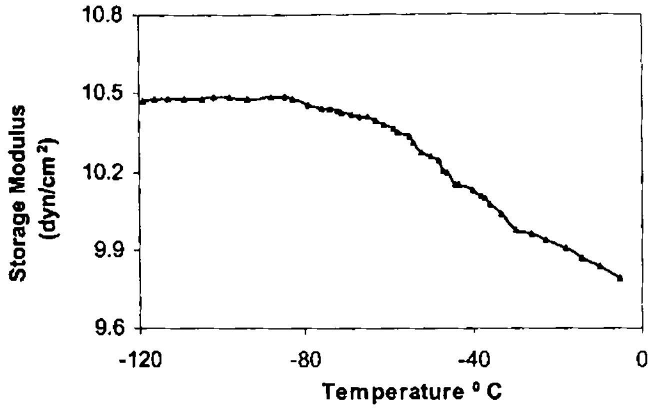


Fig VI (b) 8 Plot of Storage Modulus with temperature of dynamically vulcanized 80/20 LDPE/Butyl with Chl.PIB



observed here also. Addition of Chl.PIB to the dynamically crosslinked LDPE/butyl blend has a little influence on the mutual interaction of the blend.

Conclusion

Dynamic vulcanization of the butyl rubber phase and addition of Chl.PIB are advantageous to the PE/IIR blend to a particular extent.

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CHAPTER VII oooooooooo

CHAPTER VII

SUMMARY AND CONCLUSIONS

The overall objective of the present study was to develop novel thermoplastic elastomers based on polyethylene and elastomers such as modified latex product waste and butyl rubber. Of the two types of thermoplastic elastomers, more importance was given to those from polyethylene and modified latex product waste, since latex product waste represents a potential source of low cost, high quality rubber hydrocarbon. Considering the advantages of polyethylene/butyl rubber blends, it was decided to develop a set of thermoplastic elastomers based on them also by melt blending.

After several trials, two promising processes were developed for generating good quality rubber from the waste latex products. The modified wastes thus developed had properties such as Mooney viscosity, initial plasticity, plasticity retention index, acetone extract, volatile matter etc. comparable to those of raw natural rubber. The rubber hydrocarbon contents were slightly lower while the ash contents were slightly higher for the modified waste materials. The details of the modification process are given in Chapter III. The mechanical properties of the modified waste materials, described in the later part of Chapter III show that the modification processes proposed are good enough to produce rubber having comparable properties to those of natural rubber.

In Chapter IV (a), the utilization of the MBT modified waste in the preparation of thermoplastic elastomers with high density polyethylene is described. It was found that the modified waste could be blended up to 50 phr with HDPE and the blends had comparable or sometimes even better properties than the blends based on natural rubber and HDPE. SEM studies showed that the failure behaviour of these blends are similar to that of the HDPE/NR blend. Moreover, a more uniform dispersion of the rubber phase in the plastic phase was observed for the HDPE/modified waste blends. Rheological evaluation of these blends revealed that as the rubber content increased, the melt viscosity of the blends also increased and they exhibited pseudoplastic behaviour.

Considering the influence of crystallinity of polyethylene in blending with elastomers, the next part of the study was blending of low density and linear low density polyethylene with modified waste. LLDPE blends were found to exhibit better mechanical properties compared to LDPE blends. But higher melt viscosity was observed for LLDPE blends. Extrudate morphology studied using an optical microscope showed that the surface of the extrudates became non-uniform at higher shear rates, especially for LLDPE blends. The details of the rheological and morphological behaviours of the blends are outlined in Chapter IV (b).

Thiocarbanilide was found to be the most efficient modifier for waste latex products as explained in Chapter III. The utilization of this modified waste in developing thermoplastic elastomers with HDPE having improved properties is described in Chapter IV (c). The effect of dynamic vulcanization to the rubber phase was proved to be advantageous for the mechanical properties, especially in the case of blends with higher rubber content. The rheology and morphology of these blends are outlined in the chapter.

The properties of thermoplastic elastomer blends of the thiocarbanilide modified waste with linear low density polyethylene are outlined in Chapter IV (d). The most uniform dispersion of the elastomer phase in the plastic phase was observed in this case. The adhesion between the two phases was further improved by dynamic vulcanization, which resulted in the best properties in comparison with the earlier blends. Higher crystallinity of LLDPE resulted in higher melt viscosity, which would make the processability difficult with the increase in the shear rate.

Because of the industrial importance being gained by polyethylene/butyl rubber blends, the next phase of the study was the development of thermoplastic elastomers from butyl rubber and HDPE. Crosslinking the butyl phase dynamically was found to effective in improving the mechanical properties of the blends. Further, the tensile fractographs taken using scanning electron microscope revealed that the dynamically vulcanized blends were more resistant to deformation and this was found to be the result of a more uniform dispersion also. The rheology and morphology of these blends are outlined in Chapter V (a).

The development and property evaluation of thermoplastic elastomeric blends of comparatively low crystalline, low density polyethylene with butyl rubber is given in Chapter V (b). LDPE/butyl blends were found to be more flexible with higher impact resistance and lower permanent set than the HDPE/butyl blends. SEM studies on tensile fracture surface showed that the dynamically vulcanized blend was more elastomeric than the unvulcanized blend. Details of the rheology and morphology of these blends are also outlined in this chapter.

Because of the highly crystalline nature of linear low density polyethylene, it may be expected to form better blends with butyl rubber, which is more or less amorphous in nature. By making the butyl phase more elastomeric through dynamic vulcanization, the adhesion between the LLDPE and butyl phases could be improved. These thermoplastic elastomers exhibited high impact strength, elongation at break and low permanent set values, over the whole range of blend proportions examined. All the properties were found to be superior to those of the blends with HDPE and LDPE. Processing of LLDPE blends was a little more difficult due to the highly crystalline nature of LLDPE. Rheology and morphology of the blends are explained in Chapter V (c).

Since compatibility is the factor determining the practical utility of a polymer blend, next part of the study was to investigate the effect of certain polymers as compatibilizers in the polyethylene/rubber blends under study. It was found that the compatibilizers such as amine terminated liquid natural rubber, chlorinated polyisobutylene and chlorobutyl could improve the mechanical properties to some extent. Liquid natural rubber had pronounced effect on the polyethylene/modified waste blends. The mechanical properties of these blends are given in Chapter VI (a).

The influence of compatibilizers in PE/butyl blends was studied using dynamic mechanical analysis and the details are outlined in Chapter VI (b).

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