"STUDIES ON ELASTOMER BLENDS WITH SPECIAL REFERENCE TO NBR/BUTYL, NR/BUTYL AND NBR/EPDM BLENDS"

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CERTIFICATE

This is to certify that this thesis is a report of the original work carried out by Mr.Job Kuriakose Aerankavil 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 hereby declare that the thesis entitled "Studies on Elastomer Blends with special reference to NBR/Butyl, NR/Butyl and NBR/EPDM Blends" is the original work carried out by me under the supervision of Dr.Rani Joseph, Reader, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin 682022, and no part of this thesis has been presented for any other degree from any other institution.

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LIST OF ABBREVIATIONS

Polymers

NR	Natural rubber
IIR	Isobutylene-isoprene rubber or butyl rubber
NBR	Acrylonitrile-butadiene rubber
EPDM	Ethylene propylene ter polymer rubber
BR	Polybutadiene rubber
SBR	Styrene butadiene rubber
CR	Polychloroprene
IR	Isoprene rubber
CIIR	Chlorobutyl
EA	Elastomeric alloys
CM	Chlorinated polyethylene

Additives

ZnO	Zinc oxide
MBTS	Dibenzthiazyl disulfide
MBT	Mercapto benzthiazole
TMTD	Tetramethyl thiuram disulfide
MAH	Maleic anhydride
HAF	High abrasion furnace
DOP	Dioctyl pthalate
ATNR	Amine terminated liquid natural rubber
DEG	Diethylene glycol

TETD	Tetra ethyl thiuram disulfide
DPG	Diphenyl guanidine

Other abbreviations

ISNR	Indian standard natural rubber
ASTM	American society for testing and materials
ACN	Acrylonitrile content
rpm	Revolutions per minute
phr	Parts per hundred rubber
P_o	Initial plasticity
PRI	Plasticity retention index
T_g	Glass transition temperature
T	Temperature
ML(1+4) at 100°C	Mooney viscosity determined using large rotor after a dwell time of one minute and rotor run of four minutes at 100°C
ΔG	Free energy change of mixing
ΔH	Enthalpy change of mixing
ΔS	Entropy change of mixing
ΔE	Internal energy change of mixing
SEM	Scanning electron microscope
TEM	Transmission electron microscope
R	Gas constant
Nm	Newton meter
VGC	Viscosity gravity constant
V_r	Volume fraction of rubber network

V_{ro}	Value of V_r for filled vulcanizates
M_c	Number average molecular weight of rubber chains between crosslinks
χ	Polymer solvent interaction parameter
V_s	Molar volume of solvent
ρ_r	Density of rubber
ρ_s	Density of solvent

CONTENTS

Chapter I

INTRODUCTION

Elastomer blends are of great importance to the rubber industry. Almost all important rubber products in industry and transportation applications are used as blends. Moreover, the science and technology of elastomer blends are advancing at a rapid rate. One of the main advantages of elastomer blends is the great regulatable variability of their properties despite the limited number of initial components[1-8]. The blending technology has long been widely used in rubber industry. Compounding with blends of two or more elastomers is an attractive method for attaining properties not available in a single elastomer. While elastomer blends are an integral part of polymer blends there are many factors unique to elastomer blends which decide their properties[9-15].

Polymer blends

In recent years, research and development activities in the field of polymer science and technology have been concentrated more on the modification of existing polymeric materials rather than on synthesising new polymers[16-20].

Polymer blends are prepared by

1. Mechanical mixing of polymers in extruders, compounders, internal mixers etc.
2. Dissolving the polymers in a common solvent.
3. Dissolving or dispersing one polymer in the monomer of another and polymerising.

In large volumes polymer blends and alloys are mainly prepared by the first method[22-25]

All materials attract interest on the basis of their property-processing-cost-performance relation-ship. The most important concept in polymer blends is additivity of properties. By this we mean that when a polymer is mixed with another polymer, the resulting blend has a property which is the weighted average of the properties of the individual polymers. Modulus is one of such properties that is expected to obey some additivity relationship[26]. For blends the weighing functions of the composition will be sensitive to the morphology. A very intriguing possibility, although less frequently observed, is synergism in property, such as tensile strength, when the blend has a better property than those of the components. The success of a new material depends on several factors such as combination of properties and cost dilution. For example, when we blend a high thermal resistant polymer having poor processability with another polymer having good processability and poor thermal stability, the resulting blend may be useful for certain applications for which both the individual polymers are unsuitable. Similarly, when a costlier polymer is blended with a cheaper one it may reduce the properties to a level still acceptable for a particular application. At the same time it will bring the cost of the blend to a range which is competitive in the market. Thus blending is an attractive means to engineer a material so that the user does not have to pay for more than he needs. This is the most important driving force for developing products from polymer blends.

Since the driving force for development of polymer blends is generally some combination of economics and blend performance or properties, knowledge of the rules of mixtures for blend properties is of critical interest. These rules will again depend on the state of miscibility of the blend. The properties of miscible blends will follow relationships that are functions of composition and to some extent the degree of interaction between the blend components[27,28]. Immiscible blend properties will depend on the phase morphology and phase interaction as well as composition. There are many possible properties of interest such as mechanical, thermal, electrical and chemical.

A wide range of properties can be achieved by blending which includes mechanical, electrical and chemical properties along with processability. Compatibility is the fundamental property, deciding the practical utility of a polymer blend[29-37] In polymer blends the property (P) depends on average properties of the constituents and can be described by the following equation:

$$P \simeq P_1C_1 + P_2C_2 + IP_1P_2$$

where P is the property of the blend, P_1 and P_2 the properties of the isolated components and C_1 and C_2 the respective concentrations of the constituents. I is an interaction parameter which can be positive, zero or negative as shown in Fig.1.1. When I is positive the property is synergistic, when I is zero the property is additive and when I is negative the property is nonsynergistic.

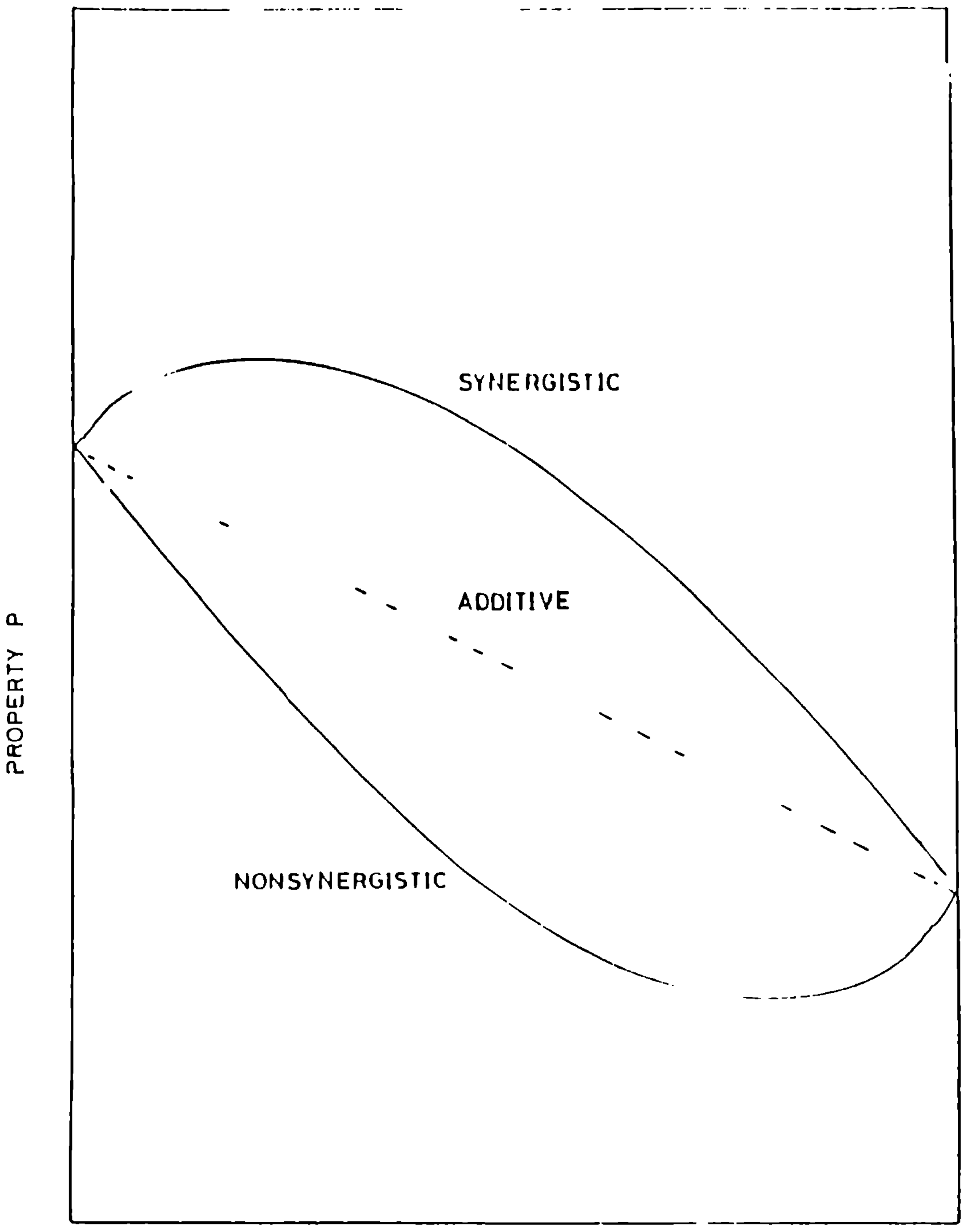

Fig.1.1: Variation of property with composition for a binary polymer blend

The most important factor governing the ultimate properties of a polymer blend is intermolecular bonding force between the molecules. The low interaction at the interface is responsible for its tendency towards phase separation under various conditions (stress, blend ratio and temperature). The poor adhesion between the molecules at the interface in a heterogeneous system does not allow efficient transfer of stress across the interface leading to premature failure under stress. Though many immiscible systems form useful products and are being successfully commercialised, the applicability of such polymer blends is limited because of the inferior macroscopic properties. So successful blending of incompatible polymer systems is gaining increasing importance both in the academic and industrial fields.

Elastomer blends

None of the commercially available elastomers satisfy the divergent requirements of various products. Hence in order to attain desirable technical compromise of properties, blending between two or more rubbers is widely practised. Pneumatic tires are examples of composite products in which the rubber compounds are made from blends of two or three elastomers as shown below[23].

Typical Elastomers in Passenger and Truck Tires

	Passenger	Truck
Tread	SBR-BR	NR-BR or SBR-BR
Belt	NR	NR
Carcass	NR-SBR-BR	NR-BR
Black sidewall	NR-SBR or NR-BR	NR-BR
White sidewall	NR-SBR-EPDM-IIR	
Liner	NR-SBR or NR-SBR-IIR	NR-IIR

One particular advantage of blending BR with NR is the effect of high curing temperatures on physical properties. This heat stability is conveyed by cis BR when blended with NR or SBR[32]. Similar improvements in thermal reversion are claimed for blends of emulsion BR with NR. The addition of cis BR is said to decrease the tensile strength and modulus of NR vulcanizates but to increase elasticity and abrasion resistance[33]. The poor processing properties of cis BR are improved by blending with liquid BR, and excellent properties for sulfur vulcanizates. are Claimed Difficulties in the processing of stereoregular poly(butadienes) are claimed to be overcome by use of specific black and or blending with NR or SBR[34,35]. Tread wear and wet skid resistance of SBR are found to improve for NR/SBR elastomer blends. Enhanced heat resistance in black filled and mineral filled stocks of EPDM/butyl blends has been established[36,37] Blending of high unsaturated rubbers with EPDM and EPM usually seeks to take advantage of the latter's ozone resistance[38]. Blends of EPDM with NR, SBR, NBR and CR give compounds with good ozone and chemical resistance and good compression set characteristics[39]. The difficulty experienced with covulcanization of butyl rubber with diene rubbers is alleviated by use of chlorobutyl and the blend can be used for inner liner ~~of~~ tubeless tires, where impermeability and damping properties of butyl rubber is exploited[40]. EPDM/NBR blends have also been considered for obtaining moderate resistance to oils and ozone, plus an acceptable level of general mechanical properties[41]. A blend of silicone and fluorosilicone polymers bonds easily with fluorosilicone adhesives and has better physical properties, better processing and is cheaper than the unblended polymer[42]. Comparison of mixing methods showed an advantage for directly compounding ingredients into the blend of elastomers, over mixing previously prepared master batches. Study of black loadings showed reinforcing furnace blacks generally to be the best type[43]. The processing behaviour ie., mixing, extruding and calendering characteristics of many stereo regular elastomers need modification to be technically acceptable for factory operations. For example processability in the case of polybutadiene, varies from very difficult to easy and may be improved by addition of oil, liquid polymers, or other broader distribution elastomers, such as NR or emulsion SBR[44].

Vulcanizate physical properties are affected by two major factors: vulcanization and filler distribution. In order to achieve a single T_g which controls blend properties such as resilience, some covulcanization between the different phases in the blend is needed. This explains the use of chlorobutyl in place of butyl rubber for blending with diene elastomers which give better general physical properties and the variation of the termonomer in EPDM influences physical properties of its blends with diene rubbers. This covulcanization (interphase crosslinking) is influenced by the type of curative system used, including its solubility in each phase and the response of the individual elastomers to the curatives. Filler disaggregation to an adequate level is needed for optimum properties but another potent factor appears to be distribution of the filler in the phases of the blend. This distribution is clearly influenced by the molecular weight of each phase.[44,45]

Properties of elastomer blends

Mechanical properties of elastomer blends may not often approach the level of average properties of the individual components which is due to the incompatibility on the molecular scale and exist in the form of two separate phases. A heterogenous blend usually results when two chemically dissimilar rubbers are mixed [46-50]. Several investigators have tried to correlate between the morphology as revealed by electron microscopic studies and the mechanical properties of the blends. It is convenient to divide the variables of a blend system into two categories direct and indirect variables[51]. The direct variables can be further subdivided into those which are important because the pure component properties depend on them and those that are unique to the blend systems. The direct variables are the fundamental ones and can be controlled by the indirect or processing variables.

The first three fundamental variables are those that also affect the pure components. They are the glass transition temperature (T_g), the molecular weight and crosslink density of the components. Among the rubbery materials, a higher T_g or molecular weight generally increases toughness for a given crosslink density[52], moreover the mechanical properties of elastomers depend very strongly on crosslink density[53]. Specifically, the energy required to rupture an elastomer in simple tension generally passes through a maximum as a function of crosslink density.

The remaining four direct variables are unique to blends. The properties obviously depend on the properties of each component in the blend. In addition, morphology of the blend may be important. One rubber, may form the continuous phase while the other is dispersed phase, or a cocontinuous structure when both phases are continuous may exist. Also, various sizes and shapes of the dispersed particles are possible.

The interfacial adhesion between the two phases may determine the path that a growing crack takes in a deformed rubber blend and also determines the extent to which stresses can be transferred between the matrix and particle phases. If the interfacial adhesion is sufficiently low, the small cavities may be opened up between the dispersed domains and the matrix when the blend is stressed. Thus the interfacial adhesion plays a key role in determining the mechanical properties. The relative stiffness between the two phases is a function of the molecular weight, T_g, and rate of crosslinking (and scission) of the two rubber phases. The micro deformation of the blend particle will depend in part on this property. It is found in many composites that the relative stiffness also affects the mechanical properties.

The morphology of a blend depends upon the condition under which the rubbers are mixed. Two methods have been used (1) solutions of rubbers stirred together, then dried or precipitated. (2) The bulk rubbers are comasticated in a Brabender plasticorder, or similar high shearing mixer. With this technique, the mixing time, temperature, and/or speed can be varied to obtain different morphologies. Annealing after mixing is another method of changing the morphology which can cause an increase in dispersed particle size or phase inversion.

Distribution of insoluble compounding ingredients

A general question which comes up in the case of of elastomer blends is regarding the distribution of filler particles between the separate zones and how are performace characteristic affected[54].

Fillers are broadly defined as reinforcing and non-reinforcing. Carbon black and silica are included in the first class, while clays and whiting are examples of the second category.

Based on a series of investigations on blend homogenity of natural rubber with some of the principal synthetic elastomers the following conclusions have been arrived at.

Filler distribution between separate polymer phases is strongly influenced by molecular features and processing variations. In 50/50 preblend with NR, the commonly used commercial types of SBR show a strong affinity for carbon black, when added to the blend at relatively high loadings (eg., 40 phr) similar to NR/BR blend containing carbon black. In unmilled solution or latex black master batch of NR and SBR no preferntial distribution of black was observed. Studies on 50/50 preblends of IR/BR and NR/BR containing precipitated silica showed that there was a strong tendency for the silica particles to locate preferentially in the isoprene phase. Similar results were also obtained with NR/SBR blends. Under high shear mixing conditions carbon black will migrate from a NR masterbatch to polybutadiene. High transfer was favoured by a relatively high black loading and low heat history for the NR black masterbatch. With a NR silica masterbatch, little or no transfer to polybutadiene was observed[55].

The effect of an appreciable volume loading of filler on the properties of cured elastomeric vulcanizates depends on whether the elastomer is stress crystallising or not. Dinsmore[54] reported that the ratio of the tensile strength, of black filled to that of gum vulcanizates is 1 to 1.5 for NR vulcanizates and 5 to 10 for vulcanizates of SBR and similar elastomers. Thus appreciable improvements in strength properties may be obtained for non stress crystallising rubbers by incorporation of carbon black. Certain elastomers have optimum filler loading for particular properties such as wear and tear resistance[54]. In a 50/50 NR/BR preblend, carbon black normally locate preferentially in the BR component and this distribution results in optimum vulcanizate performance[57,58]. The incorporation of carbon black into 50/50 elastomer preblends indicated that black affinity decreased in the order BR, SBR, CR, NBR, NR, EPDM, IIR[59]. In addition, black transfer during blending was observed from a mechanically mixed IIR masterbatch to a high unsaturation gum rubber but not from a NR masterbatch. Transfer, thus, appears to be confined to those situations in which the adsorptive capacity of the filler has not been fully realised. This may occur if the polymer filler masterbatch has minimum thermal or mechanical history or involves low molecular weight or low unsaturation elastomers, situation in which bound rubber formation is minimized[60-62].

It is apparent that the surface polarity of carbon black influences its distribution in elastomer blends, and also that the behaviour of inorganic filler is disparate eg. in cis BR-NR blends, silica tends to accumulate in the NR phase. Filler distribution is also influenced by the point of addition of filler, the viscosity levels of the elastomers, and the blending methods. The ability of rubbers to accept black and other filler is said to be an important factor in attaining good dispersion which in turn affects reinforcement and ultimate performance properties. The reinforcing ability of a filler in an elastomer can be assessed by bound rubber determination[66].

Distribution of fillers can profoundly influence the modulus in elastomer blends. At lower strains where the carbon black network structure dominates the stiffness properties, an increase in the nonuniformity of this filler distribution results in a lower stock modulus. This indicates that the transfer of a portion of the carbon black from one phase would lower its modulus proportionally more than the increase in modulus of the phase with the higher carbon black concentration. The effect of carbon black distribution on modulus is thus related to the nonlinear dependence of rubber modulus on carbon black loading[66,67] Blending of elastomers with different affinities for black provides an opportunity to control the state of aggregation and connectivity of the carbon black and thereby influence the electrical conductivity. Conductivities can be achieved in the blends which exceed those of the pure components. This is due to increased agglomeration of carbon black in the immisicible blends. Carbon black tends to redistribute when mixed into blends, particularly where it has a low affinity for one of the phases. This results in an accumulation of carbon black at the interface[68,69] and consequently higher electrical conductivity. Blends of rubber with similar affinity for carbon black do not exhibit this synergism (eg. SBR/NR).

The hysteresis of a blend is often found to be lower than the weighted average of the components, particularly in filled system with a nonuniform carbon black distribution. The phase with the lower carbon black loading will have both reduced modulus and hysteresis particularly when the softer phase is the continuous phase where a low blend hysteresis[70] may result. Most of the hysteresis reduction accompanying a non-uniform distribution of carbon black can be attributed to the nonlinear relationship between hysteresis and carbon black loading particularly at very high loading[71].

Homogenity of blends

Homogenous or miscible blends are characterised by one value of any physical parameters whereas immiscible or heterogenous blends are characterised by several values of the same parameter[72]. A homogeneous polymer blend has one glass transition temperature in between those of the two polymers. In a highly phase separated polymer blend, the transitional behaviour of the individual components will be unchanged while in a miscible blend a single and unique transition will appear.

Microscopy is unique for detailed characterisation of the phase morphology in blends[73]. Optical (visible light) contrast can arise from a number of sources such as colour, opacity, refractive index, orientation, absorption etc. With transmission electron microscope (TEM), electron scattering differences are the primary source of contrast. Scanning electron microscope on the other hand, depends primarily on surface texture for contrast. Scattering methods depend on the principle that stable homogenous mixture is transparent whereas unstable non-homogenous mixture is turbid unless the components of the mixture have identical refractive indices[3]. The utility of polymer blends obviously does not require achieving miscibility. Most of the multicomponent polymer system commercially utilised are two phase blends.

In heterogenous or phase separated blends, interfacial adhesion between the respective phases governs the ultimate mechanical properties. For polymeric constituents having limited affinity for each other, the interface represents a flaw yielding ultimate mechanical properties significantly lower than expected from constituent values. If indeed polymers are miscible excellent adhesion is expected, provided sufficient temperature and pressure are employed to allow for molecular mixing.

The primary advantage of a miscible blend compared to immiscible blend counterparts is the assurance of mechanical compatibility. The simplified average of ultimate mechanical properties is not always the observed or expected case, due to the importance of the position of the glass transition temperature (T_g) and or brittle ductile behaviour.

Blend compatibility

Although the great majority of elastomer blends are heterogeneous some technically advantageous combination or compromise of properties can be realised from the blends. However in most heterogenous rubber mixtures the mechanical properties are found to be inferior to those of the components. This is due to three types of incompatibilities generally met within these type of blends, namely thermodynamic incompatibility, viscosity mismatch and cure rate mismatch[74].

Viscosity considerations

Tokita[75] and Avegeropolous[76] have thoroughly investigated the mixing parameters required for the optimum blending of elastomers. In a blend of EPDM/NR it was concluded that smaller domain size was achieved through a higher stress field during mixing, lower interfacial tension between the phases, and diminishing concentration of the disperse phase (less coalescence). Higher mixing temperature appeared to reduced domain size by diminishing the interfacial tension. Since the temperature normally goes up during mixing, the high shear blending of polymers with similar viscosities will give the most homogenous mixtures. Further studies in EPDM/BR blends indicated that the driving force for blend homogenity was related to a similarity in the viscosities of the two phases under the specific condition of mixing. Because of the large difference in T_g between EPDM and BR it was possible to vary their relative viscosities simply by changing the shear rate and or mixing temperature, the domain size of the disperse phase (or the size of the cocontinuous phases) could thus be altered for the same blend. It was also possible to shift the disperse phase from one polymer to another eventhough that polymer was the minor component (25%). In this instance, the low viscosity phase actually encapsulate, the high viscosity component, and then becomes continuous. The shape of the domains is more nearly spherical when the high viscosity component is the disperse phase. A softer disperse phase typically gives elongated domains. Extremely large domain size of the BR phase in NR/BR and SBR/BR blends were related to significantly higher viscosity for the BR phase[77] Thus incompatibility due to viscosity mismatch which prevents or greatly delays the formation of intimate mixture can be overcome by improving the blending process either by adjusting oil or filler concentration in the two elastomers and by adjusting the individual raw polymer viscosities so that, through much of the process, the effective viscosities of the phases will no longer be mismatched[78,79]

Thermodynamic considerations

Thermodynamic incompatibility prevents mixing on a molecular scale[80,81]. Thermodynamic incompatibility of polymer blends is governed by the well-known Gibbs free energy relation

$$\Delta G = \Delta H - T\Delta S$$

where ΔG is the change in free energy of mixing, ΔH the change in enthalpy of mixing, ΔS the change in entropy of mixing and T the absolute temperature.

Polymer blends exhibit a wide range of morphological states from coarse to fine ones. In addition to the usual possibilities of obtaining separate phases, with various size, shape and geometrical arrangement of inclusions, more complex structures are possible especially in crystalline polymer blends. For such systems specific properties can be expected eg., for gradient polymers which contain crystalline elements. One of the main aspect of study on polymer blends is the dependence of the mechanical properties on composition. This is due to the fact that these complex systems exhibit a behaviour which does not simply follow the sum of the properties of the components.

It seems interesting to note that until quite recently, relatively very little attention has been given to the interaction of the components in terms of the thermal stability of the composition[2].

Polymers can be blended to form a wide variety of random or structural systems with desirable combination of properties but in practice, these theoretically expected properties are not achieved because adhesion of the phases are not created. The most pertinent dynamic properties pertaining to elastomer blends are homogenity of mixing (phase morphology) and cure compatibility.

The complete miscibility of polymers requires that the free energy of mixing be negative, which can only be achieved by exothermic mixing or a large entropy of mixing[1,3,74,19,82] Therefore, most of the blends of elastomers are immiscible because mixing is endothermic and entropic contribution is small, because of the high molecular weights. Hence an almost insignificant positive free energy of interaction is enough to overcome this small entropy of mixing. Thus two polymers do not have to be very dissimilar before they are insoluble in each other and lead to the existence of discrete zones of heterogenity upon mixing. Fortunately miscibility is not a requirement for most rubber applications. Homogenity at a fairly fine level is necessary for optimum performance but some degree of micro heterogenity is usually desirable to preserve the individual properties of the respective polymer component. Based on microscopic studies, almost all bulk mixes of elastomer blends are microheterogenous to varying degrees[83].

Miscibility implies that a lower free energy is associated with molecular dispersion of the components than with a phase separated morphology. The free energy change (excess free energy) accompanying formation of a strictly random two component mixture can be expressed as[82,84]

$$\frac{\Delta G_m}{KT} = V\left[(\phi_i/V_iN_i)\ln \phi_i + (\phi_j/V_j\, N_j)\ln \phi_j + \phi_i\phi_j\, X/V_r\right]$$

where V is the total volume, and V_i, N_i and ϕ_i the molar volume, degree of polymerisation and the volume fraction of the ith component respectively. V_r is an arbitrary reference volume that can be conventionally taken to be equal to the root mean square of the respective molar volumes of the component chain units. The first two terms on the right hand side of the above equation correspond to the ideal, or random mixing entropy. The third term represents the excess enthalpy. This mixing enthalpy is zero for an ideal mixture, that is, a mixture of molecules that have the same size, shape and in which the intermolecular forces between pairs of like segments of each type, as well as between unlike segments, are all equivalent. Such ideality is not expected in practice, and the excess enthalpy due to mixing is described by the Flory Huggins interaction parameter X.

In strictly van der Waals mixtures, phase separation can be induced by increases in one molar mass of the constituents, since the miscibility is of entropic origin. For high polymers, this combinatory entropy makes a sufficiently small contribution to the free energy such that miscibility is always limited to mixtures in which the components chemically interact and thereby effect a negative excess enthalpy. When such specific interations are present increases in molecular weight can still effect phase separation. Blends with high exothermic mixing enthalpies, on the other hand, can be expected to remain miscible at the highest of molecular weights.

Cure compatibility

While true miscibility may not be required for good rubber properties, adhesion between the polymer phases is necessary and the respective interfacial energies are important in this respect.

Covulcanization[85] was defined in terms of a single network structure including crosslinked macromolecules of both polymers. They should be vulcanized to similar levels with crosslinking across the microdomain interfaces. The nature of the polymer (eg., unsaturation, polarity) determines curative reactivity which is also influenced by solubility. Vulcanizates with components having similar curative reactivity generally give better properties than those whose components have large difference in this respect[86,87]

Curative diffusion

Curative diffusion[88-91] between the domain of an elastomer blend takes place during vulcanization. This process may deplete curatives from one side of the polymer-polymer interface and actually speed up cure on the other side. Thus, there is an interfacial layer of rubber with a different state of cure than the bulk. The net result can be a weaker layer of a rubber at the interface which may reduce adhesion.

Gardiner[89] measured a diffusion gradient (D), which represents the concentration changes as a function of distance and time, His measurements for the diffusion of accelerator (tellurium diethyldithio carbamate) and sulfur from IIR to other elastomers are shown below

Curative diffusion coefficient[92]

Curative	From	To	$Dx10^{7}$,cm^{2}/S
Accelerator (TDDC)	IIR	BR	12.66
		EPDM	1.09
		CR	1.08
		SBR	0.58
		NR	0.70
Sulfur	IIR	SBR	4.73
		SBR & 50 PHR N700 CB	17.2
		NR	2.82

Gardiner emphasised that curative migration is related to diffusion during curing and not transfer during mixing. Curative diffusion was controlled through selective (phase) mixing of curatives into the individual polymers using specific curative combinations. Cure rate mismatch occurs due to solubility differences and curative migration of ingredients in elastomer blends. Solubilities of curatives in various rubbers at 153°C are shown below[85,93,94].

	Solubility at 153°C, phr[95]		
Curatives	SBR	EPDM	BR
S	17.3	10.7	16.8
MBT	5.2	1.1	2.4
TMTD	14.3	5.0	4.9

The solubility of the common curatives is greater in highly unsaturated elastomers than in less unsaturated elastomers and migration from the latter to the former may be inevitable even when concentrations are equal initially[89]. Such migration will be accentuated by higher curative reaction rates in the high diene elastomers, causing excess material to be drawn from the adjacent phase and associated with over and undercure[90,57] In such circumstances vulcanizate properties may not approach the level attainable by either of the elastomers alone and will be well below the additive line in terms of their properties.

Blending procedures

The general mixing methods for preparing elastomer blends include, latex, solution, solution and latex, mechanical, mechanochemical and powdered rubber[19]. These methods may be further divided into two general categories of preblending and phase mixing. In the first case, the compounding ingredients are generally added to the premixed polymers in a manner similar to the mixing of a single elastomer. In a phase mix, an attempt is made to control the specific location of filler and or extender oil and curing agents. This is generally accomplished by the preparation of separate masterbatches which are then blended mechanically.

Preblending

This procedure is probably the one most commonly used for mixing of polymer blends in a Banbury. One of the polymers, may first be masticated to improve mixing behaviour and reduce viscosity difference. Evans and Partridge[96] showed that a single stage preblending procedure was a most cost effective method for preparing blends of NBR and halobutyl (CIIR). NBR has been compounded with 25% of the carbon black and two third of the extender oil. This masterbatch was then blended with the CIIR and the remaining carbon black and oil prior to adding curatives on a mill. It was found that rubber properties are not significantly different for the two compounding procedures. For the best results, the polymer components of a blend are usually mixed for a short amount of time prior to addition of the filler and other compounding ingredients[70]. Bristow[97] compared the properties of NR/BR as a function of preblending: addition of ingredients with no preblending, and the blending of separate masterbatch which contained proportionate amounts of the compounding ingredients. No major differences in final compound properties were indicated within comparison. However, no studies were carried out with uneven proportions of compounding ingredients added to the separate masterbatches.

Solution and latex mixing

Latex[98,99] and solution[78,58,100] mixing have both been employed for the preparation of elastomer blends. These methods offer distinct advantages of mixing smaller particle size carbon black in conjunction with cleanliness of operation and better utilisation of mixing facilities. However, the advantages in blend uniformity, if any, would appear to be small. Comparison of latex and solution masterbatches to mixes made in Banbury or on a two roll mill showed that former gave uniform blends, but roll mixing[101] was found to be the most effective means of blending masterbatches. The mill mixes were very uniform and indicated lower die swell in comparison to latex blending. However, most rubber properties were found to reflect the overall blend ratios of the polymers and there were no major trends associated with the mixing procedure.

Phase mixing

Separate masterbatches are employed with this type of mixing in order to locate specific types and amounts of curing agents[85,90,92,102] or filler[58,59,70,103] in the separate polymer phases. In one of the first studies of this type[58] solution mixing[104] was used to prepare NR and BR masterbatches at different carbon black loading. This is a convenient method for difficult-to-mix polymers such as cis 1,4 BR. The masterbatches were subsequently blended in a Banbury to produce tread compounds with variation in carbon black phase distributions. The phase mixing procedure assumes that the carbon black (or other ingredients) will remain in the polymer to which it has been added. But this is not always true since there are specific conditions under which carbon black has been observed to migrate from one polymer to another during mixing.

Covulcanization of elastomer blends[110]

Several investigators have tried to improve covulcanization of elastomer blends and thereby improve the properties of the blends closely along the additive line with respect to the properties of the two individual elastomers. Improved covulcanization of EPDM/NR blends[93] was achieved by Woods and Davidson by using a TETD accelerator-lead oxide activator combination. The lead salts of TETD are insoluble in both polar and nonpolar materials, which eliminates the thermodynamic driving force for curative diffusion[105]. Coran achieved better cure compatibility for EPDM/NR blends by modifying the EPDM with maleic anhydride which permits EPDM to be crosslinked independantly with zinc oxide in the accelerated sulfur vulcanizing system. An ionic crosslink network is produced in the EPDM phase. This type of crosslinking is not competitive with the accelerated sulfur system which reacts rapidly with NR compared to conventional NR/EPDM blends, those with the modified EPDM exhibited higher tensile strength and fatigue life along with reduced hysteresis and permanent set, all of which reflect better covulcanization. The maleic anhydride treatment has also been applied to IIR and EPDM by Suma[106] and coworkers for improved blending with NR. Elastomer blends can be described in terms of three types of systems[50].

1. Unvulcanized domains of polymer A in an unvulcanized matrix of polymer B (plastic behaviour).

2. Unvulcanized domains of polymer A in a vulcanized matrix of polymer B (rubber like elasticity but diluted by the A phase).

3. Vulcanized domains of polymer A in a vulcanized B matrix (maximum elasticity).

Zapp[40] obtained interfacial bonding in the CIIR/SBR and CIIR/BR blends through the use of very active thiuram and thiuram tetrasulfide curative systems, and also with bis alkyl phenol polysulfide as sulfur donors. Interfacial bonds were associated with a preponderance of monosulfidic crosslinks. Reinforcing carbon blacks indicated only a minimal effect on the sulfur bond chemistry or in the interfacial bonding. However, covulcanized carbon black loaded blends using a sulfur donor cure system displayed tensile strength and rupture energies which were significantly higher than systems cured with elemental sulfur.

Special mixing techniques

A number of mixing schemes have been developed to control more precisely the different aspects of the overall homogenity, phase morphology filler distribution and interfacial interaction of the different components of elastomer blends. Controlled heterogenity in elastomer blends has been used to improve the green strength of blends of NR with the other elastomers accomplished by blending of separately mixed major and minor components of the blend.

a) Dynamic vulcanization

The concept of dynamic curing was originally developed by Gessler for blends of CIIR and polypropylene. With this mixing technique, the elastomer phase was crosslinked to provide a vulcanizate within a thermoplastic matrix. Dynamically vulcanized blends have been defined as elastomeric alloys (EA) which represents a synergistic combination of an elastomer and thermoplastic. The resultant properties are above those that would be expected for a simple blend of the component polymers. Alloying is primarily chemical in nature with strong interaction between the elastomer and the thermoplastic. Dynamic vulcanization technique has been applied by Coran[24,105] and coworkers[107,108] to enhance properties of elastomer blends. They dynamically vulcanized EPDM/NR blends in which the EPDM was vulcanized into small domains through the use of an EPDM polymer modified with maleic anhydride. Partial dynamic precrosslinking or precuring is one of the recent technique used for NR/IIR blend homogenisation.

b) Compatibilization

The blending of highly incompatible elastomers n sometime be improved by the addition of small amounts f another polymer. Selva and White applied this technique to improve the homogenity[109] of binary and tern y blends of CR, NBR and EPM. NBR/EPM and CR/EPDM blends x much more rapidly when a small amount of chlorina d polyethylene (CM) is added to the mix. The CM can e considered to be a compatibilizing or emulsifying ag t which appears to form a skin on the EPM particles. I s helps the larger NBR chunks to adhere to them.

OBJECTIVES AND SCOPE OF THE PRESENT WORK

The main objective of the present study is o develop covulcanized elastomer blends such as NR/I , NBR/IIR and NBR/EPDM so as to improve their mechani l properties for critical applications.

Natural rubber (NR) maintains its leading posit n for applications requiring a combination of properties t is poor in air/gas retention properties and its resistance to oxidation and ozone degradation. Butyl rubber has excellent ageing behaviour and resistance to ozone cracking combined with low permeability to air and other gases. Blending and co-curing of NR and IIR is practically impossible due to the large difference in unsaturation between these rubbers. But if these two rubbers can be cocrosslinked the blend may turn out to be a very useful one.

Nitrile rubber (NBR) has excellent oil resistance, but is subject to degradation at high temperature. The high temperature ageing resistance is important for this rubber because of its frequent use in extractive media which often leach out the antioxidants in the vulcanizate. A more practically useful approach to improve the ageing resistance of NBR is by blending it with rubbers such as butyl rubber or by blending it with ethylene propylene ter polymer (EPDM) which has excellent resistance to ozone, oxygen and weathering even without antioxidants and antiozonants without sacrificing nitrile's oil resistance.

The following methods are proposed to be investigated for attaining uniform crosslinking in both elastomer phases and hence improving the mechanical properties of NR/IIR, NBR/IIR and NBR/EPDM blends.

1) Use of a novel compounding sequence

Instead of blending the rubbers first and then adding the compounding ingredients for both the rubbers as is done conventionally, the slower curing rubber of the above blends is proposed to be compounded first with its curing agents and other ingredients.

2) Partial precuring of the slower curing rubber

In order to prevent migration of the curing agents from the slower curing rubber to the faster curing one the slower curing rubber is proposed to be precured or precrosslinked to an optimum level before blending with the faster curing rubber. This procedure may also help to bring down the viscosity mismatch between the constituent elastomers in a blend. The partial precuring is proposed to be done both statically (in an air oven) and dynamically (in an internal mixer) such as Brabender plasticorder or Shaw intermix.

3) Carboxylation of the slower curing rubber

In order to make the nonpolar rubber, polar carboxylation of the nonpolar elastomer is proposed. This may reduce the tendency for curative migration and cure rate imbalance between the two constituent elastomers.

4) Use of a compatibiliser

Use of a polar rubbery compatibiliser such as amine terminated liquid natural rubber (ATNR) is yet another way proposed for improving the mechanical properties of the blend.

5) Evaluation of the efficiency of the above novel methods

In addition to measuring the mechanical properties, the efficiency of the above proposed novel methods for preparing elastomer blends will be investigated by several other techniques such as observing the dispersion of fillers and other ingredients in the blends, by optical microscopy and photomicroscopy, morphology of the blends by SEM studies of the fracture surfaces, measuring the crosslink densities by equilibrium swelling and by measuring the electrical conductivity and permeability of the blends.

The thesis is divided into following chapters:

Chapter I	Introduction
Chapter II	Experimental techniques
Chapter III	
Part I	Mechanical property improvement of NBR/IIR blends by partial precuring of IIR
Part II	Effect of acrylonitrile content on the mechanical properties of NBR/IIR blend
Chapter IV	
Part I	Studies on NR/IIR blends: Effect of partial dynamic curing of butyl before blending
Part II	Use of amine terminated liquid natural rubber as a compatibiliser in NR/NBR blend
Chapter V	
Part I	Studies on the covulcanization of NBR/EPDM blends
Part II	Morphology, permeability, dispersion and conductivity studies of NBR/IIR, NR/IIR and NBR/EPDM blends
Chapter VI	Summary and conclusions.

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Chapter II

EXPERIMENTAL TECHNIQUES

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

Elastomers

1. Natural rubber (NR)

ISNR-5 was supplied by Rubber Research Institute of India (RRII), Kottayam. The Bureau of Indian Standards (BIS) specifications for this grade of rubber are given below:

Parameters	Limits
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. Isobutylene-isoprene rubber or Butyl rubber (IIR)

Butyl rubber used was Polysar PB 301, 1.5 mol per cent unsaturation, Mooney viscosity ML(1+8) at 125°C - 48.

3. Acrylonitrile-Butadiene rubber or Nitrile rubber (NBR)

Nitrile rubber was supplied by Gujarat Apar

Polymers Ltd., Gujarat. Aparene N 553 NS had an acrylonitrile content of 33% and Mooney viscosity (ML(1+4), 100°C) 45. Aparene NSW 512 had an acrylonitrile content of 28% and Mooney viscosity (ML(1+4), 100°C) 50.

4. Ethylene-propylene diene rubber (EPDM)

EPDM rubber was supplied by Herdillia Unimers Ltd., Bombay. Herelene H-625 had a Mooney viscosity (ML(1+4), 125°C) of 65.

Compounding additives

1. Zinc oxide

Zinc oxide (ZnO) was supplied by M/s.Meta Zinc Ltd., Bombay. It had the following specifications.

Specific gravity	5.5
ZnO content	98%
Acid content	0.4% max.
Heat loss (2 hrs at 100°C)	0.5% max.

2. Stearic acid

Stearic acid used in the study was supplied by Godrej Soaps Pvt. Ltd., Bombay and had the following specifications.

Melting point	50-69°C
Acid number	185-210

Iodine number	95 max.
Specific gravity	0.85 ± 0.01
Ash	0.1% max.

3. Dibenzthiazyl Disulfide (MBTS)

Dibenzthiazyl disulfide was supplied by Bayer Chemicals, Bombay. It had the following specifications.

Specific gravity	1.34
Melting point	165°C

4. Tetra methyl thiuram Disulphide (TMTD)

Tetramethyl thiuram disulphide used was supplied by Polylefins Industries Ltd., Bombay. It had the following specifications.

Melting point	136°C
Specific gravity	1.4

5. Sulfur

Sulfur was supplied by Standard Chemical Company Pvt. Ltd., Madras and had the following specifications.

Specific gravity	2.05
Acidity	0.01% max.
Ash	0.01% max.
Solubility in CS_2	98% max.

6. Accinox ZC

Accinox ZC was supplied by ICI India Ltd., Calcutta as dark brown granules. It had the following specifications.

Specific gravity	1.02
Melting point	48°C

7. Zinc diethyl dithiocarbamate

Zinc diethyl dithiocarbamate was supplied by ICI India Ltd., Calcutta as a creamy white powder. It had a density of 1.47 gm/cm^3 and melting point 178°C and soluble in chloroform, CS_2 and benzene.

8. Diphenyl guanidine (DPG)

Diphenyl guanidine supplied by Monsanto Chemical Co., U.K. was white powder of density 1.15 g/cm^3 and melting point 145°C and soluble in chloroform.

9. Mercapto benzothiazoie

Mercapto benzothiazole having the following specificationswas supplied by Bayer India Ltd., Bombay.

Specific gravity	1.50
Melting point	161°C

10. High Abrasion Furnace Black (HAF N 330)

High Abrasion Furnace Black HAF was supplied by M/s.Carbon and Chemicals (India) Ltd., Cochin. It conforms to the following specifications

Iodine adsorption	80 mg/g
DBP adsorption	105 cm^3/100g
Mean particle diameter	32 nm

11. Aromatic oil

Aromatic oil was supplied by M/s.Hindustan Petroleum Ltd. It had the following specifications.

Colour	Viscous greenish brown oil
Aniline point	92°F

12. Paraffinic oil

Paraffinic oil was supplied by M/s.Hindustan Petroleum Ltd. It had the following specifications.

Colour	Light yellowish oil
Aniline point	198°F
Viscosity gravity constant	0.857
Density	0.861 g/cc

13. Naphthenic oil

Naphthenic oil was supplied by M/s.Hindustan Petroleum Ltd. on the following specifications.

Colour	Light coloured oil
Aniline point	164°F
Viscosity gravity constant	0.85-0.9
Density	0.932 g/cc

14. Dioctylphthalate

Commercial grade with specific gravity 0.986 and viscosity 60 cps.

15. Precipitated silica

Precipitated silica VN 3 Gran Ultrasil was supplied by Insilco. Spray dried precipitated silica had following specifications.

Specific gravity	1.98
Heat loss, %	4.7 (2 hours at 100°C)
Ignition loss, %	3.6 (2 hours at 100°C)
N_2 surface area mm^2/gm	155-195
pH (5% aq. sulfur)	5.8-6.8
Residue 45 m sieve	0.3%
SiO_2	93%

EXPERIMENTAL METHODS

1. Mixing and homogenisation

a) Using the Mixing Mill

Mixing and homogenization of elastomers and compounding ingredients were done on a laboratory size (15x33 cm) two roll mill at a friction ratio of 1:1.25. The elastomer was given one pass through the nip of (0.002x100)". Then it was given 2 passes through the nip of (0.002x10)" and allowed to band at the nip of (0.002x55)". The temperature of the rolls was maintained at 70±5°C during the band formation on the mill. After smooth band formation on the mill, the compounding ingredients were added as per ASTM D 3184 (1980) and ASTM D 3182 (1982) in the order of activators, fillers, accelerators and curing agents. Before the addition of accelerators and sulfur, the batch was thoroughly cooled to prevent scorching of the compound on the mill.

After completing the mixing the compound was homogenised by passing six times endwise through a tight nip and finally sheeted out at a nip gap of 3 mm. For the preparation of compounds of elastomer blends, NR was masticated to the Mooney viscosity level of the synthetic rubber and then the rubbers were blended. The other additives were added as described above unless otherwise specified.

b) Using Brabender Plasticorder

Dynamic precuring or precrosslinking was done on a Brabender plasticorder. This device measures the torque generated due to the resistance of a material to mastication or flow under preselected conditions of shear and temperature. The heart of the Brabender plasticorder is a jacketed mixing chamber whose volume is approximately 40 cc for the model used (PL 3S). Mixing or shearing of the material in the mixing chamber is done by two horizontal rotors with protrusions. The resistance which is put up by the test material against the rotating rotors in the mixing chamber is made visible with the help of a dynamometer balance. The dynamometer is attached to a precise mechanical measuring system which indicates and records the torque. A D.C. thyristor controlled drive is used for speed control of the rotors (0 to 150 rpm range). The temperature of the mixing chamber is controlled by circulating hot oil. The temperature can be varied upto 300°C. Stock temperature thermocouple with a temperature recorder is used for temperature measurement. Different types of rotors can be employed depending upon the nature of the polymers.

The rotors can be easily mounted and dismounted due to the simple fastening and coupling system. Once the mixing conditions(rotor type, rpm and temperature) are set sufficient time should be given for temperature to attain the set value and become steady.

c) Using Francis Shaw Intermix

Precuring was also carried out on a Francis Shaw Intermix model (KO MK3) with a working volume of 1 litre. It is a batch mixer, capable of mixing materials in a short period of time. The heart of the intermix is the mixing chamber which contains two rotors of unique design. Materials to be mixed are fed into the intermix at the top. The rotors are driven by an electric motor. Drive is transmitted from motors through a set of reduction gears. Pressure is applied on the stock from the top by a plunger or ram. Discharge door is at the bottom.

2. Cure characteristics

a) Using Goettfert Elastograph

The cure characteristics of the compounds were determined using a Goetfert Elastograph model 67.85. It is a microprocessor controlled rotorless cure meter with a quick temperature control mechanism and well defined homogenous temperature distribution in the die or test chamber. In this instrument, a specimen of definite size is kept in the

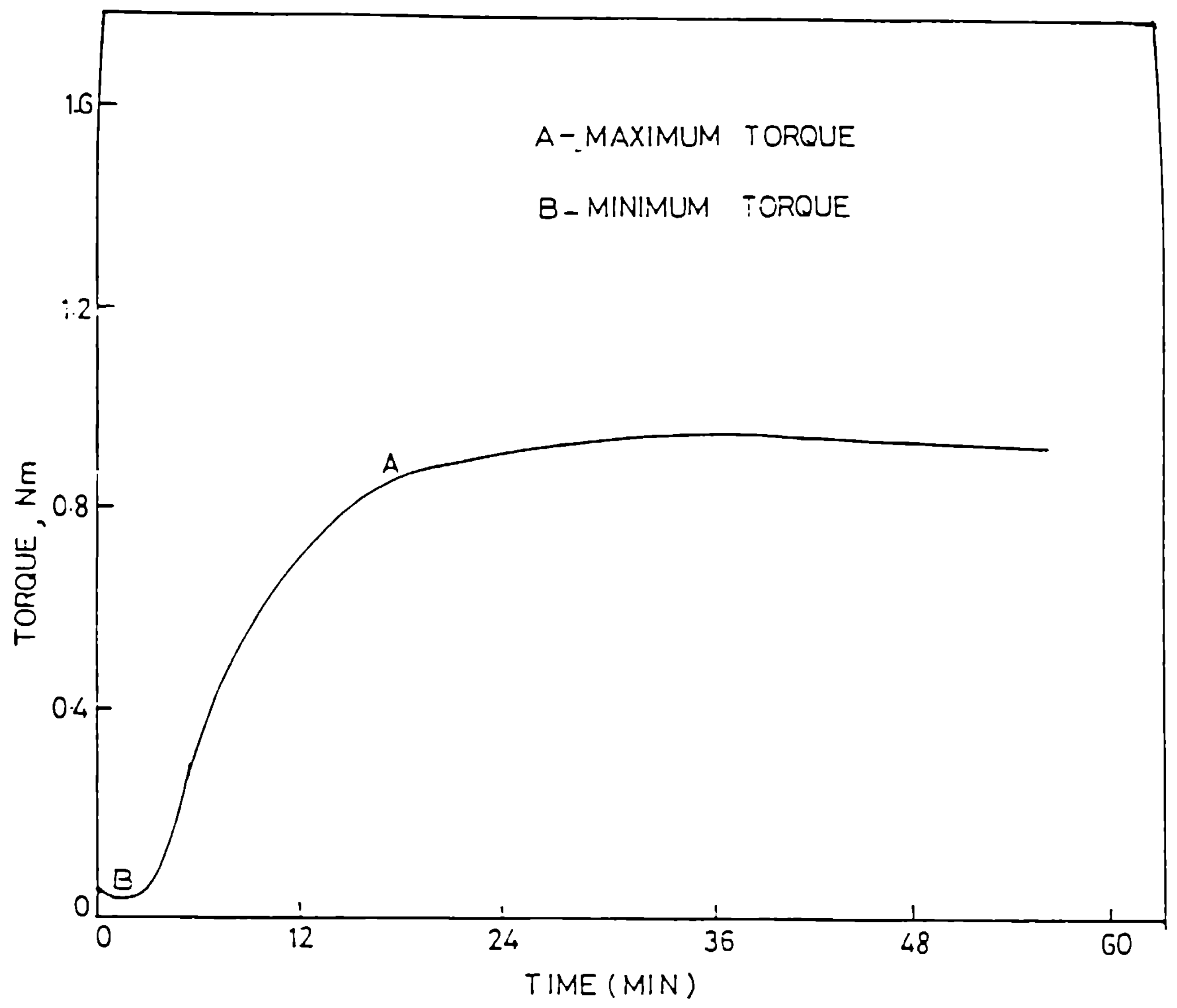

Fig.2.1: A typical cure curve of a rubber compound from Elastograph

lower half of the cavity which is oscillated through a small deformation angle (±0.2°). The frequency is 50 oscillation per minute. The torque is measured on the lower oscillating die half. A typical elastograph cure curve is shown in Fig.2.1 and the following data can be taken from the torque time cure.

(1) Minimum torque: Torque obtained by the mix after homogenising at the test temperature before the onset of cure.

(2) Maximum torque: This is the torque recorded after the curing of the mix is completed.

(3) Scorch time(t_{10}): This is the time taken for attaining 10% of the maximum torque.

(4) Optimum cure time (t_{90}): This is the time taken for attaining 90% of the maximum torque.

(5) Cure rate: Cure rate was determined from the following equation

$$\text{Cure rate (Nm/min)} = \frac{L_{max} - L_{min}}{t_{90}-t_{10}}$$

where L_{max} and L_{min} are the maximum and minimum torque respectively and t_{90} and t_{10} the times corresponding to the optimum cure time and scorch time respectively.

The elastograph microprocessor evaluates the vulcanization curve and prints out these data after each measurement.

b) Using Monsanto Rheometer

The Monsanto rheometer used in the study for determining the curing behaviour of rubber compounds was model 100 S. In this instrument the rubber compound is contained in a cylindrical cavity 50x10 mm and has embedded in it a biconical rotor of diameter 37 mm which is oscillated simultaneously through a small arc amplitude (1 to 3 degree). The cavity and the specimen are maintained to within ±0.5°C and the force required to oscillate the disc is measured. The torque time curve (vulcanization curve) of the rheometer is similar to that of the elastograph and all the relevant data could be taken accordingly.

Cure time

On examination of the graph (plot of torque vs. time) one can observe that the torque decreases initially with time due to reduction in viscosity and thixotropic effect, but increases, steadily as vulcanization starts. As vulcanization proceeds this torque shows a steady increase, attains a maximum value and then slowly decreases due to polymer degradation. For practical purposes cure time is taken as the time for the development of 90 per cent of maximum torque and is denoted as t_{90}.

Permeability measurement

The apparatus consists of a gas cell divided into two chambers by the membrane to be tested. The gas under test is admitted at known pressure from one side. The permeability can be studied either by measuring the pressure decrease at the high pressure side or the pressure increase at the low pressure side. Permeability measurements were carried out according to ASTM D 1434 - 75. Test specimens of thickness 0.25 mm were moulded and used for measurements. The equipment used was CEAST Dow cell COD 62100/000.

The prepared film was used to divide the cell of the apparatus into two chambers, and air at one atmospheric pressure was admitted from the upper compartment. The lower compartment was connected to a suction pump through a capillary U tube. Then conditioning of the test specimen was done for a definite period calculated from

$$t = b^2/2D$$

where b is the thickness of test piece in meters and D the diffusion coefficient in meter square per second. Then mercury was poured into the capillary to a fixed mark. The level of mercury into the capillary steadily decreases as air permeates, through the membrane. The level of the mercury meniscus was periodically noted and permeance in cm^3/cm^2, s mm Hg was calculated from the equation.

$$\text{Permeance} = \frac{g(h)}{t-t_o}$$

$$g(h) = \frac{62.2868}{ARTS} \; \frac{h_o-h}{1-(h_o-h)/2S} \; [a(h_2+h_3-h_o-h)V_f] \text{ where}$$

S = $P-(h_L-h_o)$ slope of the plot of $t-t_o$ vs. the function of g(h) is the permeance of the material.

a = area of capilary, 3.23 mm^2

A = area of transmission, 43 cm^2

h_o = initial height of Hg in the capillary at the start of transmission run, mm.

h = height of mercury in the capillary at the start of transmission run (mm)

h_2 = height of mercury in cell reservoir by from plane to top of mercury meniscus, 126.2 mm.

p = pressure of gas to be transmitted, 760 mm Hg.

R = Universal gas constant, 62360000 (mm^3 x mm Hg)/(Kxg mols)

t_o = time at the time start of the actual transmission run

t = time, hr

V_j = 709.424 mm^3

Air permeability of rubber is governed by factors like chain flexibility, inter molecular interaction, phase and aggregation state of a rubber, density of macromolecular packing and the extent of crosslinking. Permeability of some common rubbers to nitrogen gas at 25°C in 10^{-11} cm^3/cm^2.S mm of Hg.

NR - 80, NBR (27% ACN)- 10, Butyl- 3.25, Methyl rubber- 4.73. Permeability of elastomers to air at 25°C as a percentage relative to NR.

NR-100, NBR (27% ACN)-15, Neoprene G-15, Butyl-4.8, silicone-2700.

3. Moulding of test specimens

The test specimens for determining the physical properties were prepared in standard moulds by compression moulding on a single day light, electrically heated press having 30x30 cm platens at a pressure of 120 kg/cm^2 on the mould. The rubber compounds were vulcanized upto their respective optimum cure times at specified temperatures. Mouldings were cooled quickly in water at the end of the curing cycle and stored in a cold and dark place for 24 hours and were used for subsequent physical tests. For samples having thickness more than 6 mm (Compression set, abrasion resistance etc.) additional curing time based on the sample thickness was given to obtain satisfactory mouldings.

4. Physical test methods

At least five specimens per sample were tested for each property as follows and mean values are reported.

a) Tensile stress-strain behaviour

Tensile properties of the elastomer blends were determined according to ASTM D 412 (1980) using dumbell specimens on a Zwick universal testing machine model 1445. All the tests were carried out at 28±2°C· 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 tight by the two grips, the upper grip of which was fixed. The rate of separation of the power actuated lower grip was fixed at 500 mm/min. for elastomeric specimens. The tensile strength, elongation at break and modulus were evaluated and printed out after each measurement by the microprocessor.

b) Tear resistance

This test was carried out as per ASTM D 624 (1981) using unnicked, 90° angle test pieces. The samples were cut from the compression moulded sheets parallel to the mill grain direction. The test was carried out on a Zwick universal testing machine. The speed of extension was 500 mm/min and the test temperature 28±2°C.

c) Hardness

The hardness (Shore A) of the moulded samples was tested using Zwick 3115 hardness tester in accordance with ASTM D 2240 (1981). The tests were performed on mechanically unstressed samples of 300 mm diameter and minimum 6 mm thickness. A load of 12.5N was applied and the readings were taken after 10 seconds of indentation after firm contact had been established with the specimens.

d) Compression set

The samples (6.25 mm thick and 18 mm diameter) in duplicate, compressed to constant deflection (25%) were kept for 22 hours in an air oven at 70°C. After the heating period, the samples were taken out, cooled at room temperature for half an hour and the final thickness was measured. The compression set was calculated as follows:

$$\text{Compression set } (\%) = \frac{t_o - t_1}{t_o - t_s} \times 100$$

where t_o and, t_1 are the initial and final thickness of the specimen respectively and t_s thickness of the spacer bar used. The procedure used was ASTM D 395 (1982) method B.

3) Abrasion resistance

The abrasion resistance of the samples was tested using a DIN abrader. Sample having a diameter of 6±0.2 mm and a thickness of 6 to 10 mm was kept on a rotary sample holder and 10N load was applied. Initially a pre run was given for the sample and its weight taken. The weight after final run was also noted. The difference in weight is the abrasion loss. It is expressed as the volume of the test piece getting abraded away by its travel through 42cm on a standard abrasive surface. The abrasion loss was calculated as follows.

$$V = \frac{\Delta M}{\rho}$$

Δm = mass loss, ρ = density of the samples V = abrasion loss in cc.

Ageing studies

Dumbell and angular test specimens for the evaluation of physical properties were prepared and kept in a multicell ageing oven at predetermined temperature for specified periods. Physical properties like tensile strength, tear resistance, elongation at break etc. were measured after ageing. The percentage retention of these properties were evaluated for assessing the ageing resistance. The procedure given in ASTM D 573 was followed.

Density

The densities of the polymer samples were estimated by the method of displacement of liquid (ASTM D 792). In this method the weight of the specimen in air was first noted and then the specimen was immersed in a liquid and its loss of weight in liquid was determined. The density is given by

$$\text{Density} = \frac{\text{Weight of specimen in air x density of the liquid}}{\text{Weight loss of specimen in liquid}}$$

Ozone resistance

Ozone ageing studies were conducted according to ASTM D 518 method D in a MAST model 700-1 test chamber at

41°C. Ozone concentration in the chamber was adjusted to 50 parts per hundred million (pphm). Samples were placed in the chamber and the time for crack initiation was noted by checking the samples using a magnifying lens at regular intervals of 30 mins.

Morphology studies

a) Using optical microscope

The morphology of polymer blends was investigated using an optical microscope (Versamet 2, Union 7596). For optical microscopy a compression set test piece was cut to a convenient size and mounted on a microscope slide photographs were taken at a magnification of 330.

b) Scanning electron microscope

Scanning electron microscope (S-2400 Hitachi) was used to investigate the morphology of fractured surfaces. A thin specimen of the sample was prepared and fixed on an aluminium stub in the upright position using a double side sticker. This stub with the sample was placed in ion sputtering unit for sputtering gold on the sample to a thickness of Angstrom level at a vacuum of 0.1 and 0.01 torr.

Gold coated samples were then placed in the sample holder of the scanning electron microscope and vacuum was applied. Electron beams produced from a tungsten filament by applying a voltage (0-25 kV) were made narrow using condensor lenses bombards. Specific points of the specimen were observed as it scans its surface in a predetermined regular pattern. The secondary electrons generated carry a variety of physical, chemical and electrical information. These secondary electrons are collected by a photomultiplier and converted into a minute current that is amplified to signal (voltage) where the signal is passed into a CRT where it determines the potential of the regulating electrons which controls the current in the CRT. An image of the investigated region of the specimen is thus photographed.

The SEM observations reported in the present investigations were made on the fracture surface of tensile test specimen. The fractured surfaces of the samples were carefully cut out without disturbing the surface. These surfaces were then sputter coated with gold within 24 hours of testing.

c) Using Polaroid land camera

Dispersion of ingredients in compounded rubber stock was studied using photomicrographic technique. The technique employs an MP4 polaroid land camera with a magnification of 30. [microscopic lens (Baush & Lomb) eyepiece with 15 power and objective 2 power] with special holding assembly for the microscope. Other accessories for the microscope are the razor blade guillotine for microtoming the sample, rectangular glass sample holder with ground glass edges, fibre optics illuminator and fibre optics light guide etc.

Vulcanized rubber sample was carefully microtomed on razor blade guillotine as smooth and straight specimen which was then sandwiched between two rectangular sample holders and vise of the holder was tightened so that Then cut surface was even with the top edges of the glass holder. Sample was then positioned under the microscope. Light guide was positioned to shine across the sample, parallel to the razor cut. The angle of incident light was kept near 30 degree. Sample was viewed through reflex viewer and its surface was scanned for areas of lowest dispersion. Sample was focussed by adjusting the microscope until sample image was sharp. After assuring maximum sample illumination black and white polaroid photographs were taken. It was then compared to the set of 10 dispersion standard micrographs of equal magnification and was assigned numerical rating of 1-10 with 10 being best.

Chemical Test Methods

a) Determination of chemical crosslink density

The concentration of chemical crosslinks was estimated from the equilibrium swelling data as follows.

Samples of approximately 1 cm diameter, 0.20 cm thickness and 0.20 gm weight were punched out from the central position of the vulcanizate and allowed to swell in solvent (toluene). The swollen sample was taken out of the solvent after 24 hours and weighed. Solvent was then removed in vacuum and the sample weighed again.

The volume fraction of rubber (V_r) in the swollen network was then calculated by the method reported by Ellis and Welding from the following equation

$$V_r = \frac{(D-FT)\rho_r^{-1}}{(D-FT)\rho_r^{-1}+A_o\rho_s^{-1}}$$

where T the weight of the test specimen, D the Deswollen weight of the test specimen, F the weight fraction of insoluble components and A_o the weight of the absorbed solvent corrected for the swelling increment. The values of ρ_r and ρ_s taken were

(NR) = 0.921 g/cm ^{3}

(IIR) = 0.917 g/cm ^{3}

(EPDM) = 0.860 g/cm ^{3}

(Toluene) = 0.886 g/cm ^{3}.

In the case of vulcanizate containing HAF black, the values of V_r obtained as above, were converted into V_{ro} (the value of V_r in the absence of the black) by means of the following equation which was derived by Porter

$$V_{ro}/V_r = 0.56\ e^{-z} + 0.44$$

where z = weight fraction of filler. The crosslink density ($\tfrac{1}{2}M_c$) was then determined from V_{ro} using the Flory-Rehner equation,

$$\tfrac{1}{2}M_c = \frac{-[\ln(1-V_{ro} + V_{ro} + \chi V_{ro}^2]}{2p_r V_s (V_{ro})^{1/3}}$$

where V_s = molar volume of solvent; V_s (toluene) = 106.2 cc/mol and

χ = parameter characteristic of interaction between rubber and solvent.

Values of interaction parameters taken for calculations were the following: For NR-toluene = 0.420; IIR-toluene = 0.557, EPDM-toluene = 0.490; NBR-toluene = 0.637.

Measurement of conductivity of rubber vulcanizates compounds

The rubber compounds were vulcanized into sheet form as per standard procedure. Samples for conductivity measurements cut in pellet form, area of the specimen, and thickness were measured accurately in millimeter. This specimen is then coated with silver paint in order to avoid contact resistance of the sample.

For measuring conductivity, resistivity was measured first. Resistivity of the material was obtained by measuring the resistance and converting it to resistivity by taking the geometric consideration into account. To measure the conductivity a known voltage, say 5.5V was applied to the sample and the resultant current was measured with a digital multimeter.

Resistance was found out from the equation

$$R = \frac{V}{I}$$

where V = applied potential in volts, I = Resulting current through the circuit in ampere. Conductivity (σ) was measured by the following equation

$$\sigma = \frac{t}{Ra}$$

where t = thickness of the sample (cm), R = resistance of the samples (ohms), a = area of the sample with the electrode wire in contact (cm^2), σ = conductivity of the specimen (ohm^{-1}cm^{-1}).

Chapter III

Part I MECHANICAL PROPERTY IMPROVEMENT OF NBR/IIR BLENDS BY PARTIAL PRECURING OF IIR

Nitrile rubber (NBR) has excellent oil resistance but is subject to degradation at high temperature[1-3]. The high temperature ageing resistance is important for this rubber and fairly high doses of antioxidants may not be very effective because it is frequently used in contact with extractive media which may progressively leach out the antioxidant in the vulcanizate. This problem of degradation can be overcome if nitrile rubber is blended with butyl rubber in such proportions which do not sacrifice the former's oil resistance. But these two rubbers are incompatible due to the large difference in polarity and the resulting faster curing nature of nitrile rubber compared to butyl rubber[4-7] This cure rate mismatch in NBR/IIR blends is due to the polar nature of nitrile rubber and the comparatively slow curing nature of butyl rubber[8]. Thus NBR/IIR blends show inferior mechanical properties compared to the average properties of the constituent elastomers. The main reason for this deterioration in mechanical properties is that both rubbers do not get cured to the optimum crosslink densities or attain a covulcanized state during vulcanization[9,10]. In this chapter we propose a novel method for improving the mechanical behaviour of NBR/IIR blend viz. prevulcanizing the slow curing phase (IIR) to a low level so that the final vulcanizate will have optimum crosslink densities in both the elastomer phases after the final curing. The mechanical properties of these blends prepared by this novel route are compared with those of conventional blends.

EXPERIMENTAL

The optimum level of precuring that has to be given to IIR phase was determined from the variation of tensile properties of blends of NBR/IIR with variation of the level of precuring of the IIR. Butyl compounds were prepared on a laboratory mixing mill (6"x12") according to ASTM D 3182 (1982) as per formulation given in Table 3.1. These compounds were sheeted out in the mixing mill at a thickness of 5 mm and then partially precured or precrosslinked for different times at 130°C in a laboratory air oven. The precured compounds were then blended with nitrile rubber (NBR) in various compositions on the mill and then compounding ingredients for NBR were added. The compounds were then vulcanized upto the respective optimum

TABLE 3.1

FORMULATIONS FOR NBR/BUTYLBLENDS

NBR	100	90	70	50	30	10	-	-	-	-	-	-
BUTYL	-	-	-	-	-	-	100	90	70	50	30	10
Zinc Oxide	4	3.6	2.8	2	1.2	0.4	4	3.6	2.8	2	1.2	0.4
Stearic Acid	2	1.8	1.4	1	0.6	0.2	2	1.8	1.4	1	0.6	0.2
Accinox ZC	1	0.9	0.7	0.5	0.3	0.1	1	0.9	0.7	0.5	0.3	0.1
MBTS	1	0.9	0.7	0.5	0.3	0.1	1.0	0.9	0.7	0.5	0.3	0.1
TMTD	0.5	0.45	0.35	0.25	0.15	0.05	0.75	0.675	0.525	0.375	0.225	0.075
Carbon Black HAF N330	40	36	28	20	12	4	40	36	28	20	12	4
Parraffinic Oil	-	-	-	-	-	-	5	4.5	3.5	2.5	1.5	0.5
DOP	5	4.5	3.5	2.5	1.5	0.5	-	-	-	-	-	-
Sulfur	2.0	1.8	1.4	1.0	0.6	0.2	2	1.8	1.4	1.0	0.6	0.2

cure times and the tensile properties of the vulcanizates were determined.

Mechanical properties of NBR/IIR blends

Butyl rubber, precured upto the optimum level, was blended with nitrile rubber at various percentages. The compounding ingredients required for NBR were then added. The optimum cure time (time to reach 90% of maximum torque) was then determined on a Goettfert Elastograph model 67.85 as per ASTM D 1646 (1981). The compounds were then vulcanized upto their optimum cure times in an electrically heated laboratory hydraulic press, at 150°C. Dumbell shaped tensile test specimens were punched out of these compression moulded sheets along the mill grain direction. The tensile properties were measured on a Zwick universal testing machine model 1445 using a crosshead speed of 500 mm/min as per ASTM D 412 (80).

Angular test specimens were punched out of the compression moulded sheets and tear resistance of the blends was measured on a Zwick universal testing machine according to ASTM D 624. Samples for abrasion resistance, compression set and hardness were moulded and tested as per relevant ASTM standards. The ageing resistance of the vulcanizates was studied after ageing the sample at 100°C for 24 hours in a multi cell ageing oven.

RESULTS AND DISCUSSION

Table 3.2 shows the variation in tensile strength and elongation at break of 50/50 NBR/IIR blend with the level of precuring of the butyl rubber at 130°C for various times. Precuring time which gives the maximum tensile strength was taken as the optimum time. It can be seen that tensile strength increases with precuring time, reaches a maximum value and then decreases So the optimum time for precuring was taken as 30 min. at 130°C. This shows that after the optimum level of precuring butyl phase gets further cured and then it only acts similar to an overcured or scorchy rubber. Aged samples also indicate the same trend. Blends prepared by partially precuring the butyl rubber and then blending with NBR are hereafter referred to as modified blends to distinguish them from the blends prepared by blending butyl and NBR conventionally.

Table 3.3 shows the cure characteristics of modified and conventional blends. When NBR forms the major constituent there is not much change in the cure time between the conventional and modified blends but the scorch

TABLE 3.2

50/50 NBR /BUTYL BLENDS : DETERMINATION OF OPTIMUM TIME FOR PRECURING

Time for precuring at 130°C (mins.)	Tensile Strength N/mm^2	Elongation at break (%)
0	7.49	110.
5	8.28	130.
25	10.83	188.
30	13.89	211.
35	11.48	182.
45	9.18	123.

AFTER AGEING FOR 24 HRS AT 100°C

Time for precuring at 130°C (mins.)	Tensile Strength N/mm^2	Elongation at break (%)
5	7.69	102.
25	11.49	163.71
30	11.09	179.
35	9.47	185.73

TABLE 3.3
CURE CHARACTERISTICS OF NBR/BUTYL BLENDS

NBR	100	90	70	50	30	10	0	90	70	50	30	10
IIR	0	10	30	50	70	90	100	-	-	-	-	-
Modified IIR	-	-	-	-	-	-	-	10	30	50	70	90
Cure time t90 at 140 °C min.	11.6	9.3	9.0	15.0	14.0	22.3	43.0	9.3	9.0	9.3	9.0	11.0
Scorch time min	5.0	4.5	3.4	3.3	3.0	3.5	12.0	3.4	3.3	2.3	1.4	1.0
Max. torque lb-in	76	42	37	37	37	28	24	42	42	34	33	21

time is lower for modified blends. As butyl content increases cure time decreases for modified blends. This is expected because the curing behaviour is likely to be more influenced by the major constituent. Reduction in cure time for modified blends indicates that there is not much curative migration to NBR phase and curatives are trapped in the butyl phase itself due to precuring.

Fig.3.1 shows the variation in tensile strength of NBR/IIR conventional and modified blends with composition. The modified blends show much better tensile strength compared to the conventional blends. This improvement in tensile strength is probably due to the optimum crosslink densities in both NBR and IIR phases and in the interphase. Improvement is found to be most pronounced in the 90/10 butyl/NBR blend which shows that it was this composition that was most seriously affected due to curative migration in conventional blending. In this case curatives for the 90 parts of butyl were almost totally consumed by the 10 parts of nitrile phase and hence the nitrile phase got overcured. Ageing resistance is also found to be superior for the modified blends. Fig.3.2 shows the variation of tear strength of modified and conventional NBR/IIR blends. The modified blends show superior tear strength compared to

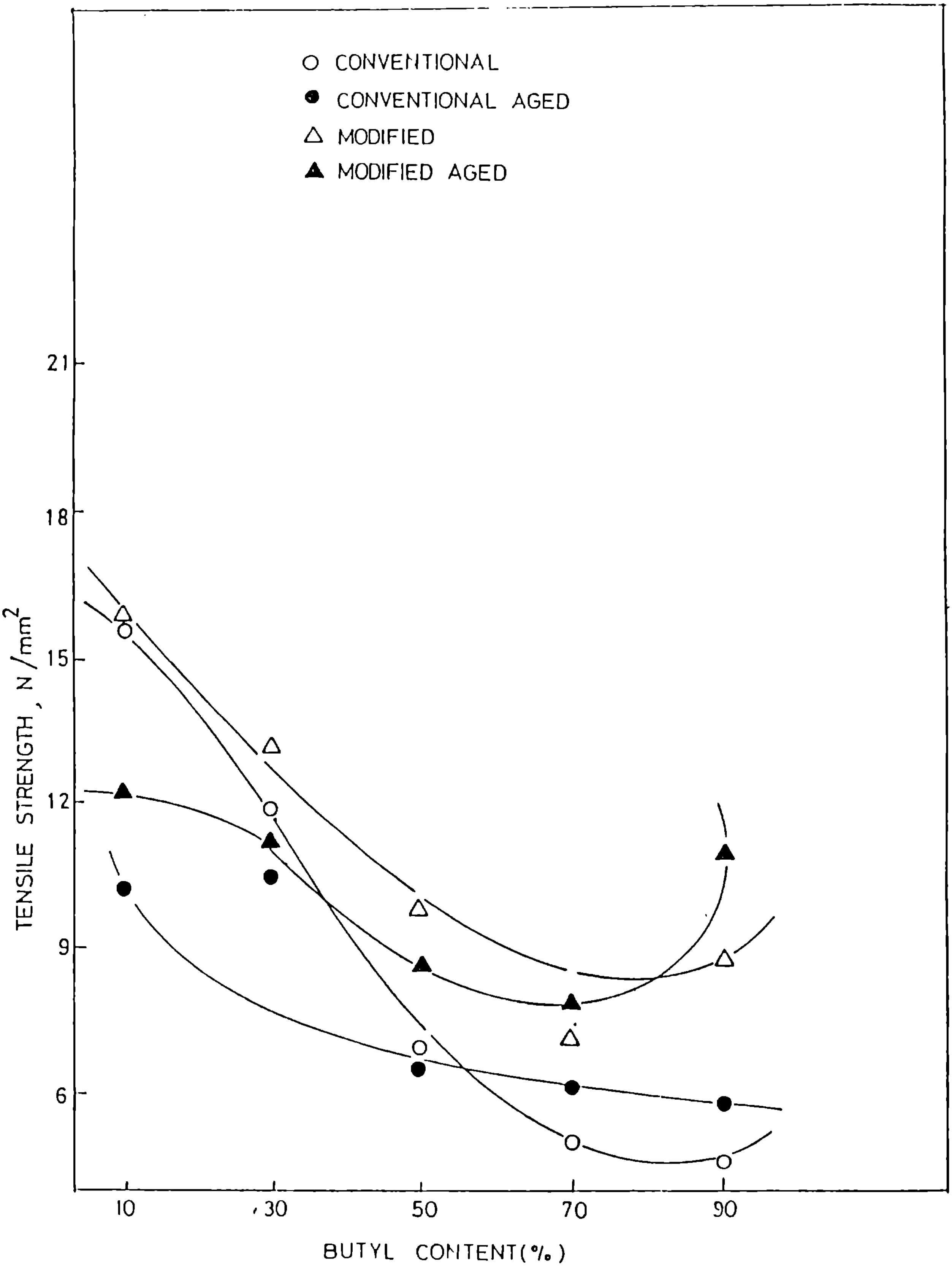

Fig.3.1 Variation of tensile strength with butyl content of modified and conventional NBR/IIR blends.(48% ACN)

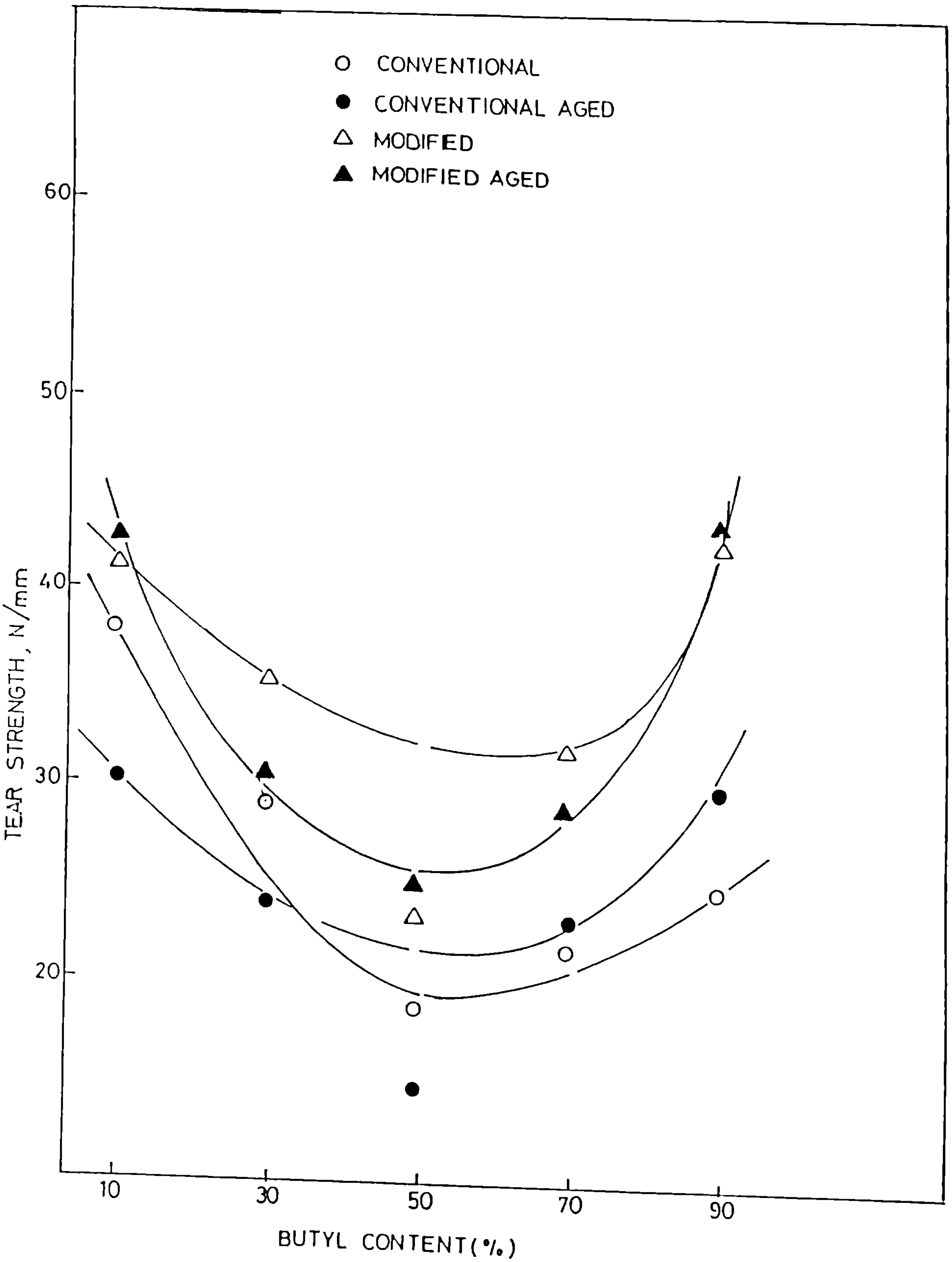

Fig.3.2 Variation of tear strength with butyl content of modified and conventional NBR/IIR blends(48% ACN)

conventional blends before and after ageing as in the case of the tensile strength. This further points towards optimum crosslink densities in the rubber phases and in the interphase. Further reasons for the improved strength may be uniform filler distribution due to the reduction in the viscosity mismatch between NBR and IIR phases in the case of modified blends due to the precuring. The 90/10 NBR/IIR blend shows poor ageing resistance but as the concentration of IIR in the blend increases the ageing resistance of the blend is also improved.

Fig.3.3 shows the variation in elongation at break of the modified and conventional NBR/IIR blends. The modified blends display higher elongation at break too. Since the elongation at break is controlled by the continuous elastomer phase, the lower value in the case of conventional blends probably results from the overcure of the continuous elastomer phase. In the conventional curing of the blends NBR gets a higher proportion of curing agents resulting in overcure. The 90/10 IIR/NBR blend shows higher elongation at break since butyl rubber is the major component. Fig.3.4 shows the variation of abrasion loss with blend composition. The modified blends show better abrasion resistance than the conventional blends. This is

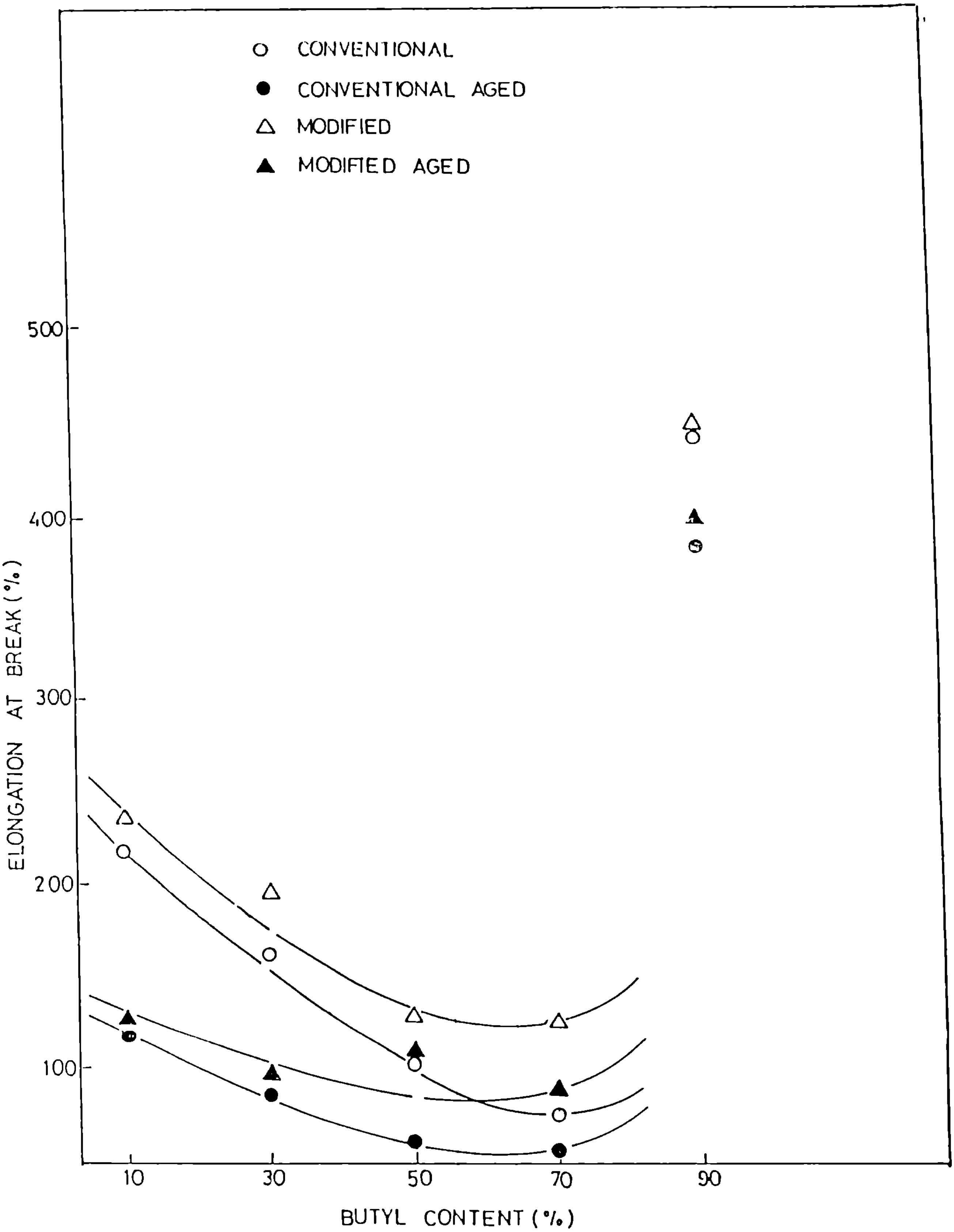

Fig.3.3 Variation of elongation at break with butyl content of modified and conventional NBR/IIR blends(48% ACN)

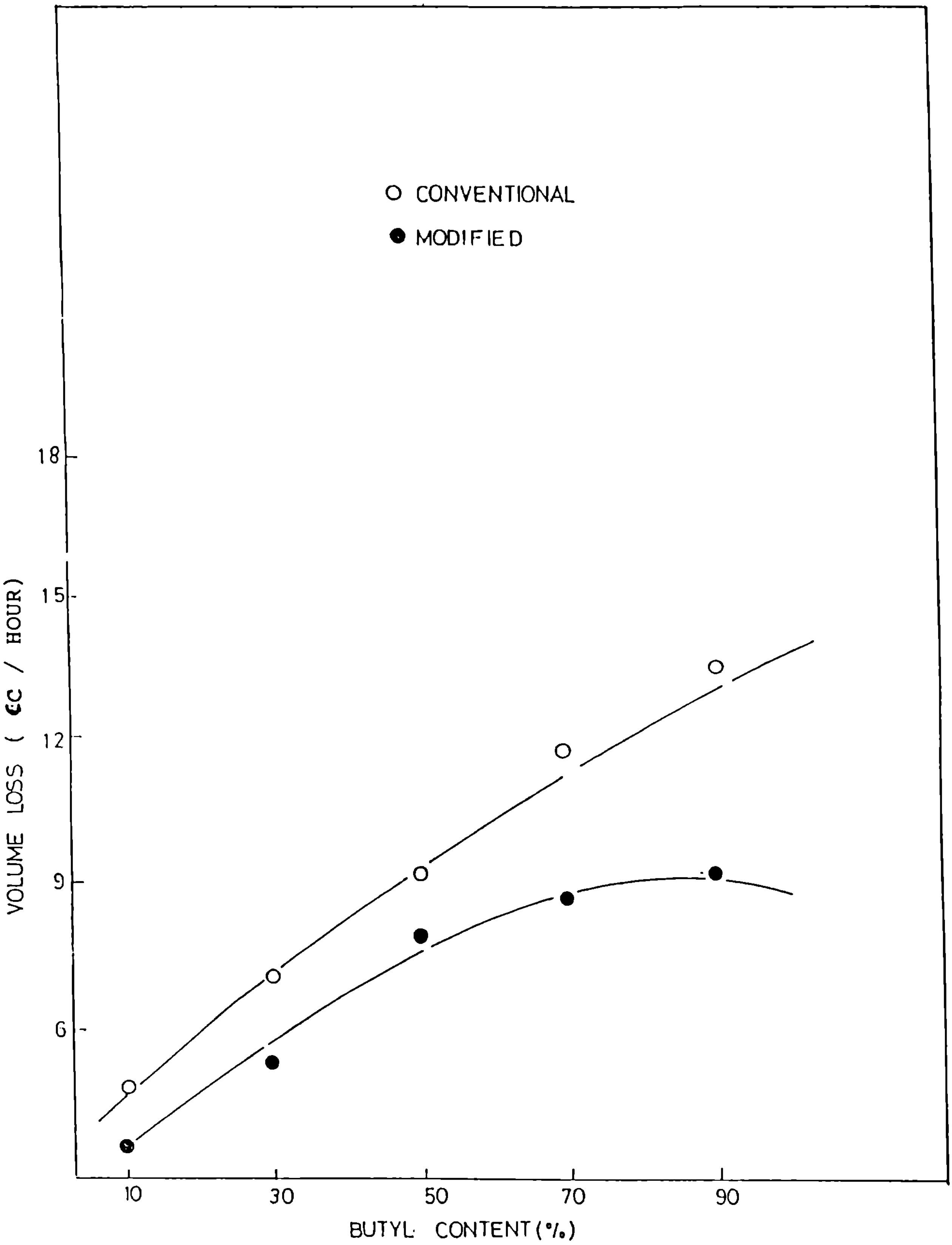

Fig.3.4 Variation of volume loss by abrasion with butyl content of modified and conventional NBR/IIR blends(48% ACN)

TABLE 3.4

NBR/BUTYL BLENDS: VARIATION OF COMPRESSION SET AND HARDNESS

NBR	100	90	70	50	30	10	0	90	70	50	30	10
IIR	0	10	30	50	70	90	100	-	-	-	-	-
Modified IIR	-	-	-	-	-	-	-	10	30	50	70	90
Hardness Shore A	70	69	69	68	71	75	72	70	70	71	73	74
Compression set %	31	26	52	41	52	66	64	32	35	40	50	62

probably due to the even filler distribution in the two elastomers which results from the better viscosity matching of the precured IIR and NBR.

Table 3.4 shows the compression set and hardness of the NBR/IIR blends with composition. As the butyl content increases compression set increases for both modified and conventional blends which is an inherent property of butyl rubber, but modified blends display lower compression set values compared to conventional blends which shows the better homogenity of the modified blends. Hardness is also found to be superior for modified blends due to uniform crosslinking and uniform filler distribution in both phases.

CONCLUSION

Introducing a low degree of precuring in the IIR phase before blending with NBR is an attractive means for achieving co-crosslinked state in the NBR/IIR blends. Partial precuring helps to improve the compatibility of NBR/IIR blends. Mechanical properties which are influenced by the crosslink densities in both the phases and in the interphase are markedly improved by precuring.

Part II EFFECT OF ACRYLONITRILE CONTENT ON THE MECHANICAL PROPERTIES OF THE NBR/IIR BLENDS

Acrylonitrile content of the NBR is an important parameter in deciding the oil resistance and blending characteristics of the rubber with other rubbers[11-14]. In NBR/IIR blends, using an NBR grade of higher acrylonitrile content oil resistance can be improved, but increased curative migration from the butyl phase to the nitrile phase can occur due to the enhanced polarity resulting in inferior mechanical properties. In this chapter NBR/butyl blends were prepared using two grades of NBR viz., 33% and 48% acrylonitrile content. The effect of partial precuring of the slow curing butyl phase and then blending it with two grades of NBR is evaluated[15]. The mechanical properties of these blends prepared by this technique are compared with those of the conventional blends.

EXPERIMENTAL

Precuring of the butyl phase

Mixing was done according to ASTM D 3182 (1982) as per formulation given in Table 3.5. Butyl rubber was compounded on a laboratory two roll mixing mill (6"x12") using a friction ratio 1:1.25 with cold water circulation.

TABLE 3.5

FORMULATIONS FOR NBR/BUTYLBLENDS

NBR	100	90	70	50	30	10	-	-	-	-	-	-
BUTYL	-	-	-	-	-	-	100	90	70	50	30	10
Zinc Oxide	4	3.6	2.8	2	1.2	0.4	4	3.6	2.8	2	1.2	0.4
Stearic Acid	2	1.8	1.4	1	0.6	0.2	2	1.8	1.4	1	0.6	0.2
Accinox ZC	1	0.9	0.7	0.5	0.3	0.1	1	0.9	0.7	0.5	0.3	0.1
MBTS	1	0.9	0.7	0.5	0.3	0.1	1.0	0.9	0.7	0.5	0.3	0.1
TMTD	0.5	0.45	0.35	0.25	0.15	0.05	0.75	0.675	0.525	0.375	0.225	0.075
Carbon Black HAF N330	40	36	28	20	12	4	40	36	28	20	12	4
Parraffinic Oil	-	-	-	-	-	-	5	4.5	3.5	2.5	1.5	0.5
DOP	5	4.5	3.5	2.5	1.5	0.5	-	-	-	-	-	-
Sulfur	2.0	1.8	1.4	1.0	0.6	0.2	2	1.8	1.4	1.0	0.6	0.2

The butyl compounds were sheeted out from the mixing mill at a thickness of about 5 mm and then partially precured at 130°C for 30 mins, in a laboratory air oven as in the case of the earlier studies. The precured compounds were then blended with two grades of nitrile rubber in various compositions on the mill and then the compounding ingredients for NBR were added. The compounds were then vulcanized upto their respective optimum cure times and the tensile properties of the vulcanizates were determined.

Evaluation of mechanical properties

Butyl rubber precured upto the optimum level was blended with the two grades of NBR at various percentages. The compounding ingredients required for NBR were then added and the compound was sheeted out (Blends prepared in this manner are hereafter referred to as modified blends). The optimum cure time (time to reach 90% of the maximum torque) was determined on a Monsanto rheometer model 100 as per ASTM D 2084-1988. These compounds were then vulcanized upto their optimum cure times in an electrically heated laboratory hydraulic press at 140°C. Dumbell shaped tensile test specimens were punched out of these compression moulded sheets along the mill grain direction. The tensile properties were measured on a Zwick universal testing machine model 1445 using a crosshead speed of 500 mm/min as per ASTM D 412-80.

Angular test specimens were punched out of these compression molded sheets and the tear resistance of these blends was measured on a Zwick universal testing machine according to ASTM D 624. The ageing resistance of the vulcanizates was studied, after ageing the samples at 100°C for 24 hours in a multicell ageing oven.

RESULTS AND DISCUSSION

Fig.3.5 shows the variation of tensile strength of the modified blends in comparison to that of conventional blends employing NBR of medium ACN content while Fig.3.6 shows the tensile strength of the blends employing NBR of high ACN content. In both the cases modified blends show significantly higher tensile strength resulting from the optimum crosslink densities in both NBR and butyl phases and in the interphase. High ACN NBR/IIR modified blends show higher tensile strength when NBR is the major component compared to the conventional blend. This shows that the tendency for curative migration towards NBR phase is more in high ACN NBR/IIR blends and that modification by precuring the butyl rubber effectively reduces the curative migration resulting in higher tensile strength. This

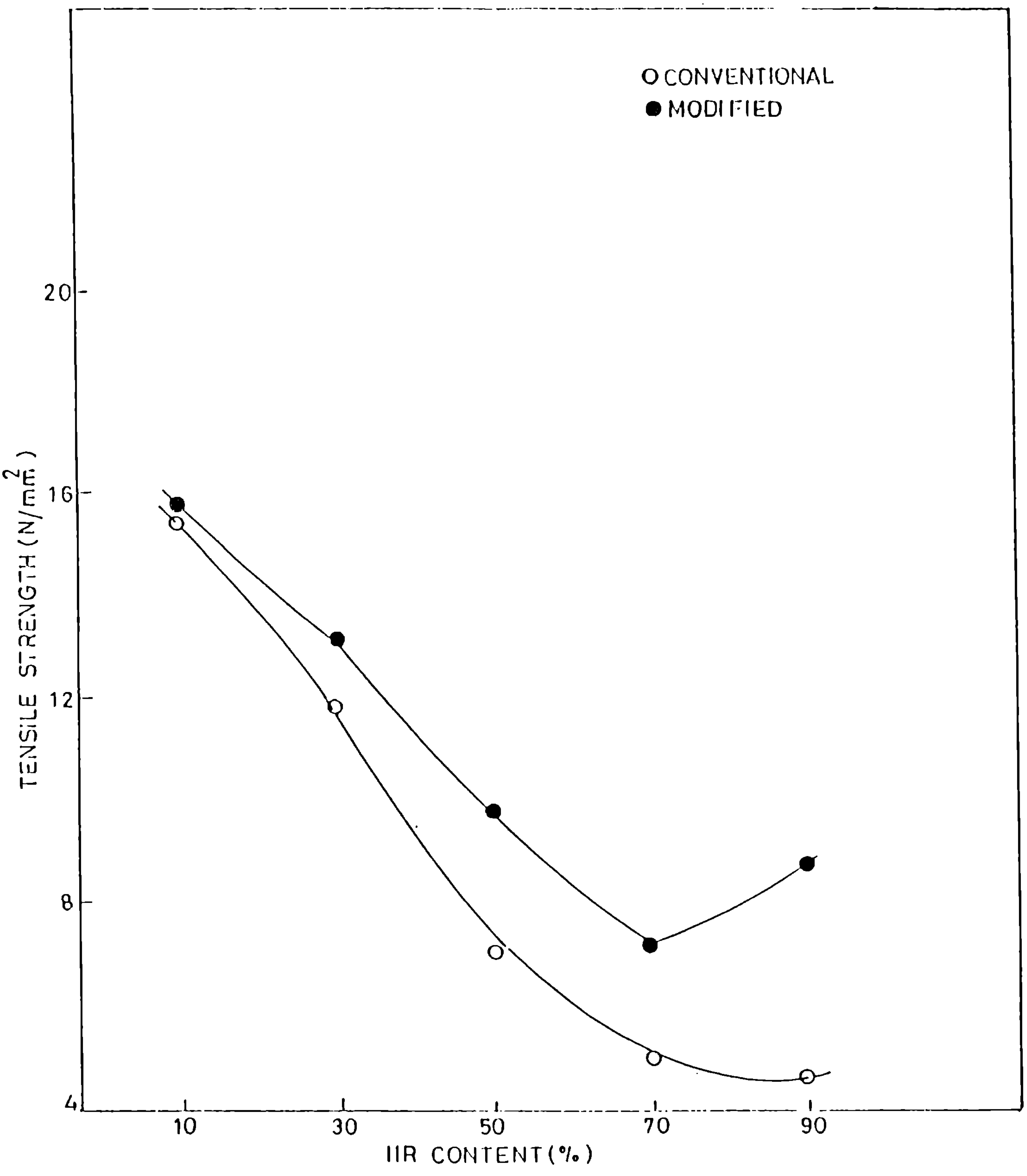

Fig.3.5 Variation of tensile strength with butyl content of modified and conventional medium NBR/IIR blends.

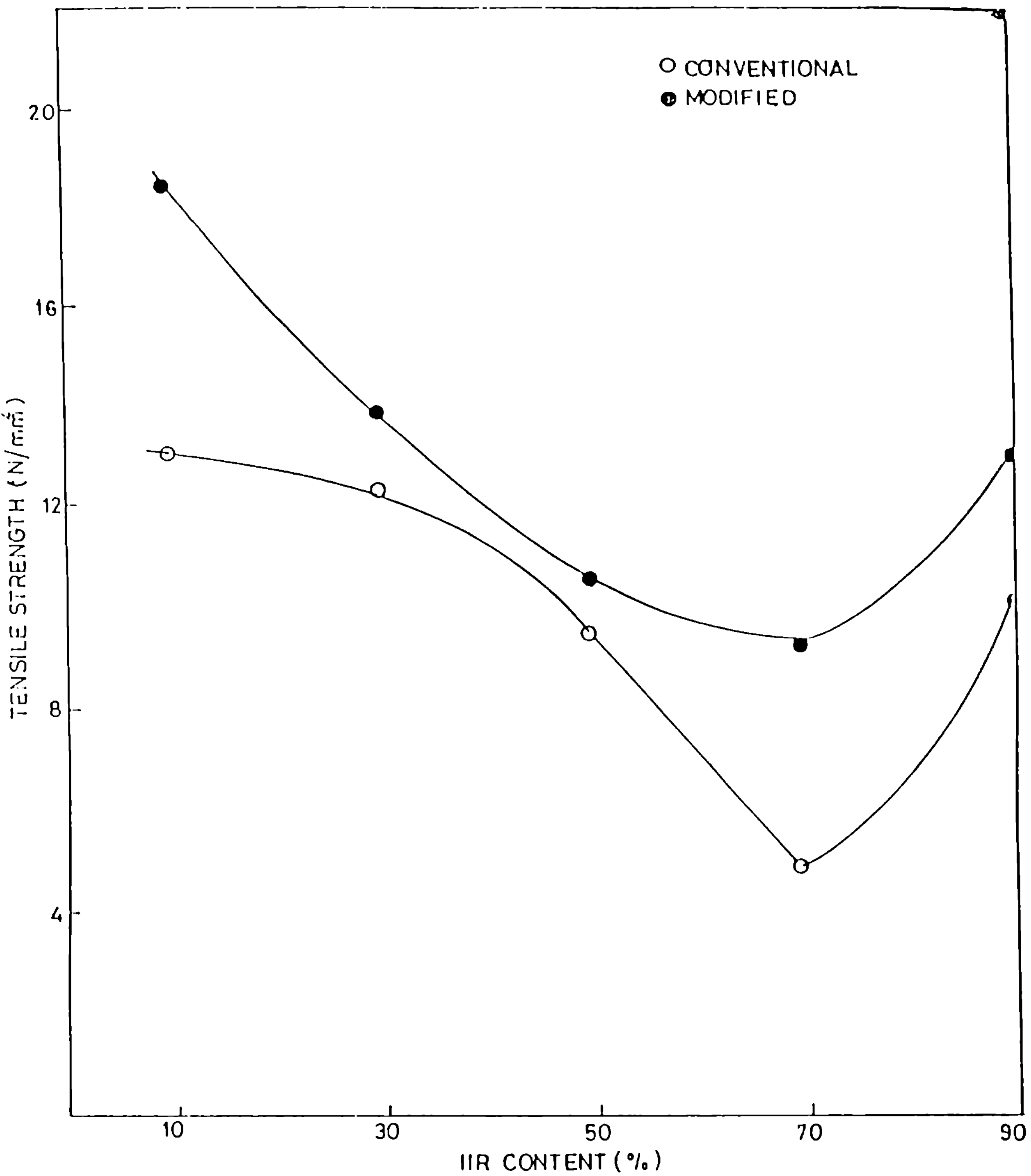

Fig.3.6 Variation of tensile strength with butyl content of modified and conventional high NBR/IIR blends.

effect decreases as butyl content of the blend increases. Figs.3.7 and 3.8 show the tensile strength after ageing of NBR/IIR blends of medium and high ACN NBR respectively. Modified blends show better ageing properties compared to conventional blends except where butyl forms the major component in which cases the modification is less effective. Figs.3.9 and 3.10 show the tear strength of NBR/IIR blends of medium and high ACN NBR respectively for conventional and modified blends. Modified blends are found to display higher tear strength compared to conventional blends. With the exception of a few ratios, it is found that tear strength of high ACN NBR/IIR blends is higher than for the blends with low ACN NBR/IIR. Figs.3.11 and 3.12 show the variation of tear strength of modified and conventional blends of medium and high ACN NBR/IIR blends respectively after ageing. Ageing resistance of the blends is found to better for modified ones for both cases and those blends with medium ACN NBR are found to possess higher ageing resistance compared with high ACN NBR. The reason for the improvement in physical properties for the modified blends may be the uniform filler distribution and the reduction in the viscosity mismatch between the NBR and butyl phases due to precuring. Figs.3.13 and 3.14 represent the elongation at break of the modified and conventional blends of medium and high ACN NBR

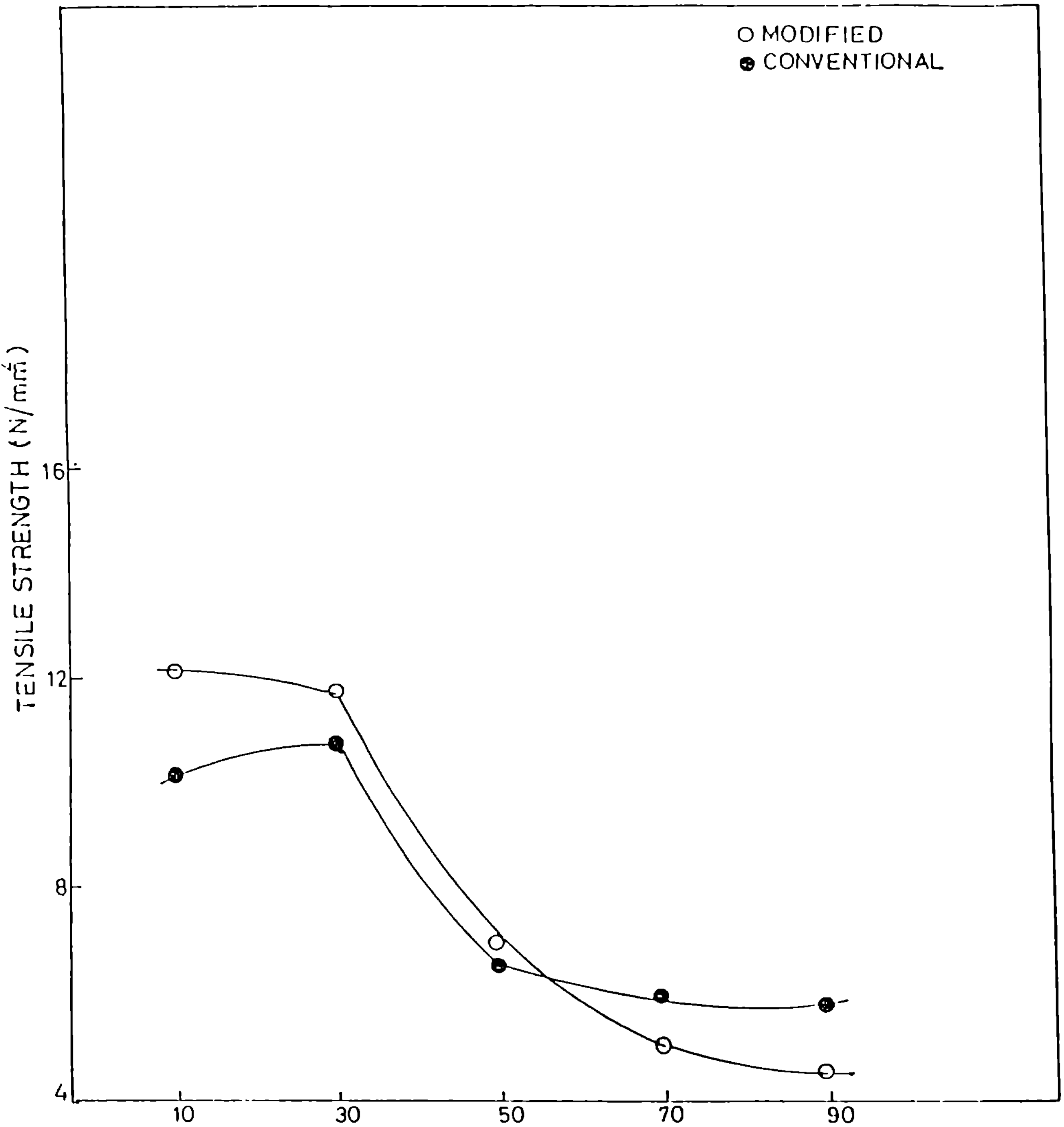

Fig.3.7 Variation of aged tensile strength with butyl content of modified and conventional medium NBR/IIR blends.

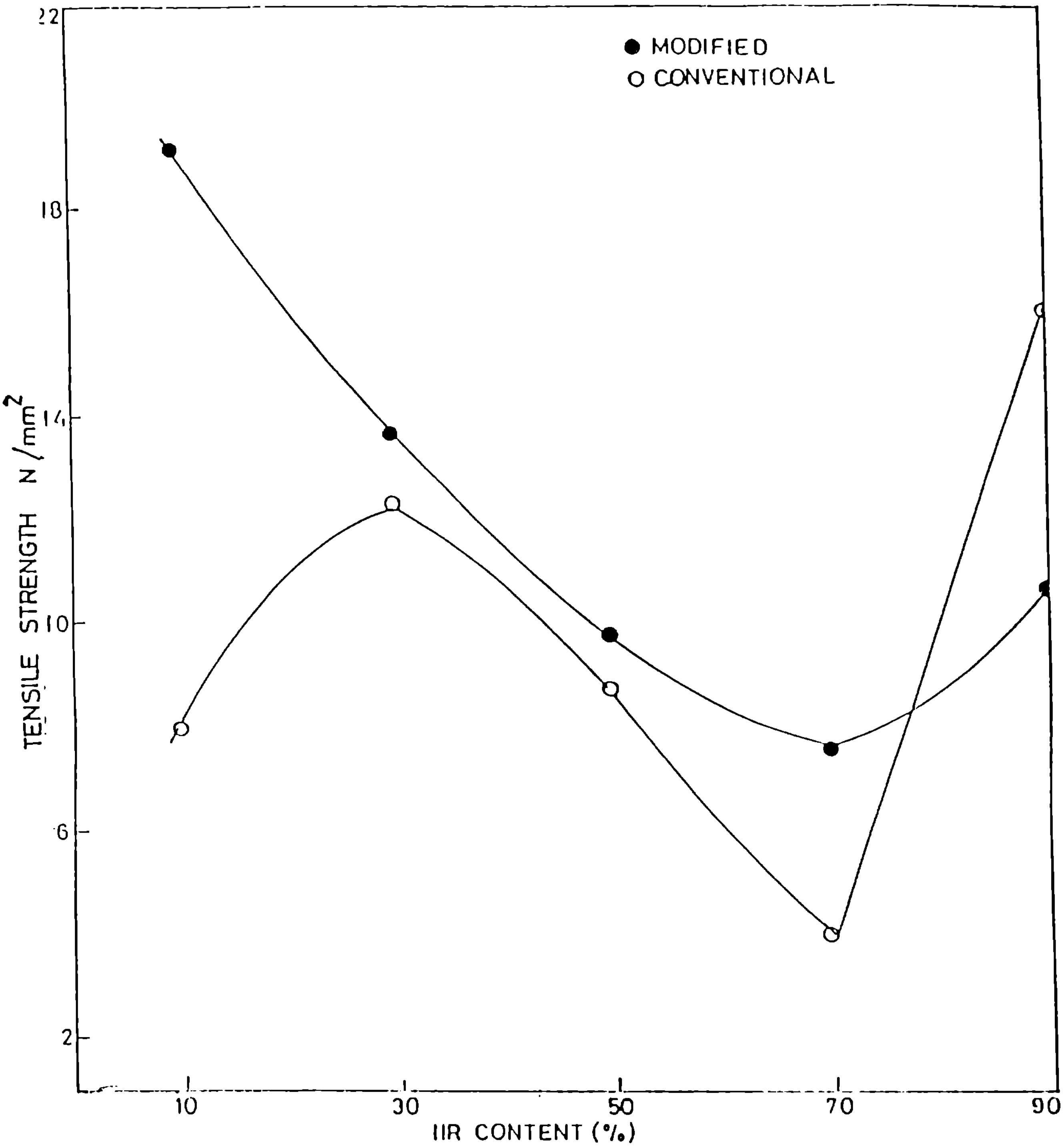

Fig.3.8 Variation of aged tensile strength with butyl content of modified and conventional high NBR/IIR blends.

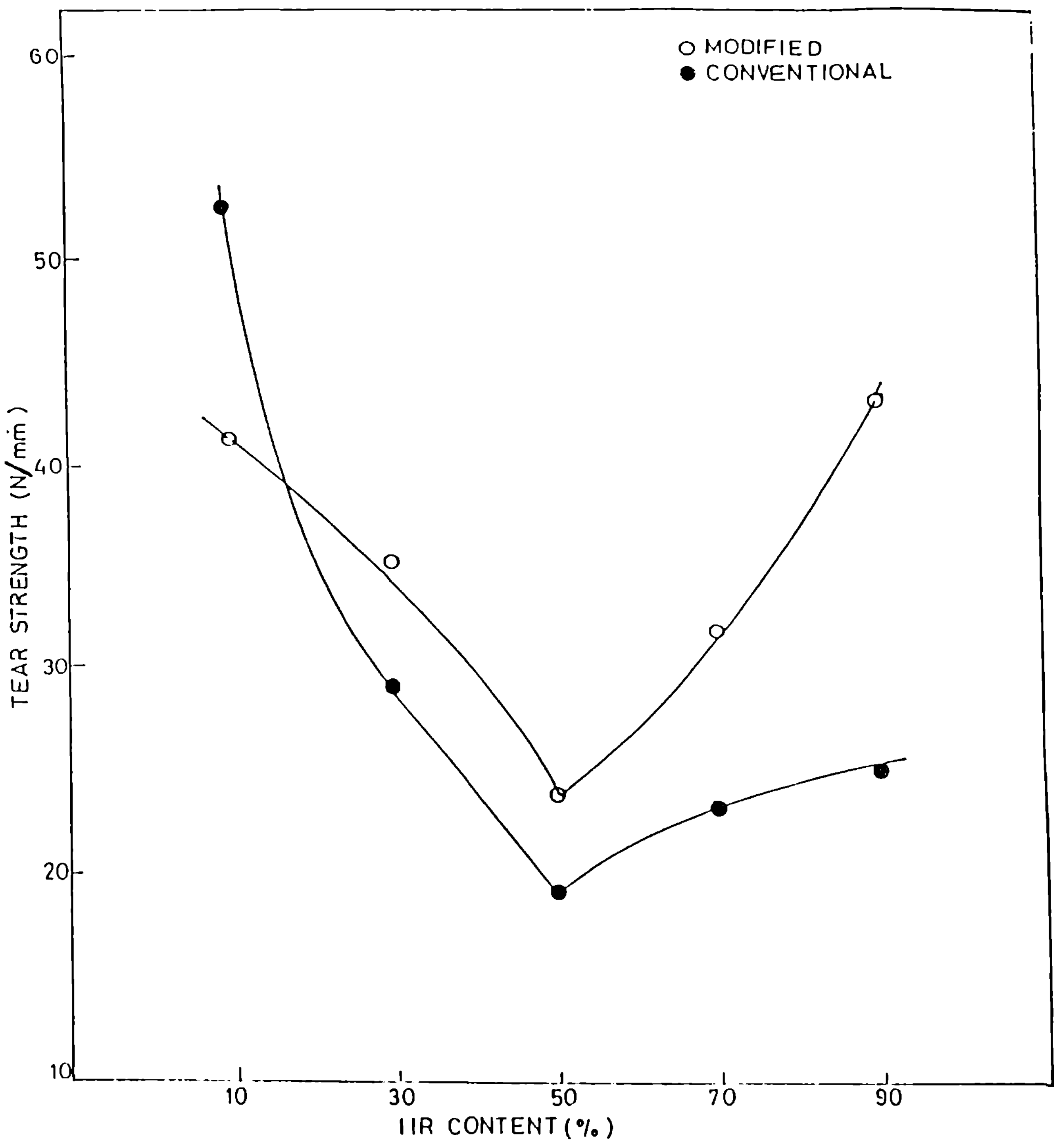

Fig.3.9 Variation of tear strength with butyl content of modified and conventional medium NBR/IIR blends.

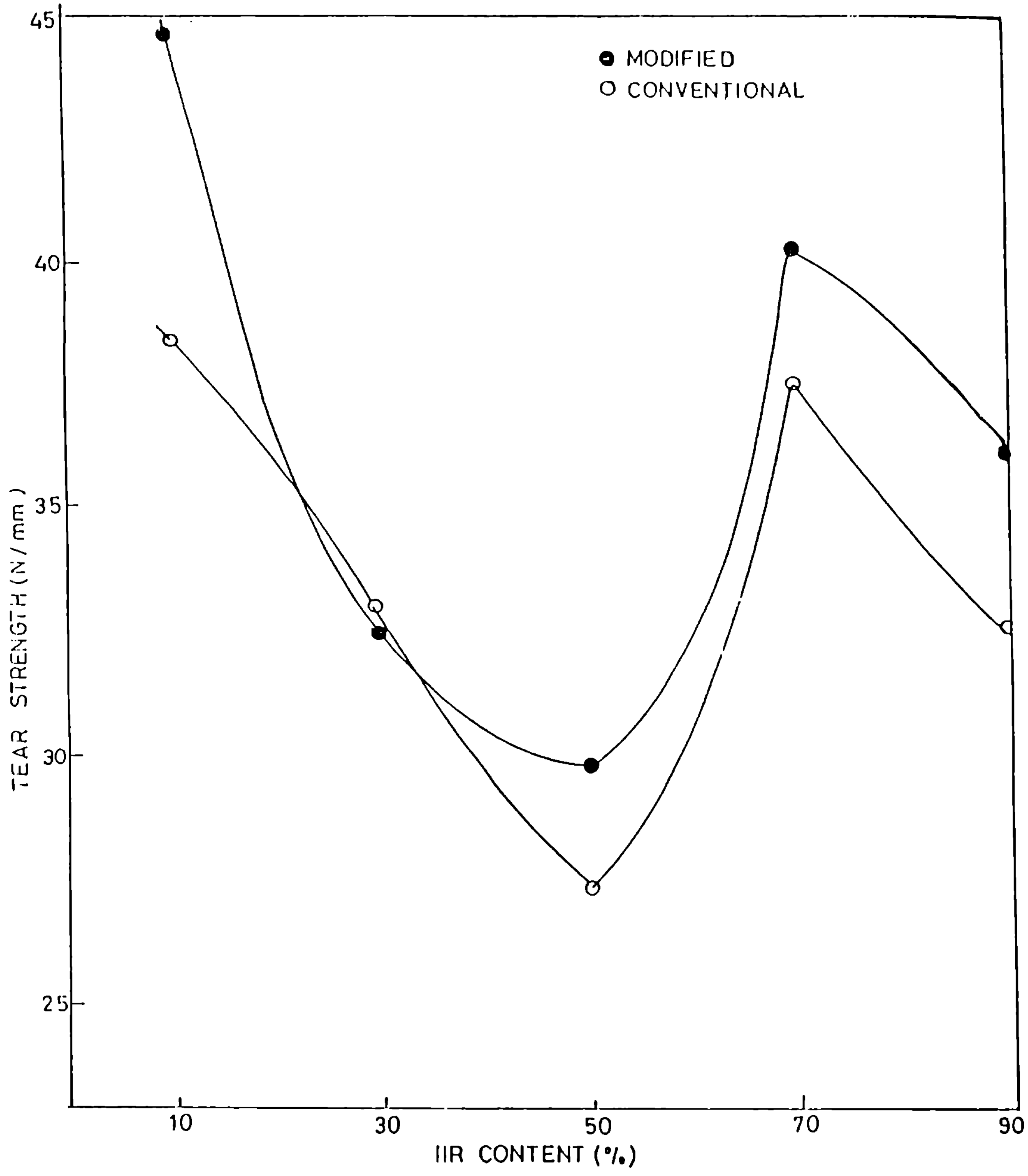

Fig.3.10 Variation of tear strength with butyl content of modified and conventional high NBR/IIR blends.

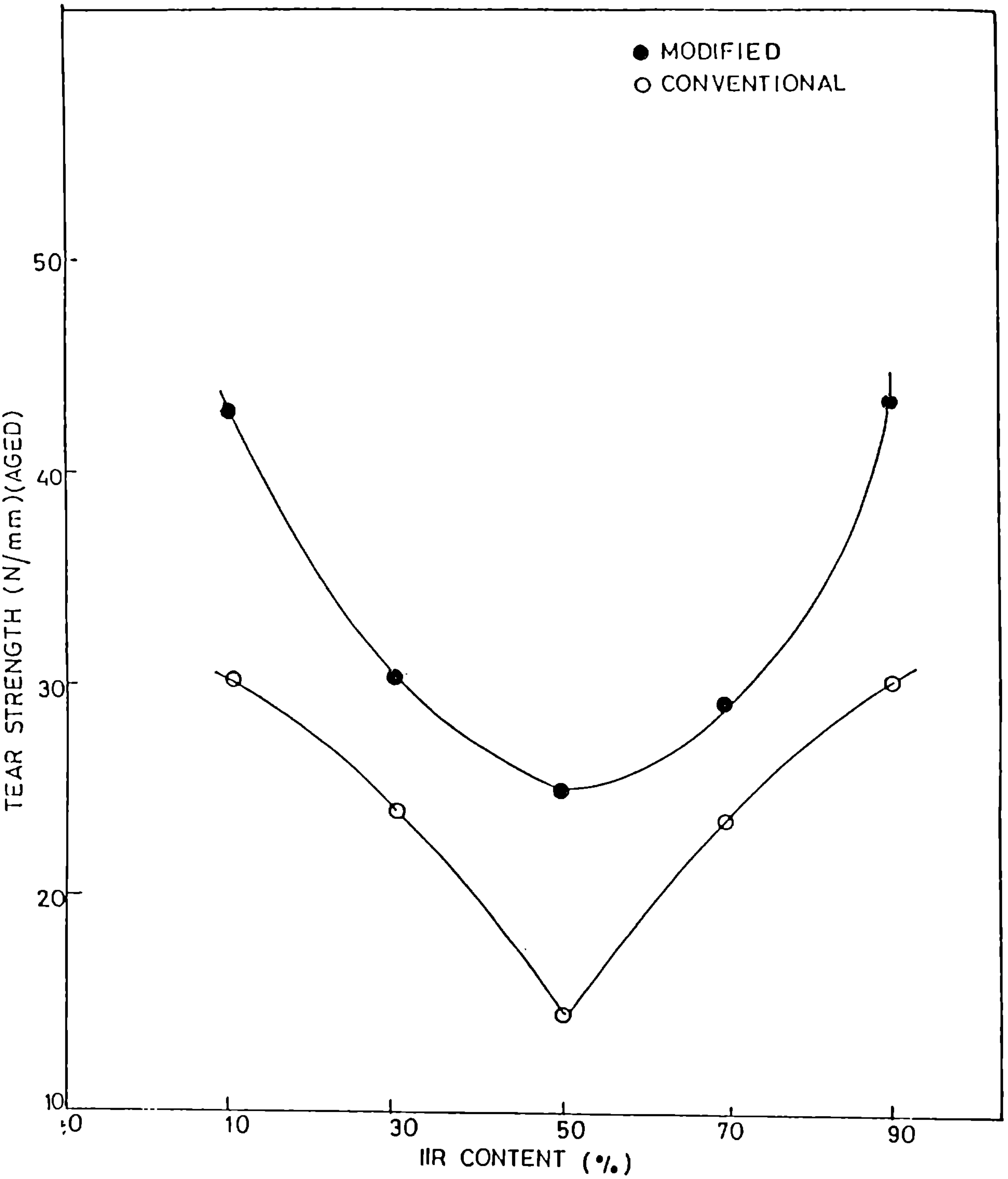

Fig.3.11 Variation of aged tear strength with butyl content of modified and conventional medium NBR/IIR blends.

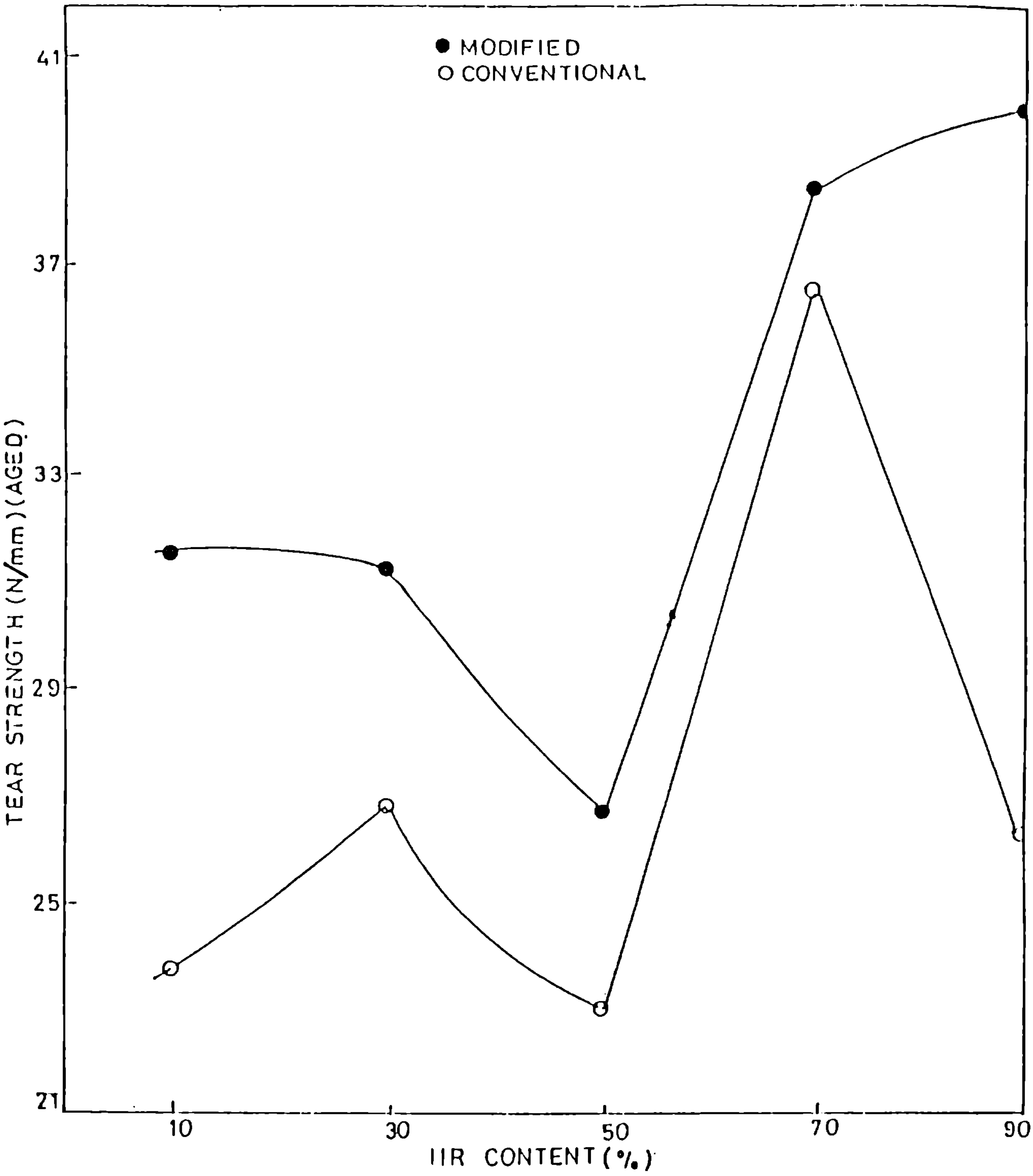

Fig.3.12 Variation of aged tear strength with butyl content of modified and conventional high NBR/IIR blends.

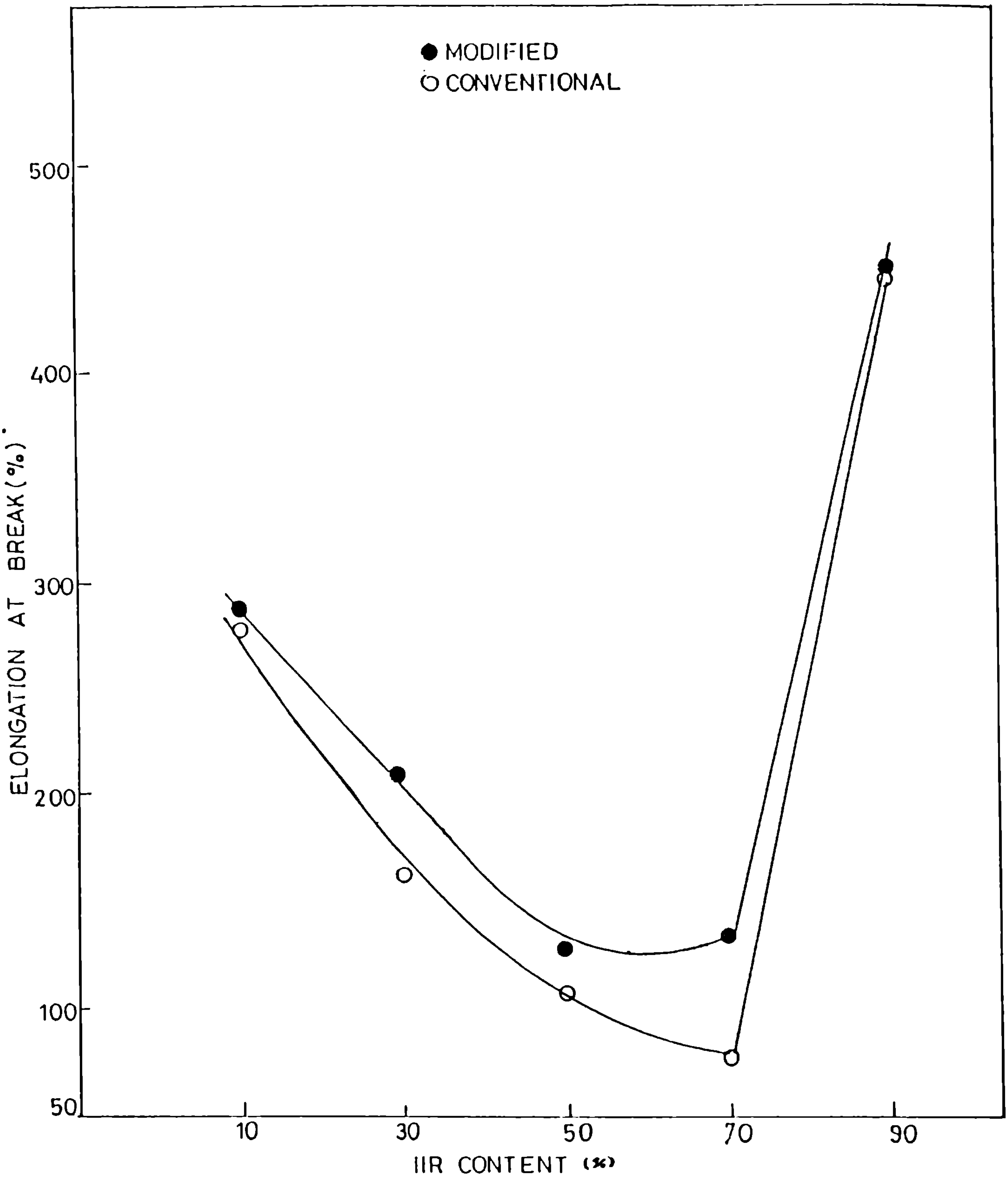

Fig.3.13 Variation of elongation at break with butyl content of modified and conventional medium NBR/IIR blends.

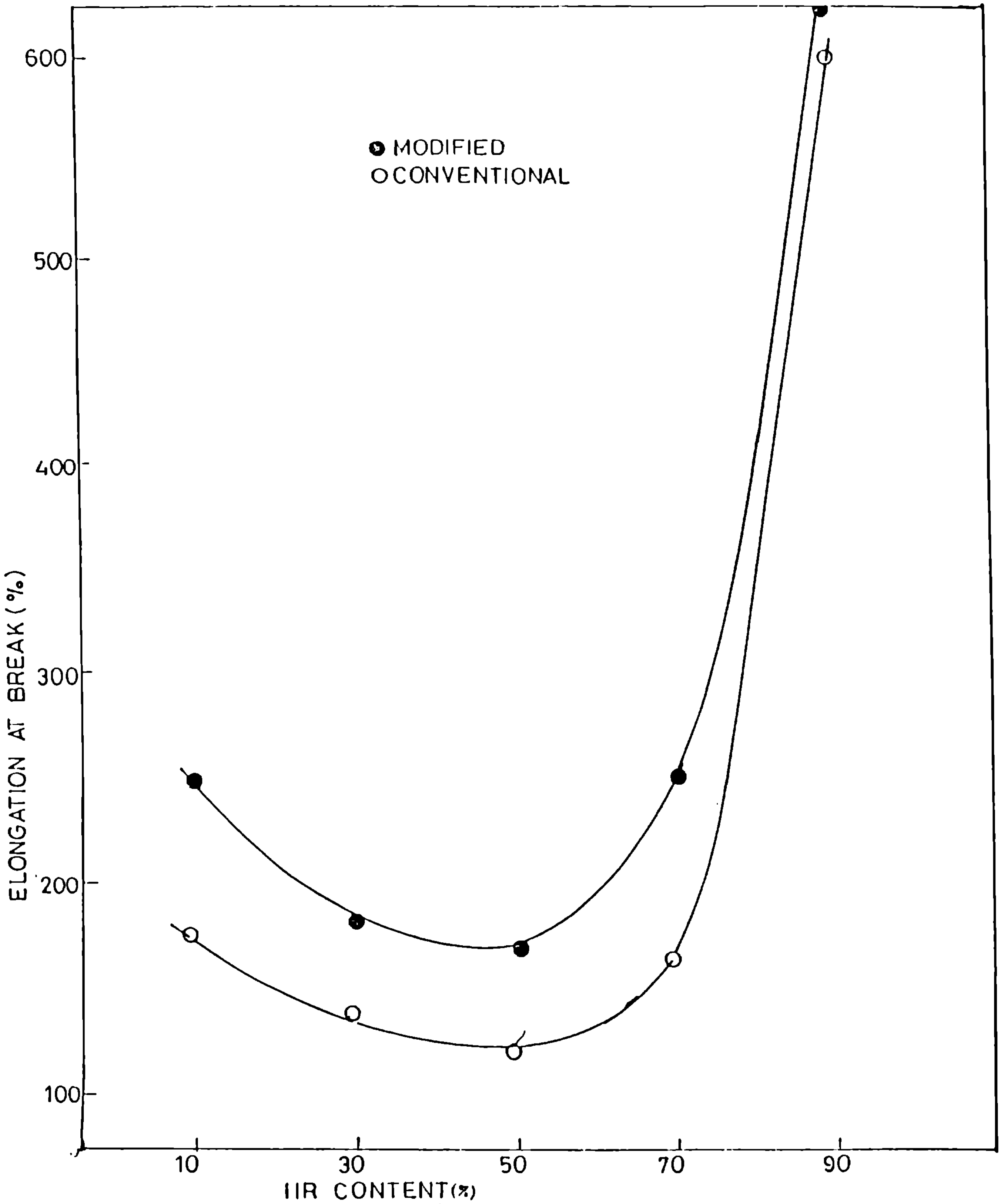

Fig.3.14 Variation of elongation at break with butyl content of modified and conventional high NBR/IIR blends.

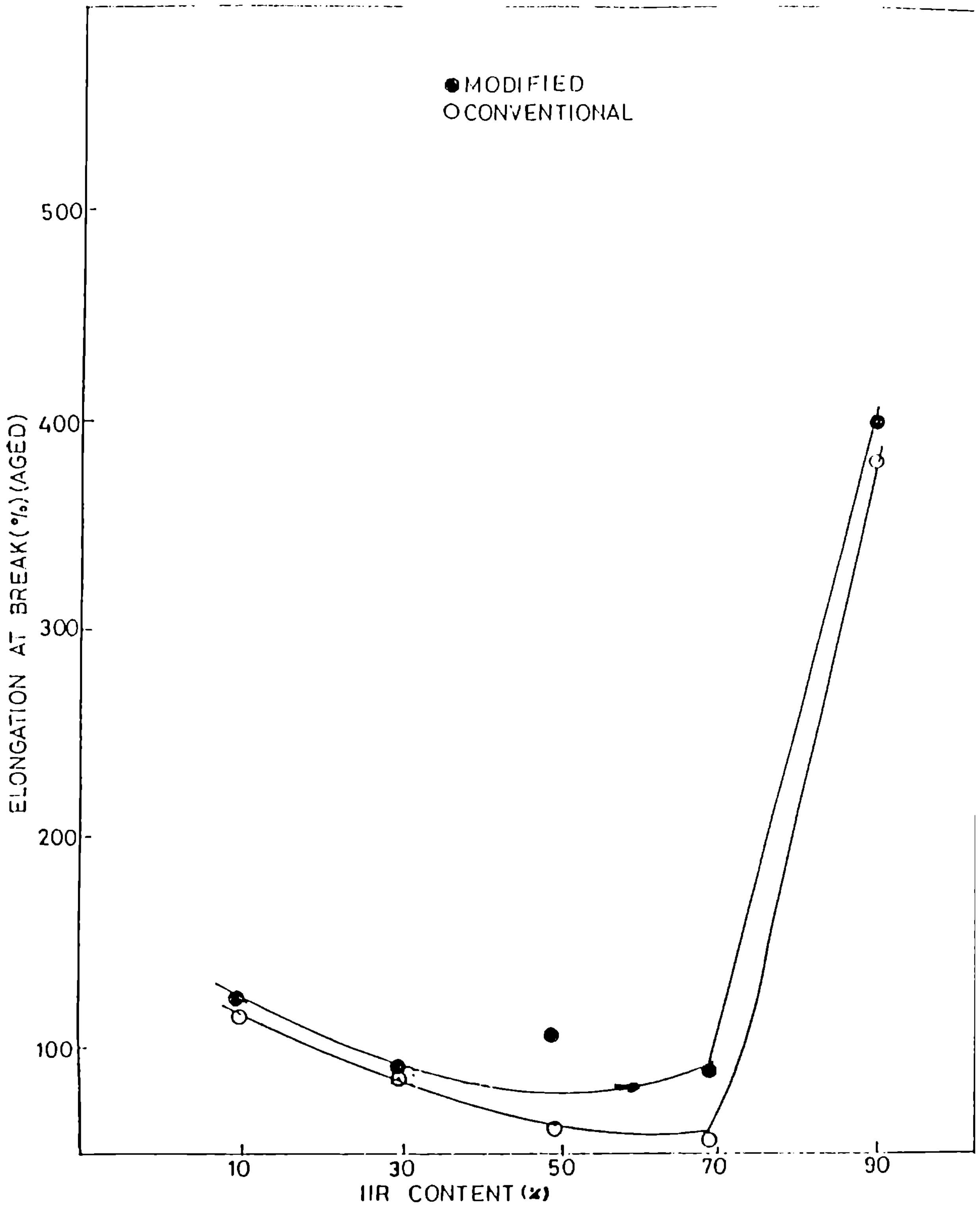

Fig.3.15 Variation of aged elongation at break with butyl content of modified and conventional medium NBR/IIR blends.

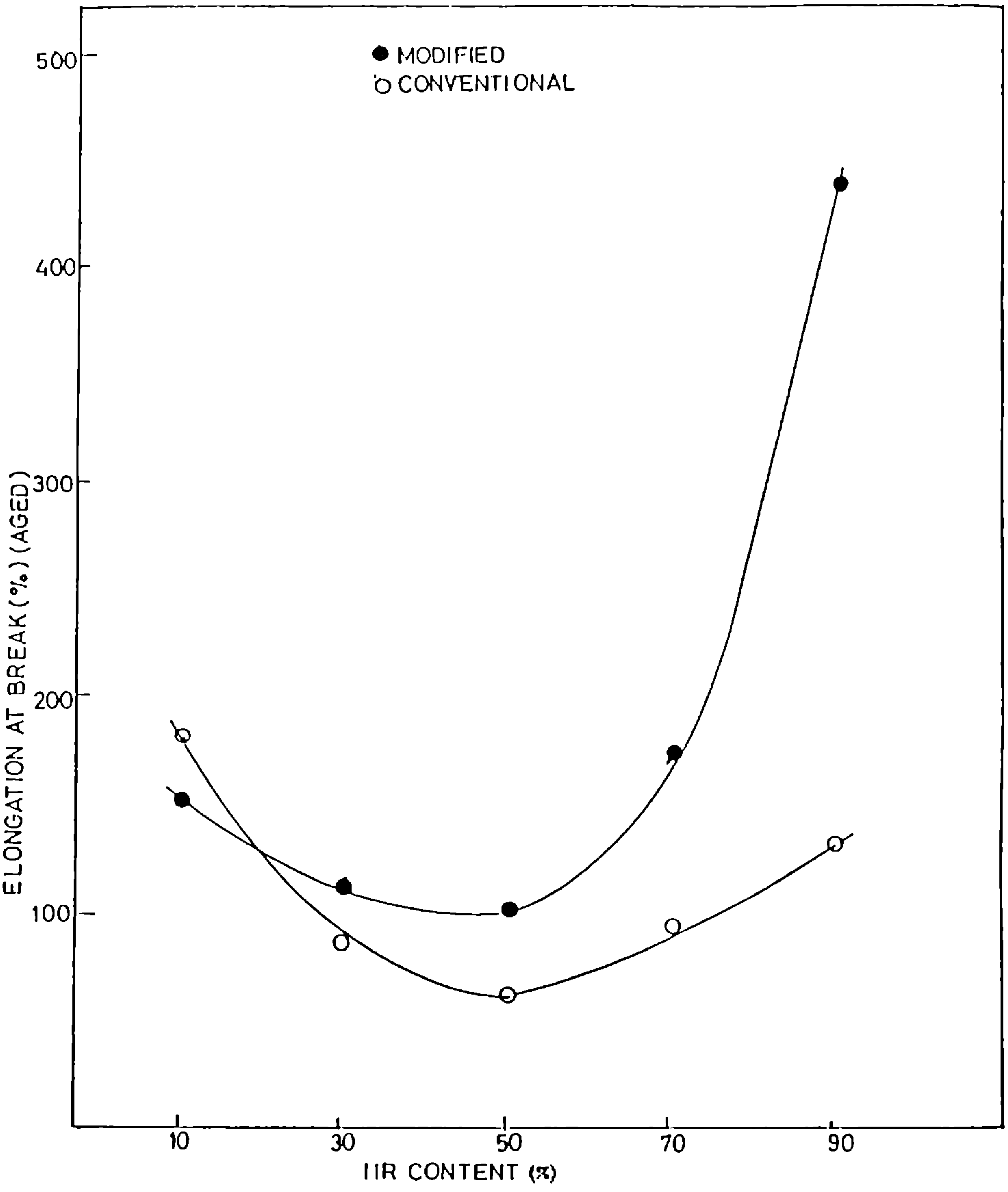

Fig.3.16 Variation of aged elongation at break with butyl content of modified and conventional high NBR/IIR blends.

respectively. Conventional blends show lower values due to the overcure of the continuous elastomer phase. Higher values are observed when butyl becomes the continuous phase, as expected. High ACN NBR/IIR blends also show higher EB compared to medium ACN NBR/IIR blends since curative migration is likely to be more in the case of high ACN NBR/IIR blends. Figs.3.15 and 3.16 show the elongation at break of conventional and modified blends for medium and high NBR respectively after ageing. As in the case of tensile and tear strength the modified blends show better retention in elongation at break also.

CONCLUSION

Precuring butyl to a low level, blending with NBR and then curing the blend is an efficient way of obtaining optimum crosslink density in both the elastomer phases and in the interphase irrespective of the NBR grade. This novel route is found to improve the mechanical properties of NBR/butyl blends significantly over their conventional counterparts.

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Chapter IV

Part I STUDIES ON NR/IIR BLENDS: EFFECT OF PARTIAL DYNAMIC CURING OF BUTYL BEFORE BLENDING

Natural rubber (NR) maintains its leading position for applications requiring a combination of end properties and good processing characteristics. But its resistance to heat, oxygen and ozone and its air/gas retention are not good and hence is not employed in demanding applications[1]. Butyl rubber (IIR) which has only a low level of unsaturation has excellent ageing behaviour and resistance to ozone cracking combined with low permeability to air and other gases[2]. Blending and cocuring NR and butyl is practically impossible due to the large difference in unsaturation[3-5]. NR is highly unsaturated and fast curing while butyl rubber is slow curing, due to its low unsaturation and the net result is cure rate imbalance and poor vulcanizate properties of blends compared to the constituent elastomers[6-10]. In this chapter we propose a novel technique for reducing the incompatibility due to the cure rate mismatch between NR and IIR and thus to improve the mechanical properties of these blends. viz. precuring butyl rubber dynamically to a low level depending upon the composition in an internal mixer and then blending it with NR and its compounding ingredients before final curing.

EXPERIMENTAL

The optimum level of precuring that has to be given to the slow curing butyl phase was determined from the variation in tensile properties of 50/50 NR/IIR blends with the level of partial precuring in the butyl phase. Butyl rubber was compounded in the mixing mill according to ASTM D 3182 (1982) as per formulation given in Table 4.1. The compound was sheeted out from the mixing mill at a thickness of 4-5 mm and cut into small pieces. These pieces were then fed into a Brabender Plasticorder (Model PL 3S) chamber at a preset temperature and subjected to dynamic crosslinking for times varying from 8-12 mins. at 40 rpm depending upon the composition (Fig.4.1). The precured compounds were then blended with masticated NR on the mill and then compounding ingredients for NR were added, blend was homogenised and then sheeted out. To study the effect of the nature of shearing, dynamic precuring of butyl rubber was also done in a Francis Shaw Intermix and properties of the blends prepared were compared with those prepared by precuring in a Brabender plasticorder.

TABLE 4.1

FORMULATIONS FOR NR/BUTYL BLENDS

INGREDIENTS	Phr											
NR	100	90	70	50	30	10	-	-	-	-	-	-
BUTYL	-	-	-	-	-	-	100	90	70	50	30	10
Zinc Oxide	4	3.6	2.8	2	1.2	0.4	4	3.6	2.8	2	1.2	0.4
Stearic Acid	2	1.8	1.4	1	0.6	0.2	2	1.8	1.4	1	0.6	0.2
Accinox ZC	1	0.9	0.7	0.5	0.3	0.1	1	0.9	0.7	0.5	0.3	0.1
MBTS	0.7	0.63	0.49	0.35	0.21	0.07	1.0	0.9	0.7	0.5	0.3	0.1
TMTD	-	-	-	-	-	-	0.75	0.675	0.525	0.375	0.225	0.075
Carbon Black HAF N330	40	36	28	20	12	4	40	36	28	20	12	4
Parraffinic Oil	-	-	-	-	-	-	5	4.5	3.5	2.5	1.5	0.5
Aromatic Oil	5	4.5	3.5	2.5	1.5	0.5	-	-	-	-	-	-
Sulfur	2.5	2.25	1.75	1.25	0.75	0.25	2	1.8	1.4	1.0	0.6	0.2

Phr - Parts per hundred rubber

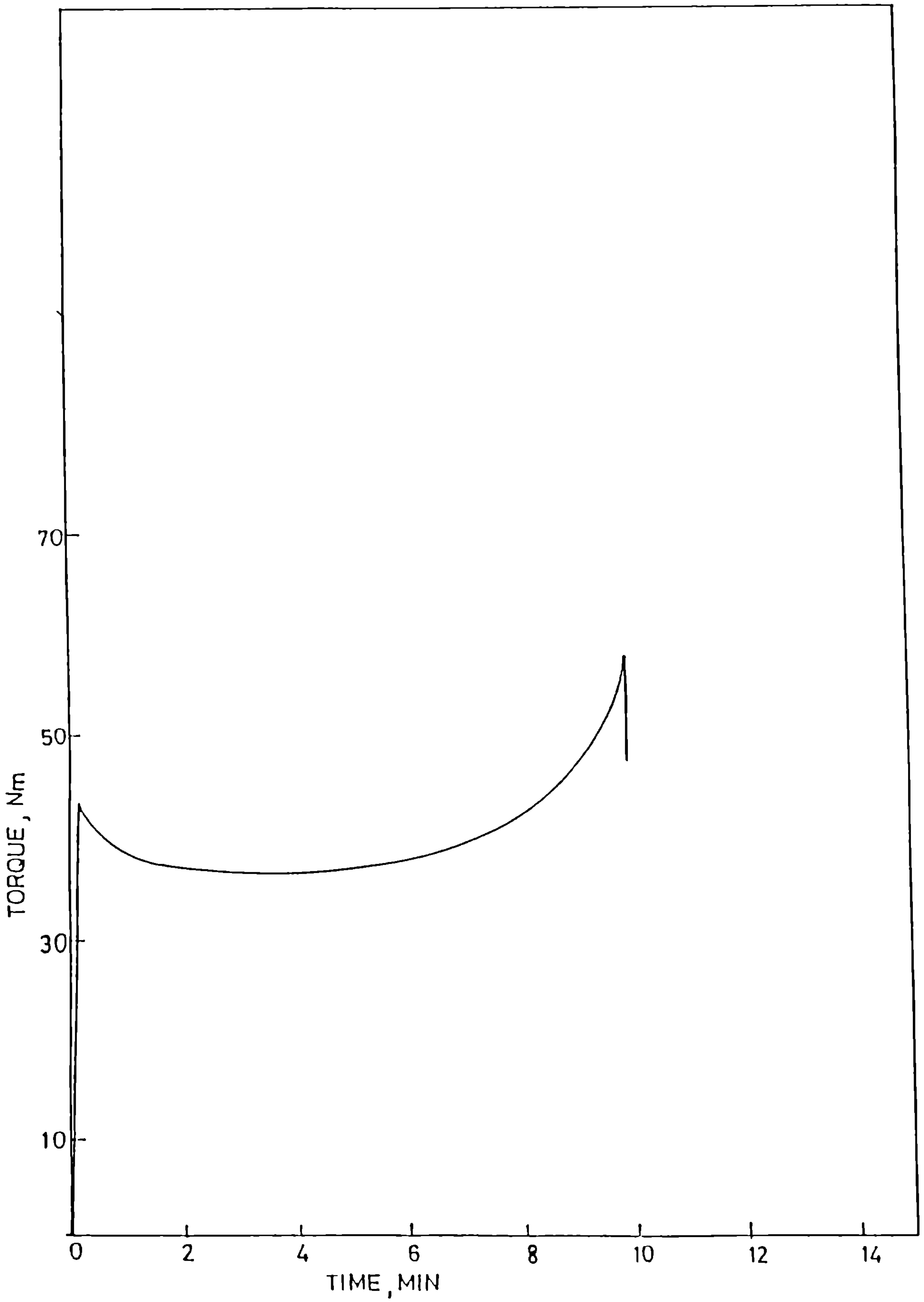

Fig.4.1 Brabender torque curve showing the optimum time for partial dynamic crosslinking of butyl compound.

Butyl rubber which was partially crosslinked dynamically upto an optimum level as determined from above, was blended with NR at various percentages. The compounding ingredients required for NR were then added and the compound sheeted out.

Optimum cure times of the blends were determined according to ASTM D 2084-88. The compounds were then vulcanized upto their respective cure times in an electrically heated hydraulic press at 140°C. Dumbell shaped tensile specimens were punched out of compression moulded sheets and were tested for the tensile properties on a Zwick UTM model 1445 at a crosshead speed of 500 mm/min as per ASTM D 412-80. Angular test specimens were punched out of the compression moulded sheets and tear resistance of the blends was measured on the Zwick universal testing machine according to ASTM D 624. Samples for compression set were moulded and tested as per relevant ASTM standards. Samples for abrasion resistance were moulded and volume loss/hr was determined on a Zwick abrader according to DIN 53 514. Hardness of the samples was measured and expressed in Shore A units. The ageing resistance of the vulcanizates was studied after ageing at 100°C for 48 hrs in a multicell ageing oven.

FIG 4.2 A CONVENTIONAL MIXING

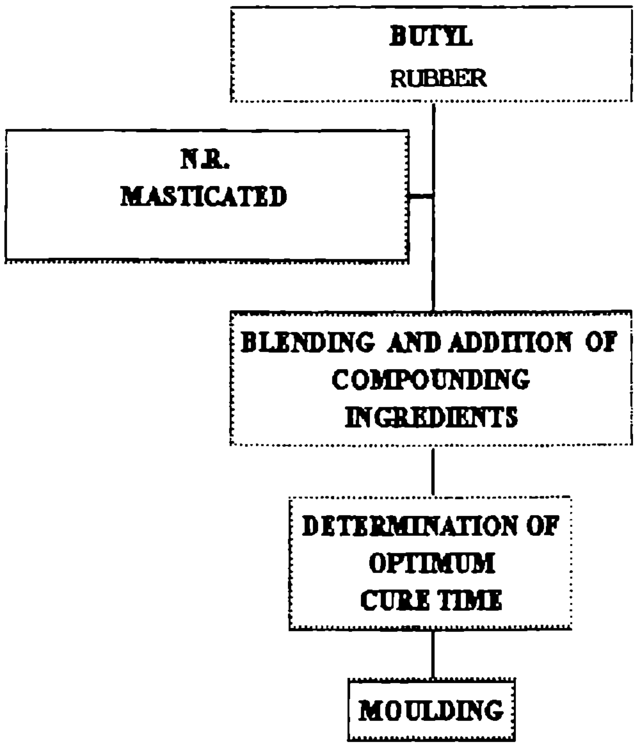

FIG 4.2 B MODIFIED MIXING

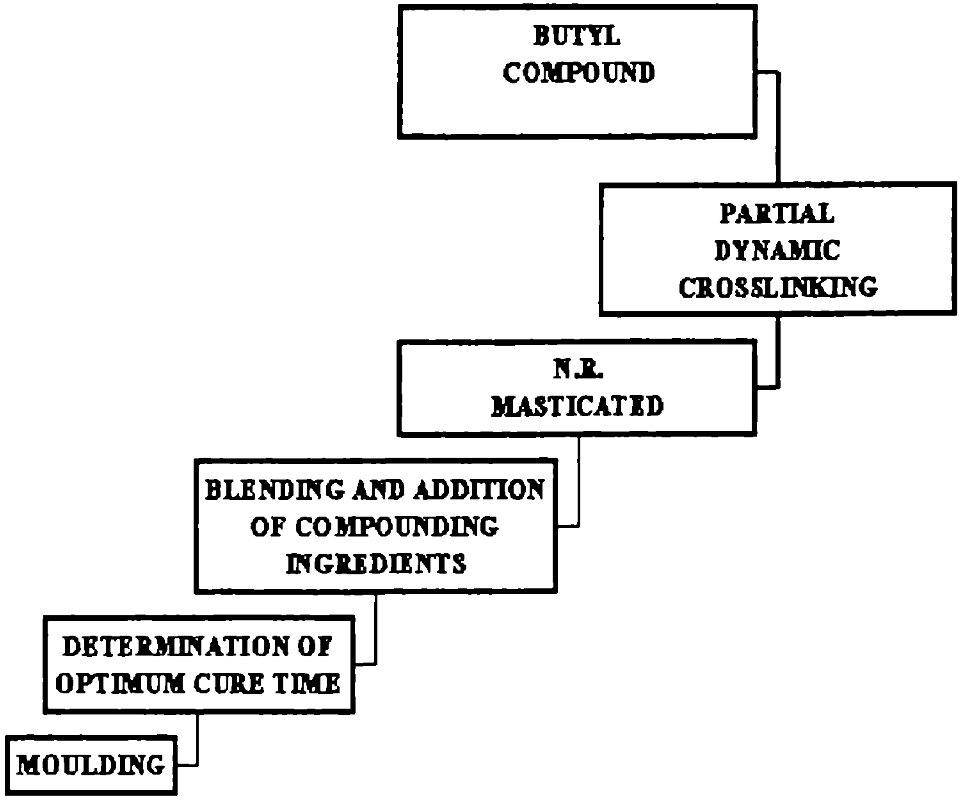

TABLE 4.2

NR/BUTYL BLENDS -VARIATION OF PHYSICAL PROPERTIES WITH THE LEVEL OF DYNAMIC CROSSLINKING ON BRABENDER PLASTICORDER

Initial temperature °C	Final temperature °C	Total precuring time, mins	Tensile strength N/mm^2	Elongation at break %
140	160	10	13.5	358.77
130	160	10	15.95	334.27
140	170	11	16.95	328.90
150	165	10	17.13	417.96
138	155	10	17.61	410.07
140	162	10.15	18.10	404.98
140	163	10.3	18.32	360.92

Fig.4.2 shows the flow diagram for the preparation of modified and conventional NR/IIR blends.

RESULTS AND DISCUSSION

Table 4.2 shows the variation in tensile strength of 50/50 NR/precured IIR with the level/time of dynamic crosslinking.

Fig.4.3 shows the variation in tensile strength with the blend composition. The NR/precured IIR blend shows improved tensile strength before and after at all compositions compared to the conventional NR/IIR blends. This shows that precuring the IIR phase reduces the migration of the curing agents into the NR phase and helps to attain a certain level of crosslinking in the IIR phase and also at the interphase. As butyl content increases tensile strength increases for both modified and conventional blends which may be due to the lower tendency for the curatives to preferentially migrate to the NR phase.

Fig.4.4 shows the tensile strength of modified and conventional NR/IIR blend after ageing. Better ageing resistance is observed in the case of modified blends.

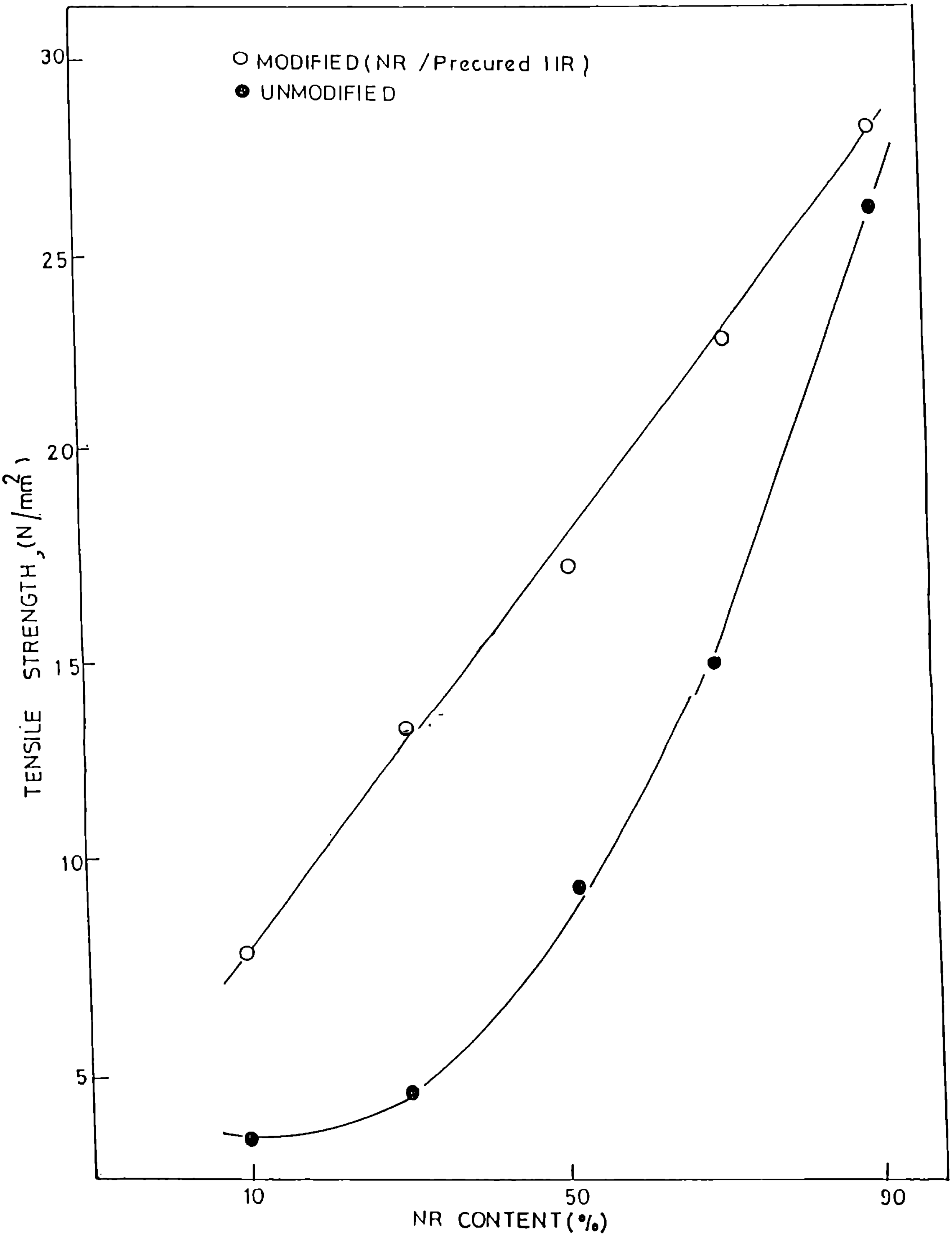

Fig.4.3 Variation of tensile strength with NR content of modified and conventional NR/IIR blends.

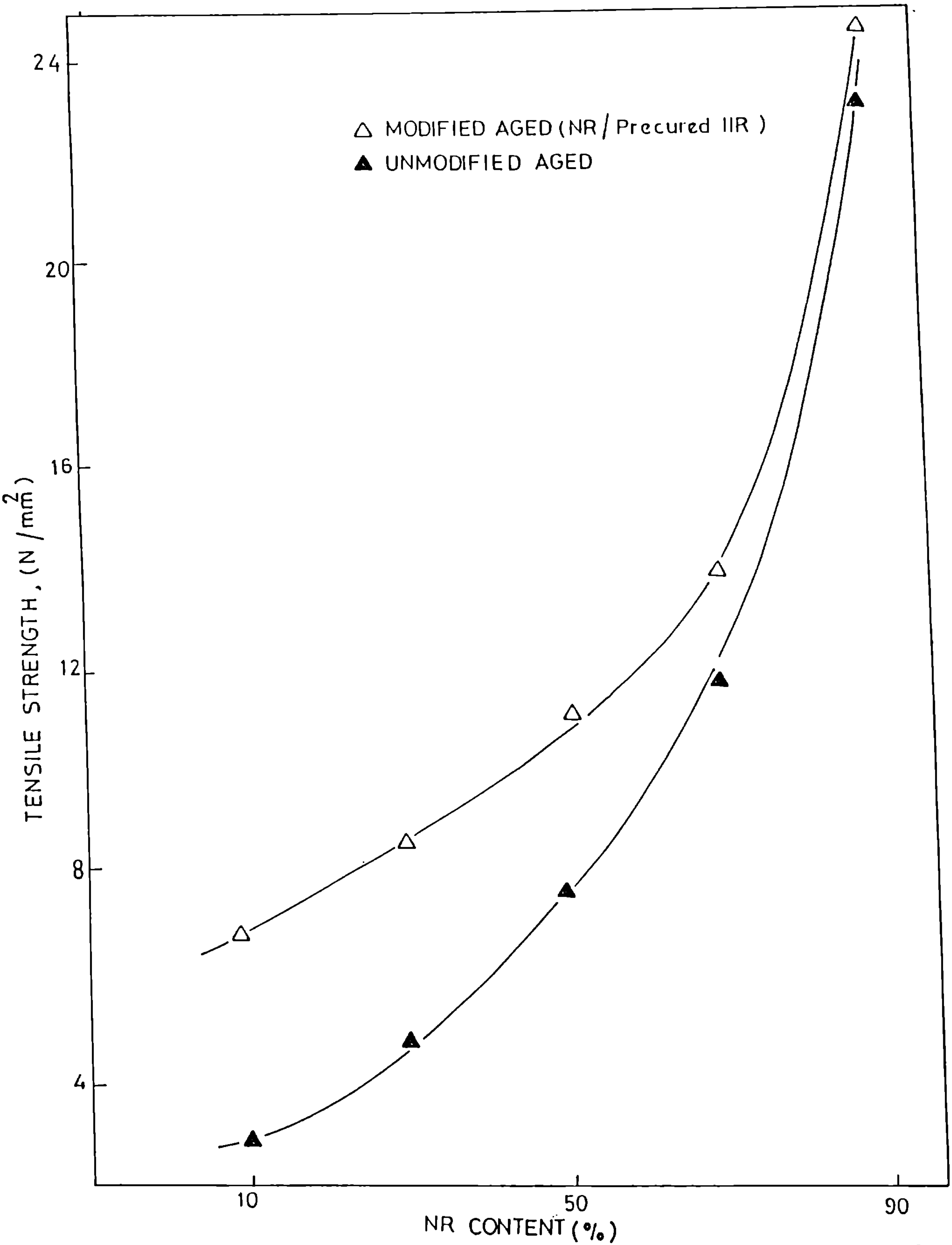

Fig.4.4 Variation of aged tensile strength with NR content of modified and conventional NR/IIR blends.

Fig.4.5 shows the variation of tear strength of modified and conventional NR/IIR blends with blend composition. Higher tear strength values in the case of modified blends may be attributed to the co-crosslinking of both phases. Fig.4.6 shows the tear strength of modified and conventional blends of NR/IIR blends after ageing. Modified blend shows better ageing resistance compared to the conventional blends.

Fig.4.7 shows the elongation at break for modified and conventional blends of NR/IIR blend. As butyl content increases elongation at break increases, modified blends show higher elongation at break compared to conventional blends, except at lower butyl content. This is obviously due to uniform cross-linking of both the phases resulting from dynamic precuring. Same trend is also shown for the elongation at break for modified and conventional blends after ageing (Fig.4.8).

Fig.4.9 shows the abrasion loss of modified and conventional blends of NR/IIR blends. Modified blends show lower loss compared to conventional blends due to uniform crosslinking in both the phases and also due to interphase

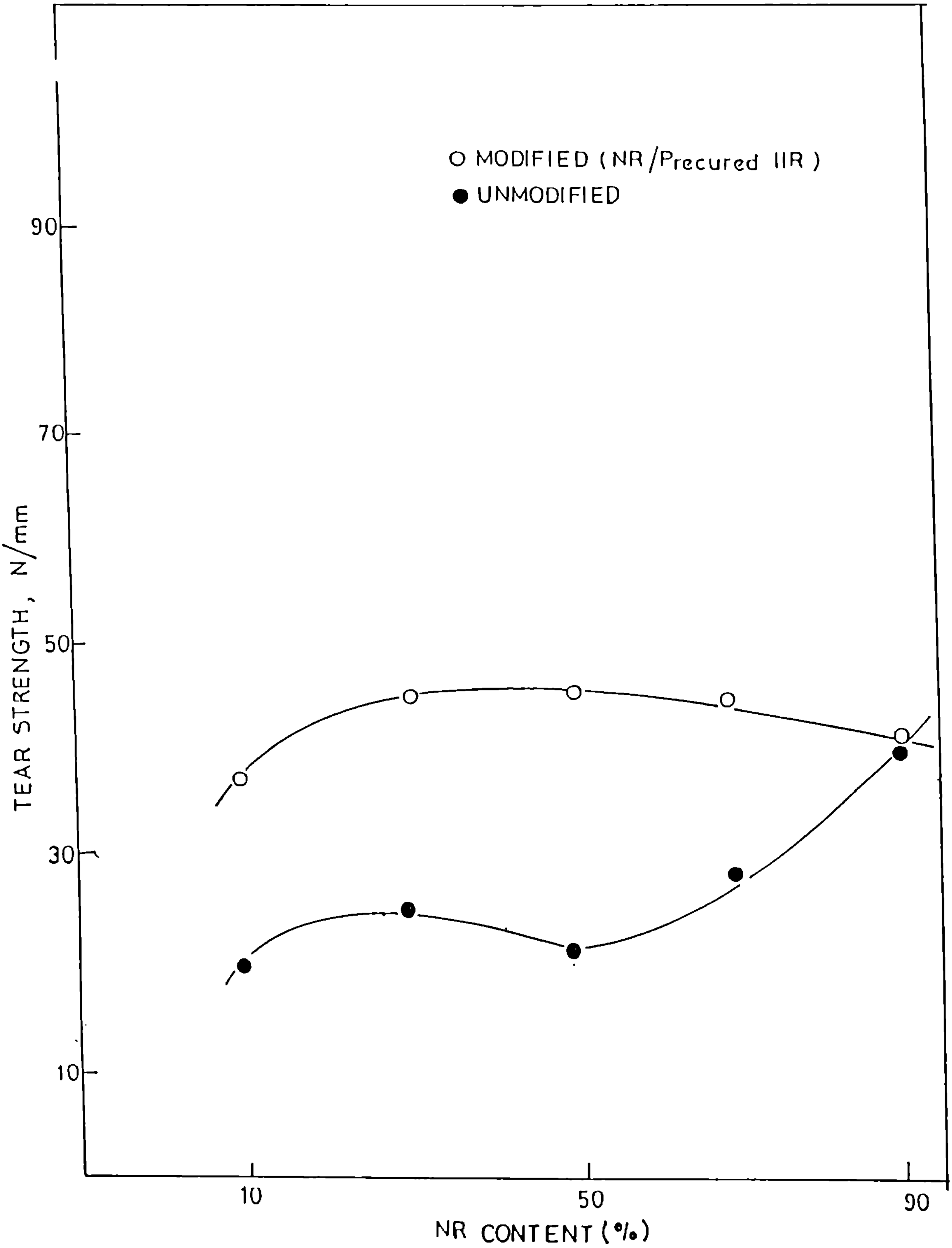

Fig.4.5 Variation of tear strength with NR content of modified and conventional NR/IIR blends.

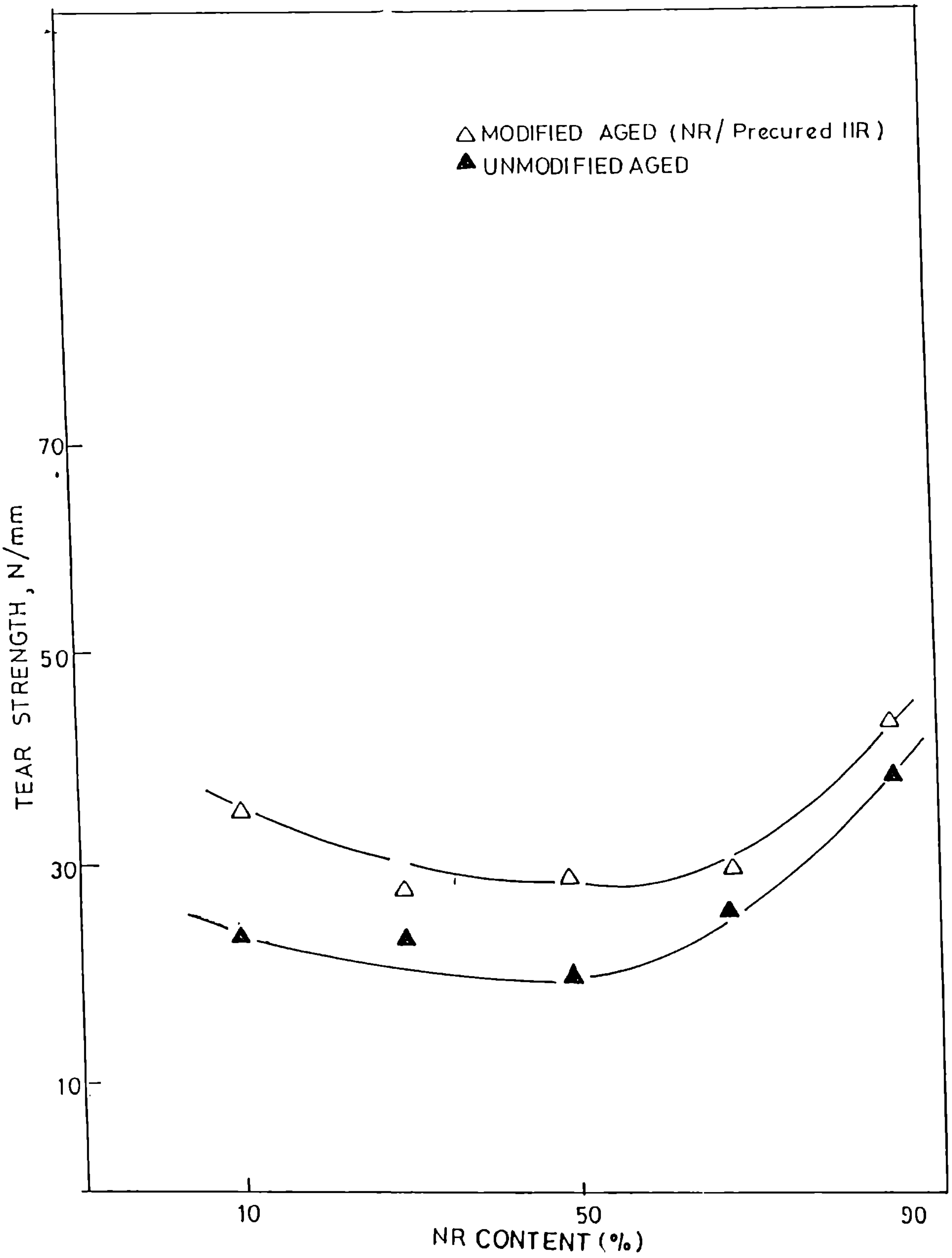

Fig.4.6 Variation of aged tear strength with NR content of modified and conventional NR/IIR blends.

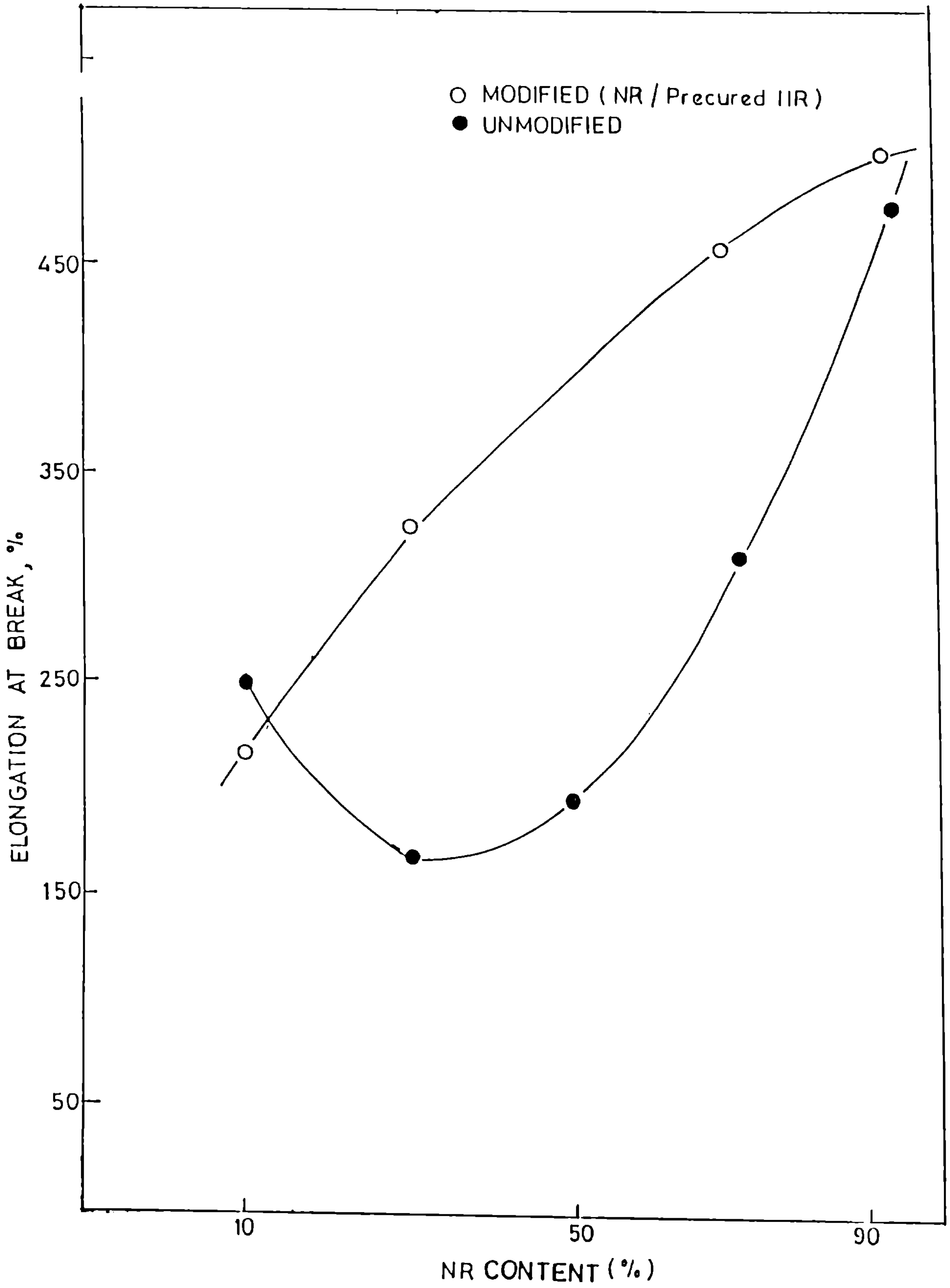

Fig.4.7 Variation of elongation at break with NR content of modified and conventional NR/IIR blends.

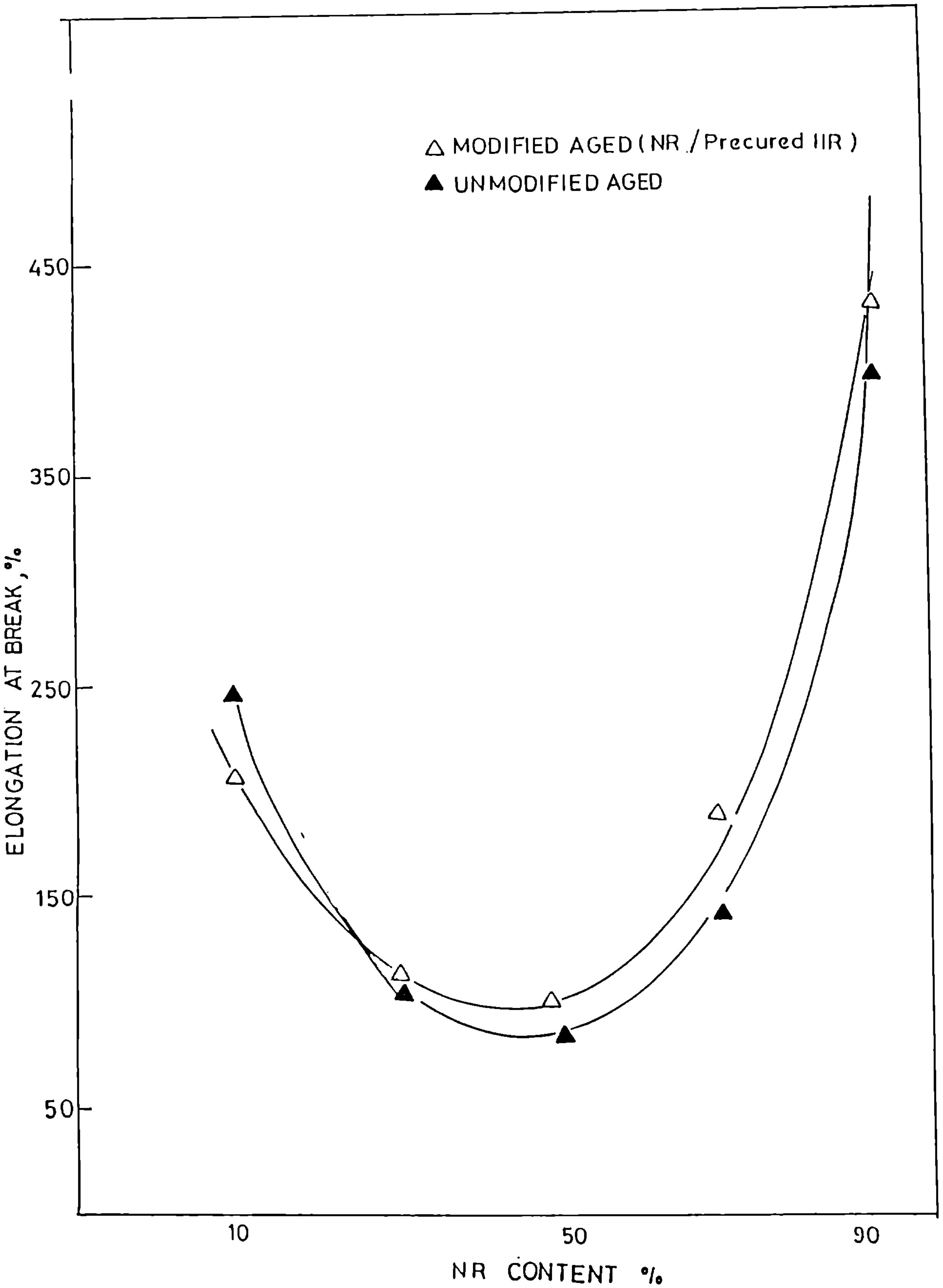

Fig.4.8 Variation of aged elongation at break with NR content of modified and conventional NR/IIR blends.

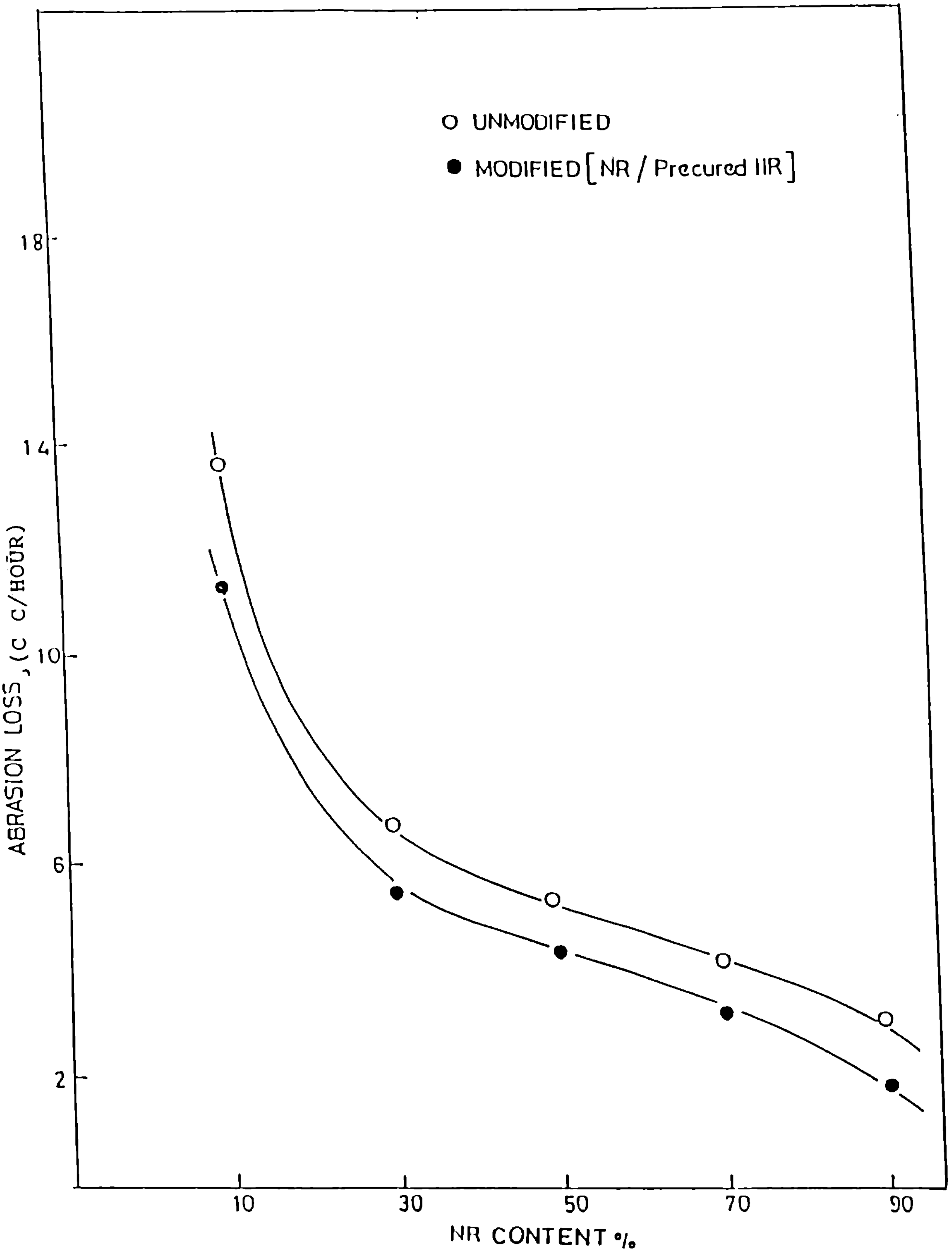

Fig.4.9 Variation of abrasion loss with NR content of modified and conventional NR/IIR blends.

crosslinks. Abrasion loss is high in the case of unmodified blends probably since NR phase is overcured and IIR phase is undercured due to curative migration.

Table 4.3 shows the cure time and scorch time at 140°C of the modified and conventional blends. Cure time and scorch time are found to be reduced for modified blends due to precuring and uniform curing of both phases.

Table 4.4 shows the hardness and compression set values for modified and conventional NR/IIR blends. Modified blends show higher hardness compared to conventional blends. As butyl content increases the blends show lower compression set values which indicate uniform curing of blends.

Fig.4.10 shows the photograph of the effect of ozone on modified and conventional blends at the end of 18 hours. No cracks are observed on the modified blends (shown on the right side of the photograph) while conventional blends developed cracks (shown on the left side of the photograph). The modified blends prepared by dynamic curing in the Shaw intermix also showed similar results as those prepared in the Brabender plasticorder, which indicates that minor changes in shear do not affect the dynamic curing.

(L) Conventional (R) Modified

Fig.4.10 Photograph of 50/50 NR/IIR Ozone Aged Samples after 18 hours.

TABLE 4.3
CURE CHARACTERISTICS OF NR/BUTYL BLENDS

NR	100	90	70	50	30	10	0	90	70	50	30	10
IIR	0	10	30	50	70	90	100	-	-		-	-
Modified IIR	-	-	-	-	-	-	-	10	30	50	70	90
Cure time t90 at 140°C min.	14.0	13.	5.9	7.1	9.0	10.0	43.0	16.9	6.4	5.3	3.4	5.6
Scorch time min	4.9	4.7	2.8	2.5	2.8	2.4	12.0	5.8	2.2	1.6	1.2	0.7
Max. torque Nm.	0.45	0.43	0.54	0.53	0.34	0.37	0.38	0.34	0.64	0.78	0.45	0.33

TABLE 4.4

NR/BUTYL BLENDS: VARIATION OF COMPRESSION SET AND HARDNESS

NR	100	90	70	50	30	10	0	90	70	50	30	10
IIR	0	10	30	50	70	90	100	-	-	-	-	-
Modified IIR	-	-	-	-	-	-	-	10	30	50	70	90
Hardness Shore A	64	52	62	69	63	70	70	60	64	71	63	64
Compression set %	25	27	44	43	44	37	68	41	28	35	28	23

CONCLUSIONS

A low degree of dynamic crosslinking in the IIR phase in NR/IIR blends helps to attain a covulcanized state in these blends after final curing.

Mechanical properties which are influenced by uniform crosslinking of both the phases and in the interface are remarkably improved by the dynamic precuring.

Part II: USE OF AMINE TERMINATED LIQUID NATURAL RUBBER AS A COMPATIBILISER IN NR/NBR BLENDS

Natural rubber possesses excellent physical properties and good processing characteristics, but its poor resistance to oil, solvents and chemicals restricts its use in the areas which require resistance to these agents. Nitrile rubber, a copolymer of butadiene and acrylonitrile is valued both for its oil resistance and for its chemical resistance, but especially for the former[11-14]. Nitrile has good resistance to a wide variety of nonpolar oils, fats and solvents. This property is advantageously made use of in preparing products for the automotive and oil industry with NBR. Blending of NR with nitrile can give rise to products having a compromise of properties of both these rubbers[15].

TABLE 4.5

FORMULATION OF NR/NBR BLENDS

INGREDIENTS	Phr									
NBR	80	80	60	60	50	50	40	40	20	20
NR	20	20	40	40	50	50	60	60	80	80
ZnO	4.2	4.2	4.4	4.4	4.5	4.5	4.6	4.6	4.8	4.8
STEARIC ACID	2	2	2	2	2	2	2	2	2	2
ACCINOX ZC	1	1	1	1	1	1	1	1	1	1
MBTS	0.94	0.94	0.88	0.88	0.85	0.85	0.82	0.82	0.76	0.76
TMTD	0.4	0.4	0.3	0.3	0.25	0.25	0.2	0.2	0.10	0.10
SULFUR	2.1	2.1	2.2	2.2	2.25	2.25	2.3	2.3	2.4	2.4
CARBON BLACK N330	40	40	40	40	40	40	40	40	40	40
AROMATIC OIL	-	5	-	5		5	-	5	-	5
ATNR	10	-	10	-	10	-	10	-	10	-

But natural rubber is highly unsaturated and nitrile rubber is highly polar leading to differences in cure rates resulting in separation of the phases and lack of interphase crosslinks resulting in inferior physical properties[16,17] In this chapter, the effect of amine terminated liquid natural rubber as a compatibilizer in NR/NBR blends for improving their mechanical properties is reported[18-20].

EXPERIMENTAL

NR/NBR blends were prepared on a laboratory mixing mill (6"x12"). Unmodified blends (without adding amine terminated liquid natural rubber) were prepared as per formulations shown in Table 4.5 using aromatic oil. In the modified blends, amine terminated liquid natural rubber (ATNR) was used in place of aromatic oil.

Amine terminated liquid natural rubber (ATNR) was prepared as reported[21], by dissolving 100 gm of masticated natural rubber in 450 ml toluene, 50 ml of ethylene diamine and 50 ml tetrahydrofuran and mixed thoroughly. This solution was kept under sunlight for irradiation for 60 hours in a quartz jar. ATNR obtained was then precipitated using methanol and used as a compatibilizer. The optimum cure times of the blends were determined on a Goettfert

TABLE 4.6

NR/NBR BLENDS

NBR GRADE	ATNR Phr	CURE TIME (T 90)min	TENSILE STRENGTH N/mm^2	TEAR STRENGTH N/mm	ELONGATI ON AT BREAK (%)
512	0	4.7	21.04	59.17	407.
512	5	3.1	24.07	57.56	434.
553	0	4.9	20.61	44.43	419
553	5	3.1	22.88	58.53	428.
553	10	3.33	23.49	66.61	386..

Elastograph model 67.85 as per ASTM D 1646 (1981). The compounds were then vulcanized upto their optimum cure times in an electrically heated laboratory hydraulic press at 150°C.. Dumbell shaped tensile test specimen and angular test specimens were punched out of these compression moulded sheets along the mill grain direction and their properties were measured on a Zwick universal testing machine as per relevant ASTM standards.

RESULTS AND DISCUSSION

Table 4.6 shows the effect of ATNR on 50/50 NR/NBR employing two different grades of NBR (553 and 512) at levels of 5 parts of ATNR and 10 parts ATNR. Tensile and tear strength improve with 10 parts of ATNR in 553, while with 5 parts of ATNR, there is only slight increase. Cure time is less with 5 parts ATNR compared to the blend without ATNR which shows that ATNR has improved the compatibility of the blends and accelerates the curing. In NBR 512 improvement in tensile and tear is good even with 5 parts of ATNR with reduction in cure time. Fig.4.11 shows the variation of tensile strength of NR/NBR blends with 10 parts of ATNR. A steady increase in tensile strength is noticed for the blends containing ATNR compared to the blends without it except in the blends where NBR is a major

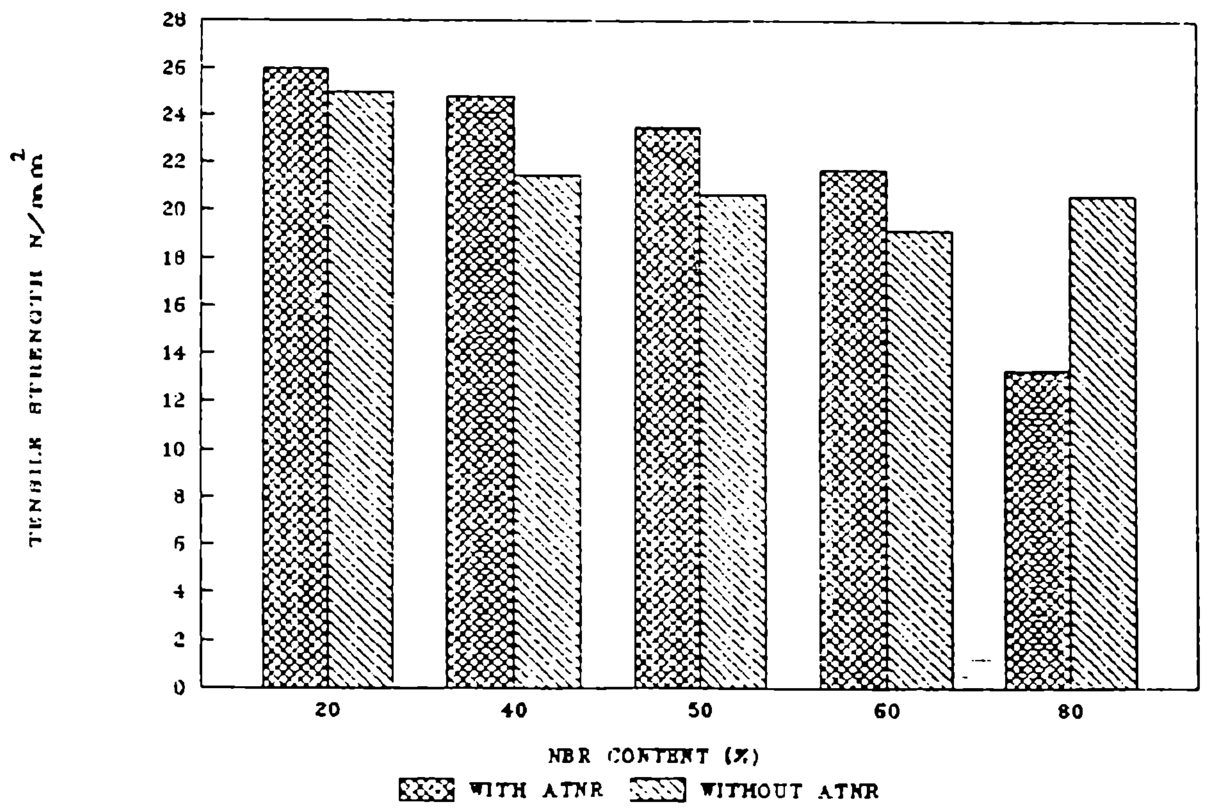

Fig.4.11 Variation of tensile strength with NBR content for NR/NBR blends with ATNR and without ATNR.

component This shows that the compatibility between NBR/NR has been improved by the incorporation of ATNR in the blend, except in cases where NBR is a major component.

Fig.4.12 shows the tear strength of NR/NBR blends with 10 parts ATNR. Except for 50/50 NR/NBR blend all other ratios show a decrease in tear strength when ATNR is incorporated compared to those blends without ATNR.

Fig. 4.13 shows the elongation at break values as NBR content increases. EB values show an increasing trend in blends with ATNR compared to blends without ATNR.

Table 4.7 shows the physical properties of 50/50 NR/NBR with silica filler. Blends with silica filler and 10 parts ATNR show improved tensile strength, less cure time but lower tear strength. NR/NBR blends with 10 part ATNR, silica filler and without diethylene glycol plasticiser show higher tensile strength and tear strength and less cure time compared to those blends with diethylene glycol. NR/NBR blends with 8 parts ATNR and silica powder show only marginal increase in tensile strength and elongation at break and lower tear strength compared to those blends with

TABLE 4.7

50/50 NR/ NBR BLENDS WITH 40 SILICA

ATNR Phr	DEG Phr	Cure time t90 at 150°C min.	Tensile strength N/mm^2	Tear strength N/mm	Elongation at break (%)
0	1.0	9.1	9.45	27.69	294.
10	1.0	4.1	12.89	26.34	439.
10	0	2.1	14.09	41.21	449.
8.0	0	2.3	12.61	36.63	430.
6.5	0	2.0	12.45	39.22	383.
6.5	0	3.3	11.59	39.11	487.

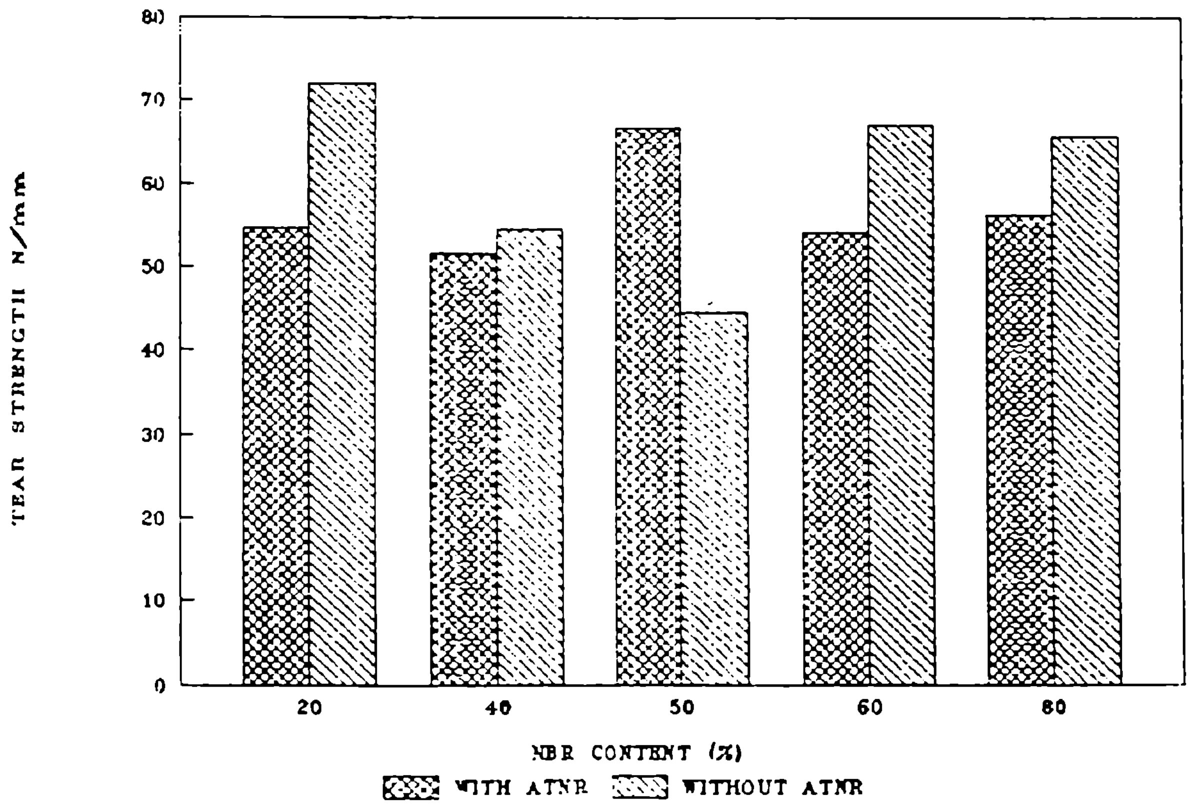

Fig.4.12 Variation of tear strength with NBR content for NR/NBR blends with ATNR and without ATNR.

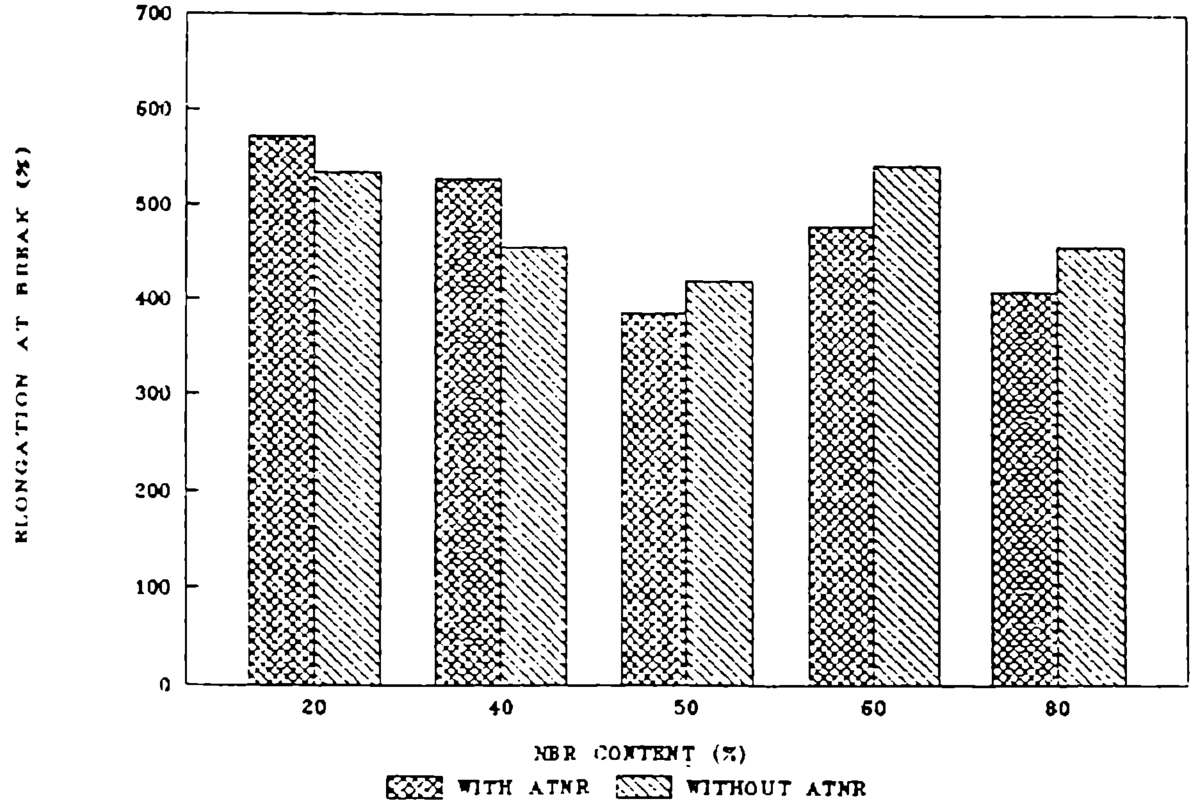

Fig.4.13 Variation of elongation at break with NBR content for NR/NBR blends with ATNR and without ATNR.

6.5 parts ATNR which shows that on increasing ATNR tear strength decreases. Blends compounded with granulated silica and without diethylene glycol show lower physical properties. Thus compounding with ATNR without using any other plasticisers can improve the compatibility of NR/NBR blends.

CONCLUSIONS

Covulcanization of acrylonitrile butadiene rubber and natural rubber by incorporation of amine terminated liquid natural rubber (ATNR) reduces the cure time of the blends and improves the tensile strength. In blends using silica filler without diethylene glycol plasticiser improved tensile strength and tear strength are observed at optimum ATNR concentrations.

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Chapter V

Part I STUDIES ON THE COVULCANIZATION OF NBR/EPDM BLENDS

Ethylene propylene ter polymers (EPDM) have a fully saturated backbone giving excellent resistance to ozone and oxygen and hence excellent weatherability even without antioxidants or antiozonants[1]. Nitrile rubber (NBR) has excellent oil resistance but is subject to degradation at high temperature and addition of antidegradants is not effective. Further, NBR is a polar elastomer and is fast curing compared to EPDM. Due to the large difference in polarity and unsaturation between NBR and EPDM, migration of curatives towards NBR phase from EPDM occurs resulting in inferior mechanical properties[2-6]. Blending of EPDM with NBR may be attractive if sufficient mechanical strength can be developed by reducing the cure rate imbalance between the two rubbers to develop satisfactory network structure in each of the phases and in the interphase[7-10]. Studies were done to improve the mechanical properties of these immiscible elastomers by employing the technique of

(1) prevulcanizing the slow curing EPDM phase to an optimum level to prevent curative diffusion and then blending it with NBR.

(2) Covulcanization of NBR/EPDM blends using carboxylated EPDM.

(3) Covulcanization of NBR/EPDM blends using two different accelerator systems in two phases.

The mechanical properties of the blends prepared by these three routes are compared with those of the conventional blends.

EXPERIMENTAL

a) Covulcanization of NBR/EPDM using carboxylated EPDM

EPDM was carboxylated using maleic anhydride with MBT as a promoter and zinc oxide for ionic crosslinking. Mixing was done on a Brabender plasticorder PL 3 S at 60 rpm and at an initial temperature of 170°C and mixing was continued to a temperature of 210°C. Thermal stability of the ionic crosslinks formed was evaluated by taking the cure curves of modified EPDM at 40°C. The modified EPDM was then blended with NBR on a laboratory mixing mill and the curatives and other compounding ingredients for both the rubbers were added. Cure curves of the blends were determined at 140°C on a Geottfert Elastograph. Formulations of the mixes are shown in the Table 5.1.

TABLE 5.1

A. CARBOXYLATED EPDM

INGREDIENTS	Phr
EPDM ROYALENE 301-T	100
MALEIC ANHYDRIDE	4
MBT	0.4
ZnO	4

Mixed in Brabender at 170°C ; Cure time 6.36 mins. at 40°C

B.50/50 NBR/EPDM BLENDS

INGREDIENTS	Phr
NBR	50
CARBOXYLATED EPDM	50
ZnO	6.5
STEARIC ACID	2.0
MBTS	0.6
TMTD	0.5
SULFUR	2.0
CARBON BLACK HAF N330	40.
DOP	5.0

b) Covulcanization of NBR/EPDM blends using two different accelerators for each rubbers

In this technique the fast curing NBR phase was compounded initially with slow accelerators along with other compounding ingredients, while slow curing EPDM phase was compounded with ultra accelerators along with other compounding ingredients. These compounds were then blended together and physical properties determined.

Five sets of blends were prepared by varying the type and contents of the sulfur and accelerators as below

1. NBR 1.5 phr DPG, 2.0 sulfur
   EPDM 1.5 phr TMTD, 2.0 sulfur

2. NBR 1.5 phr DPG, 2.0 sulfur
   EPDM 1.0 phr MBTS, 0.5 TMTD, 2.0 sulfur

3. NBR 1.5 phr MBTS, 2.0 sulfur
   EPDM 1.5 phr ZDC, 2.0 sulfur

4. NBR 1.5 phr DPG, 2.0 sulfur
   EPDM 1.2 phr ZDC, 2.0 sulfur

5. NBR 1.0 phr MBTS, 0.5 TMTD, 2.0 sulfur
   EPDM 1.0 phr MBTS, 0.5 TMTD, 2.0 sulfur

Cure characteristics were determined on a Goettfert Elastograph at 140°C and physical properties determined on a Zwick UTM shown in Table 5.2.

c) Covulcanization using precuring technique

In this technique, the slow curing EPDM phase was given a certain amount of precuring before blending it with NBR. The amount of precrosslinking that has to be given to EPDM phase was determined from the variation of tensile properties of blends of NBR/EPDM with variation of precrosslinking. Mixing was done on a laboratory two roll mixing mill of friction ratio 1:1.25 with cold water circulation as per formulations given in Table 5.3. EPDM compounds were sheeted out from the mixing mill at a thickness of about 4-5 mm and then precured in an oven at 130°C for 30 minutes. The precured compounds were then blended with NBR and compounding ingredients for NBR were added. Blended compounds were then vulcanized upto their optimum cure times and physical properties were determined.

TABLE 5.2

DIFFERENT CURE SYSTEMS FOR NBR/EPDM BLENDS

	I		II		III		IV		V	
	NBR	EPDM	NBR	EPDM	NBR	EPDM	NBR	EPDM	NBR	EPDM
ELASTOMER	100	100	100	100	100	100	100	100	100	100
CARBON BLACK N330	40	40	40	40	40	40	40	40	40	40
ZINC OXIDE	4	4	4	4	4	4	4	4	4	4
STEARIC ACID	2	2	2	2	2	2	2	2	2	2
ACCINOX ZC	1	1	1	1	1	1	1	1	1	1
MBTS	-	-	-	1.0	1.5	-	-	-	1.0	1.0
TMTD	-	1.5	-	0.5	-	-	-	-	0.5	0.5
ZDC	-	-	-	-	-	1.5	-	1.2	-	-
DPG	1.5	-	1.5	-	-	-	1.5	-	-	-
SULFUR	2	2	2	2	2	2	2	2	2	2
PARAFINIC OIL	0	5	0	5	0	5	0	5	0	5
DOP	5	0	5	0	5	0	5	0	5	0
BLEND CURE TIME,T90 min	14.1		4.6		10.3		12.3		4.2	
BLEND TENSILE STRENGTH N/mm^2	7.25		9.53		11.19		11.10		5.61	
BLEND ELONGATION AT BREAK (%)	349		325.		260.		237.		184.	

TABLE 5.3

FORMULATIONS FOR NBR/EPDM BLENDS

NBR	100	90	70	50	30	10	-	-	-	-	-	-
EPDM	-	-	-	-	-	-	100	90	70	50	30	10
Zinc Oxide	4	3.6	2.8	2	1.2	0.4	4	3.6	2.8	2	1.2	0.4
Stearic Acid	2	1.8	1.4	1	0.6	0.2	2	1.8	1.4	1	0.6	0.2
Accinox ZC	1	0.9	0.7	0.5	0.3	0.1	1	0.9	0.7	0.5	0.3	0.1
MBTS	1	0.9	0.7	0.5	0.3	0.1	1.0	0.9	0.7	0.5	0.3	0.1
TMTD	0.5	0.45	0.35	0.25	0.15	0.05	0.5	0.45	0.35	0.25	0.15	0.05
Carbon Black HAF N330	40	36	28	20	12	4	40	36	28	20	12	4
Parraffinic Oil	-	-	-	-	-	-	5	4.5	3.5	2.5	1.5	0.5
DOP	5	4.5	3.5	2.5	1.5	0.5	-	-	-	-	-	-
Sulfur	2.0	1.8	1.4	1.0	0.6	0.2	2	1.8	1.4	1.0	0.6	0.2

The optimum cure times (time to reach 90% of the maximum torque) of all these blends were determined on a Goettfert Elastograph. The compounds were then vulcanized upto their optimum cure times in an electrically heated laboratory hydraulic press at 140°C. Dumbell shaped tensile test specimens were punched out of these compression moulded sheets along the mill grain direction. The tensile properties were measured on a Zwick universal testing machine model 1445 using a crosshead speed of 500 mm/min.

RESULTS AND DISCUSSION

A. Carboxylation of EPDM with MBT as a promoter in the presence of ZnO

Curing was observed only at 40°C which is obviously due to the lack of thermal stability of the ionic crosslinks at high temperature and thus this technique failed to prevent curative migration. When blended with NBR on the mill at a temperature of 70°C and moulded at 140°C the vulcanizate showed lower tensile strength for the modified NBR/EPDM blends, compared to unmodified blends of NBR/EPDM blends, which were blended directly on the mill as shown in Table 5.4.

B. Effect of varying the curing systems

In the case of NBR and EPDM both being blended with 1.0 part MBTS and 0.5 parts TMTD curative migration

TABLE 5.4

NBR/ EPDM 50/50 BLENDS

BLEND	CURE TIME (T_{90}) min, at 140°C	TENSILE STRENGTH N/mm^2	MODULUS 100%	ELONGATION AT BREAK (%)
CONVENTIONAL	4.2	5.61	3.45	184.
MODIFIED	14.9	4.82	1.49	354.

occurs resulting in poor tensile properties due to polar nature of NBR resulting in faster curing compared to EPDM. When this system was replaced by 1.5 parts DPG in NBR phase and 1.5 part TMTD in EPDM phase improvement in tensile properties is noticed but cure time (t_{90}) is found to be higher. So in the next trial EPDM phase was given 0.5 parts of TMTD and 1.0 parts MBTS while in the NBR phase 1.5 part DPG was kept constant which reduced the cure time and improved tensile strength. Third and fourth set showed maximum tensile strength with ultra accelerator ZDC in EPDM phase, when 1.5 parts DPG was used in NBR phase and 1.2 ZDC in EPDM phase. Cure time was found to be slightly higher and tensile properties slightly lower compared to the blend with 1.5 part ZDC in EPDM phase and 1.5 parts MBTS in NBR phase. Thus it is observed that by proper selection of curatives for each of the phases depending on their cure rate, it is possible to improve the physical properties of the blend by reducing curative migration between the phases. Blend 5 which uses the same amount and type of sulphur and accelerator, for both EPDM and NBR results in the least strength and blend 3 which seems to be best combination of curatives for these two rubbers, tensile strength is almost the double the value.

C. Partial precuring of the slow curing rubber viz., EPDM

Fig. 5.1 shows the variation in tensile strength of NBR/precrosslinked EPDM blends (hereafter referred to as modified blends) with composition in comparison to that of conventional NBR/EPDM blends prepared by direct blending of NBR and EPDM on the mill. Modified blends show much better tensile strength compared to the conventional blends. The improvement in tensile strength may be due to the reduction in cure rate mismatch between NBR and EPDM.

Fig.5.2 shows the tensile strength after ageing of NBR/EPDM blend for modified and conventional blends. Improvement of tensile strength after ageing is noted for certain blend ratios in the case of modified blends.

Tear resistance of the modified and conventional NBR/EPDM blends shown in Fig.5.3. Modified blends show better tear strength compared to conventional blends which further points towards optimum crosslink densities in both the phases due to precrosslinking of EPDM.

Fig.5.4 shows the variation of elongation at break of NBR/EPDM blends which also demonstrates higher elongation at break value for modified blends due to uniform filler

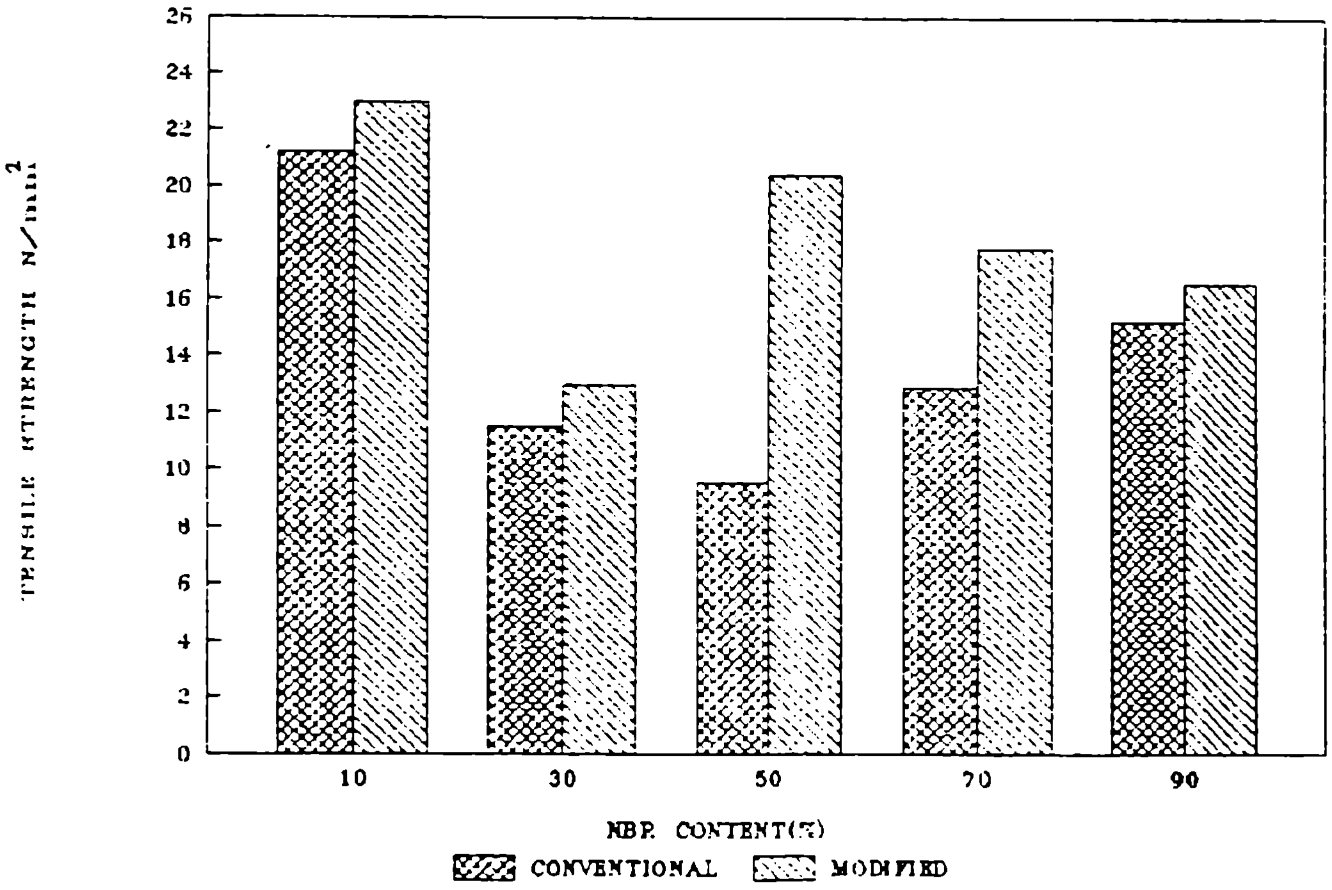


Fig.5.1 Variation of tensile strength with NBR content of modified and conventional NBR/EPDM blends.

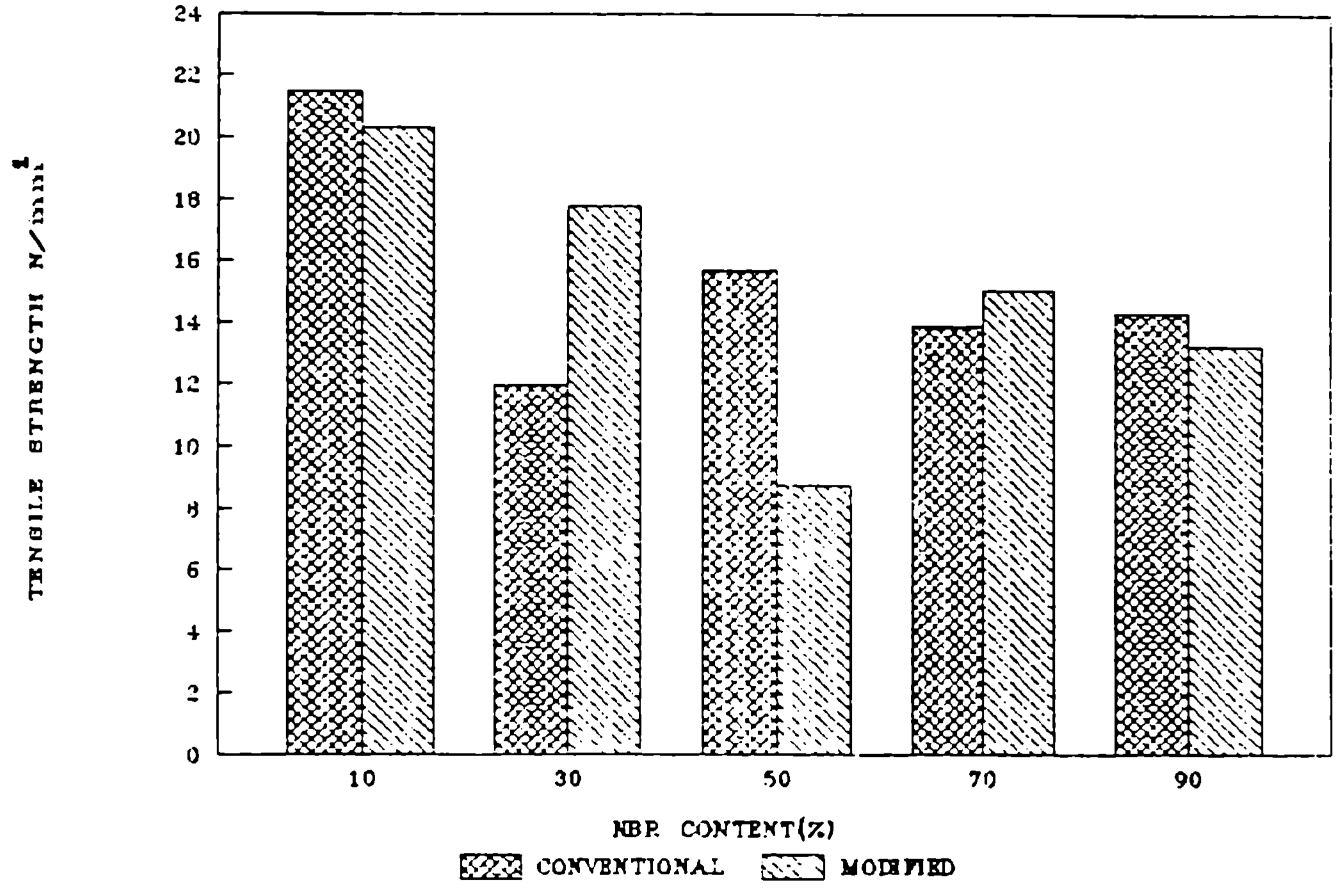


Fig.5.2 Variation of aged tensile strength with NBR content of modified and conventional NBR/EPDM blends.

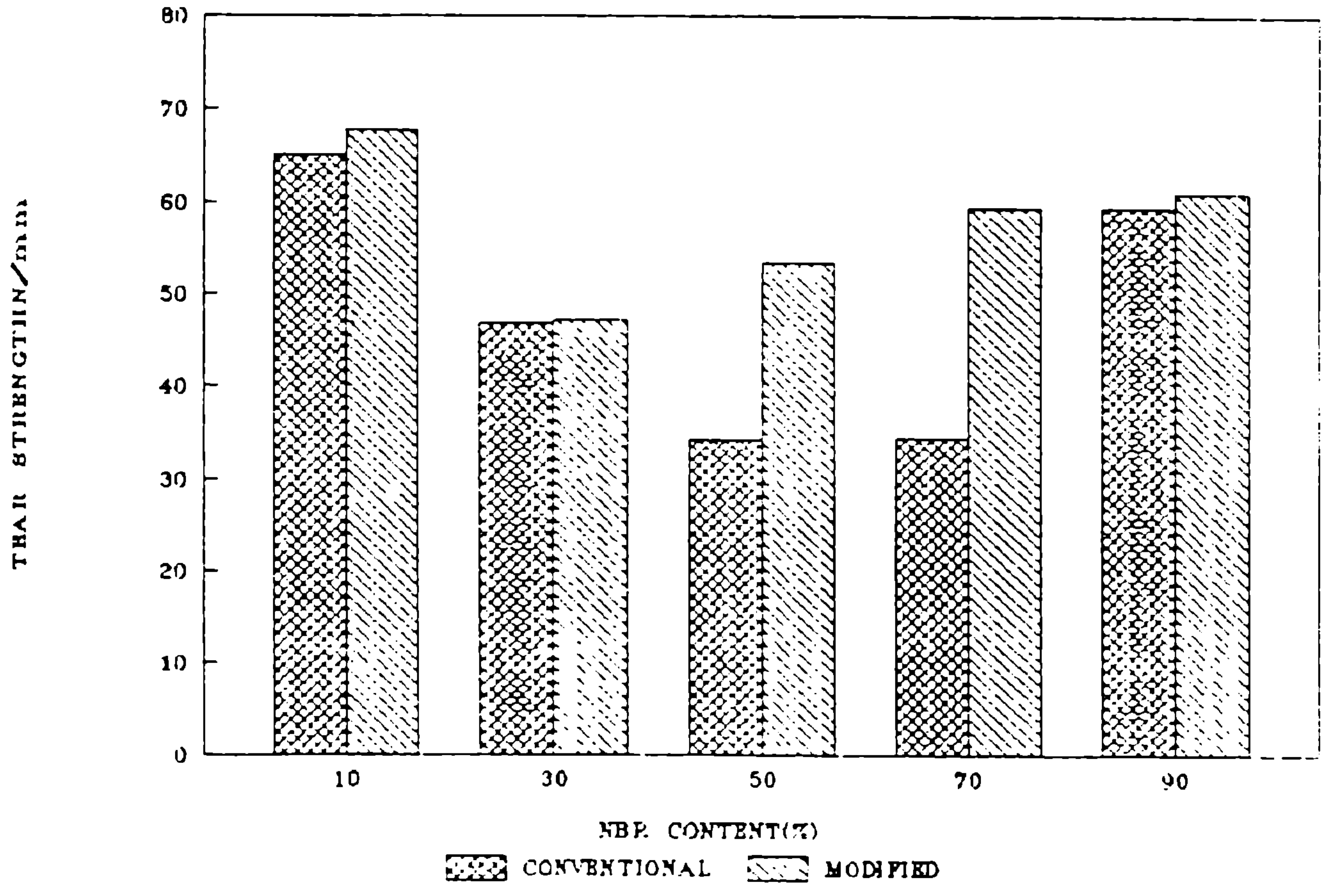


Fig.5.3 Variation of tear strength with NBR content of modified and conventional NBR/EPDM blends.

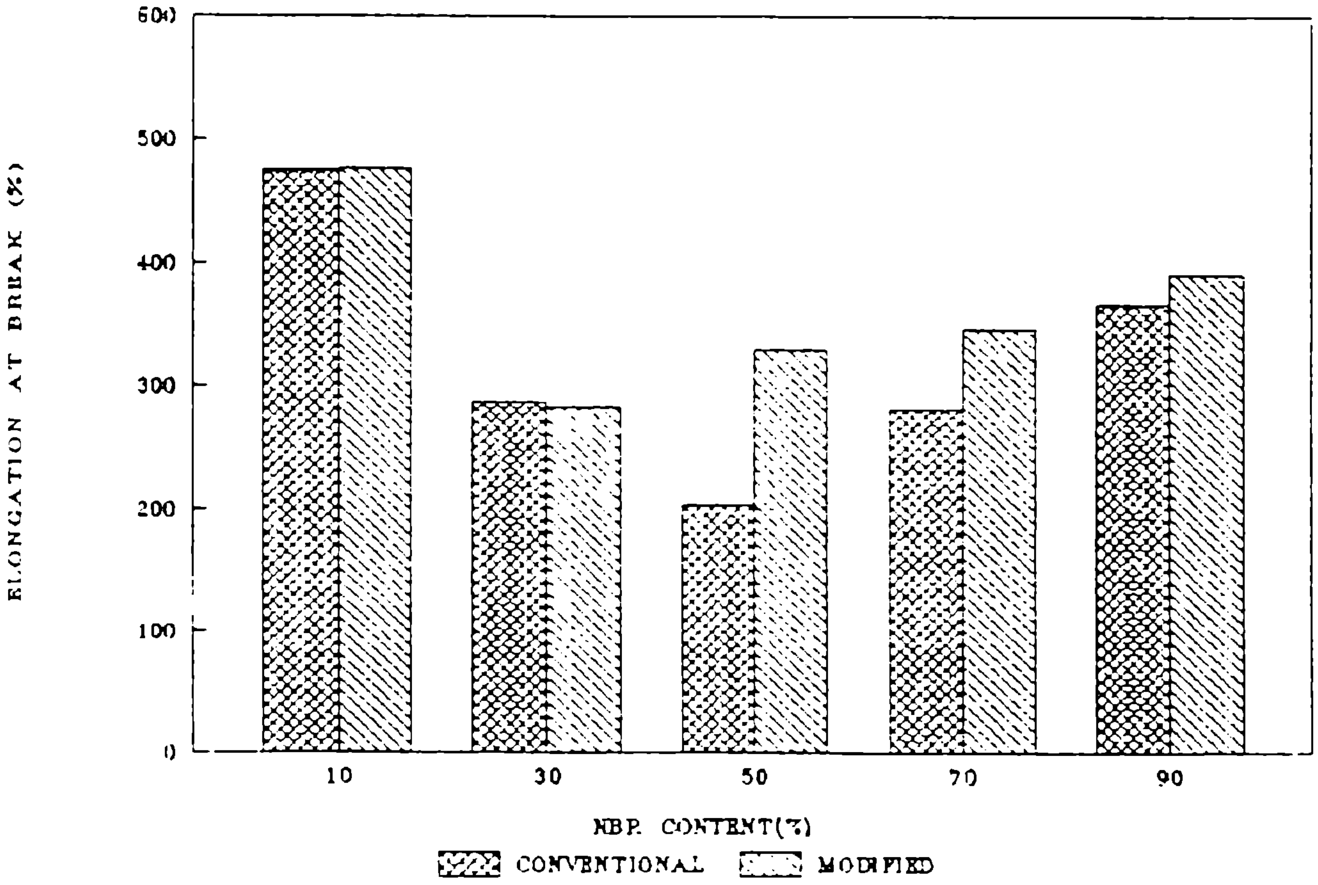


Fig.5.4 Variation of elongation at break with NBR content of modified and conventional NBR/EPDM blends.

distribution in both phases, as indicated by polaroid dispersion studies (Part II).

Table 5.5 shows the hardness values obtained for modified and conventional NBR/EPDM blends. Values obtained for modified blends are higher than those of the conventional blends.

In the ozone resistance studies conducted in the 80/20 NBR/EPDM blends crack initiation was observed after 4 hours and 30 minutes in the conventional blend while after 4 hours 50 minutes in the modified blends as shown in Figs.5.5(1) and 5.5(2) respectively. All the other blend ratios with higher EPDM content viz., 20/80, 40/60, 60/40 (NBR/EPDM) no crack initiation was observed even after 98 hours for both modified and conventional blends as shown in Fig.5.5(3).

Circular specimen of 6.5 mm thickness of modified and conventional blends were moulded and allowed to swell in n-hexane solvent for 120 hours and resulting changes in appearances are shown in Fig.5.6. In conventional blends (1) due to lack of interphase crosslinks, phase separation occurs while for modified blends (2) uniform curing and presence of interphase crosslinks prevents phase separation.

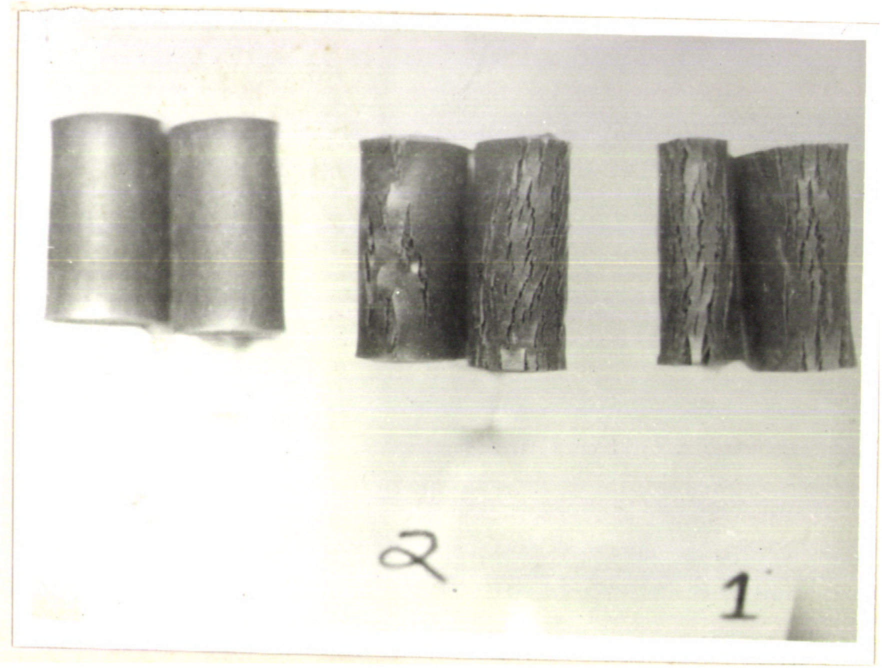


Fig.5.5 Photograph of Ozone Aged Samples.
(1) 80/20 NBR/EPDM conventional blend.after 4 hours and 30 minutes.
(2) 80/20 NBR/EPDM modified blend. after 4 hours and 50 minutes.
(3) 60/40 NBR/EPDM modified blend after 98 hours.

(1) Conventional (2) Modified

Fig.5.6 Photograph of 50/50 NBR/EPDM vulcanizate swollen samples.

TABLE 5.5

HARDNESS (Shore A)

NBR Content %	CONVENTIONAL	MODIFIED
20	57	63
40	62	63
60	58	62
80	61	69

TABLE 5.6

NBR/EPDM BLENDS

A) WEIGHT AFTER 48 HOURS IN GEAR OIL

NBR Content %	CONVENTIONAL gms..	MODIFIED gms.
20	0.10	0.11
40	0.08	0.08
60	0.05	0.06
80	0.02	0.03

NBR/EPDM BLENDS

B) WEIGHT AFTER 48 HOURS IN ENGINE OIL

NBR Content %	CONVENTIONAL gms..	MODIFIED gms.
20	0.08	0.11
40	0.06	0.04
60	0.01	0.02
80	0.00	0.01

TABLE 5.7

COMPRESSION SET (%)

NBR Content %	CONVENTIONAL	MODIFIED
20	26	21
40	26	22
60	23	21
80	28	25

TABLE 5.8

CURE TIMES AT 160°C

NBR Content %	CONVENTIONAL(t90)mins.	MODIFIED (t90) mins.
20	3.8	4.6
40	6.0	1.9
50	10	3.0
60	1.6	1.4
80	1.5	1.5

Table 5.6 shows the swelling of conventional and modified blends in (a) in gear oil and (b) in engine oil for 48 hrs. No appreciable difference is noted since oil resistance is the property of the polymer. Table 5.7 shows the compression set values for modified and conventional blends and Table 5.8 shows the respective cure times of blends.

CONCLUSIONS

1. Carboxylation of EPDM and blending with NBR do not improve physical properties of the blends.

2. By properly selecting sulfur and accelerator types and amounts for EPDM and NBR and then blending them individually before final mixing improve physical properties of their blends.

3. Precuring EPDM to a certain level and then blending with NBR is the most promising method for improving physical properties of NBR/EPDM blends.

Part II MORPHOLOGY, DISPERSION, PERMEABILITY AND CONDUCTIVITY STUDIES OF NBR/IIR, NR/IIR AND NBR/EPDM BLENDS

INTRODUCTION

The homogenity and morphology of elastomer blends can be studied by various techniques such as optical microscopy, scanning electron microscopy (SEM) and photomicrography. Optical and scanning electron microscopy were extensively used by Walters to study the blending of gum and lightly loaded elastomers involving the use of phase contrast to differentiate the components[11]. In investigating filled elastomer blends workers such as Hess[12,13] and Marsh[14] have resorted to electron microscopic techniques including differential swelling of the component phases to provide contrast. Phase contrast optical microscopy requires specimens which can be prepared by cryosectioning. The general rule for compatibility is - smaller the average disperse area, the more compatible is the blend[15-17]

The most straightforward method for examining the structure of multiphase polymeric systems is direct observation in electron microscope. The use of SEM generally involves much simpler specimen preparation of the fracture surface[18]. Contrast is achieved by imaging with back scattered electrons where emission increases in the direction of higher atomic number elements[19,20].

Most suitable method for dispersion studies is the photo micrographic studies using polaroid land camera with 30 times magnification. The photo micrograph of the samples is compared to a set of ten dispersion standards of equal magnification. The photo can be assigned numerical rating of 1-10 with 10 being the best rating. In this part of the study we report the optical microscopic, scanning electron microscopic and photo micrographic study of the blends.

EXPERIMENTAL

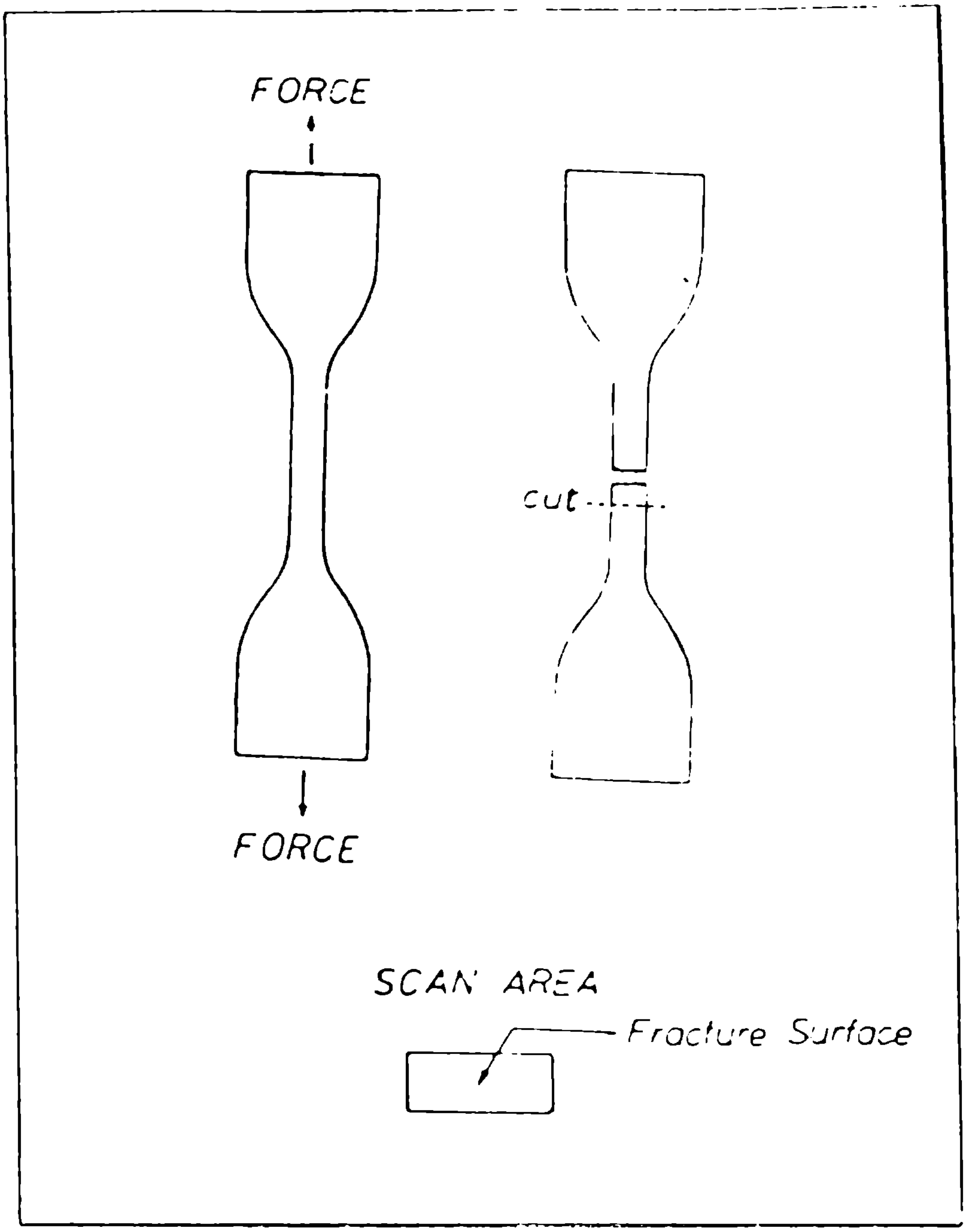
Blends prepared by direct blending of the two rubbers on a laboratory mixing mill are designated as conventional blends and those prepared by precuring the slower curing rubber to an optimum level and then blending it with the other fast curing rubber is designated as modified blends. Both the blends were vulcanised in an electrically heated hydraulic press at 140°C upto their optimum cure times. Dumbell shaped tensile test specimens were punched out of compression moulded sheets and tested on a Zwick UTM with a crosshead speed of 500 mm/min. Fracture surfaces of the specimens (as in Fig.5.7) were then stored in a desiccator to avoid contamination from dust particles. Fracture surfaces were then sputter coated with gold within 24 hours. SEM observations and the photographs were taken using a Hitachi model scanning electron microscope.

Specimens for optical microscopy and photo microscopy studies were prepared by carefully microtoming a thin section of the sample by using a razor blade. The specimen mounted on the microscopic slide and optical micrographs was viewed at a magnification of 330 using optical microscope, Versamet 2 Union 7596.

The specimens for photo micrographs were sandwiched between two rectangular glass sample holders and observed under the microscope with a magnification of 30 and photographs were taken using a polaroid MP4 land camera.

Samples for permeability, crosslink density and conductivity determination were prepared as per relevant standards.

FIG 5.7 TENSILE FRACTURE SURFACE



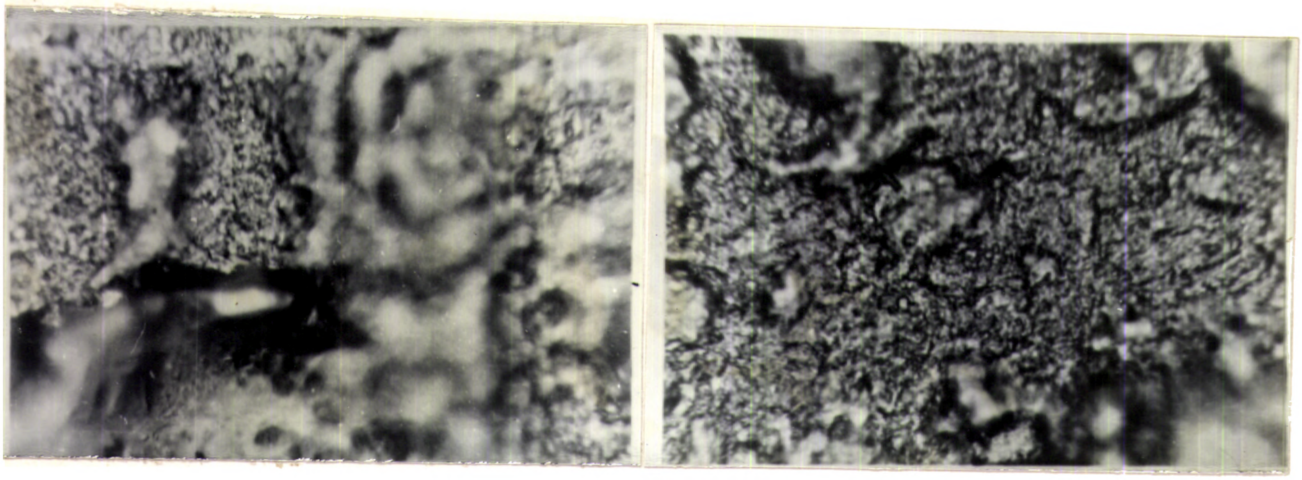
RESULTS AND DISCUSSION

a) Optical microscopy

Figs.5.8a and b show the optical microscopic photograph of 90/10 NBR/butyl (a) conventional and (b) modified blend. Poor blend compatibility and poor adhesion between the phases result in the large zones, in the case of conventional blends, while for modified blends a more uniform distribution of ingredients can be seen.

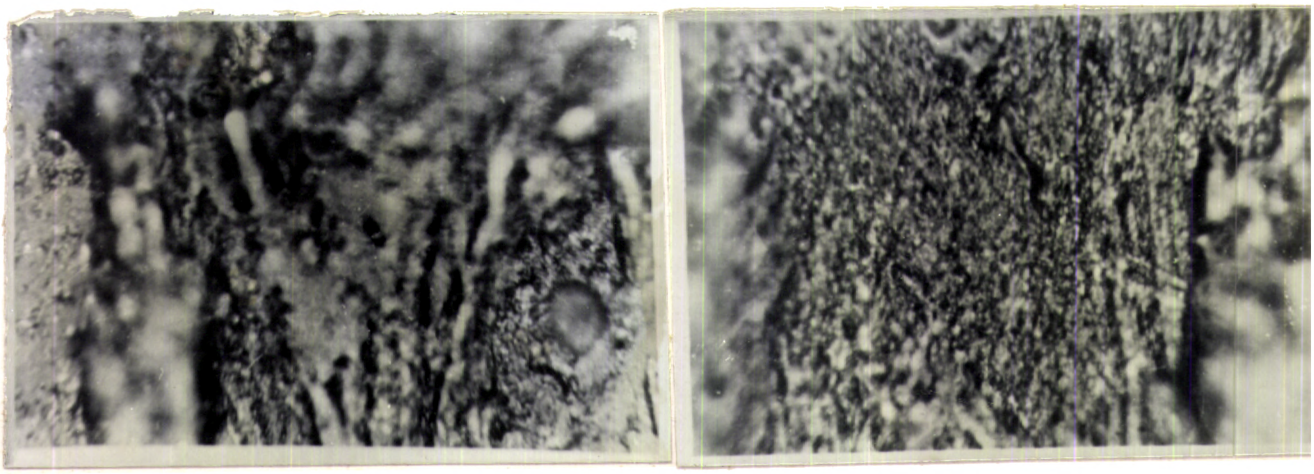
Photographs 5.9a and b show the 70/30 NBR/butyl conventional and modified blends respectively. It can be seen that a marked degree of immiscibility exists in the conventional blend while in the modified blends the average disperse area is found to be small indicating more compatibility of the blends.

Photographs 5.10a and b show 50/50 NBR/butyl conventional and modified blends respectively. Conventional blend shows discrete separate phases while modified blend shows good dispersion and uniform blending represented by even pattern in the micrograph. These observations are in accordance with the improved mechanical properties of the modified blends.



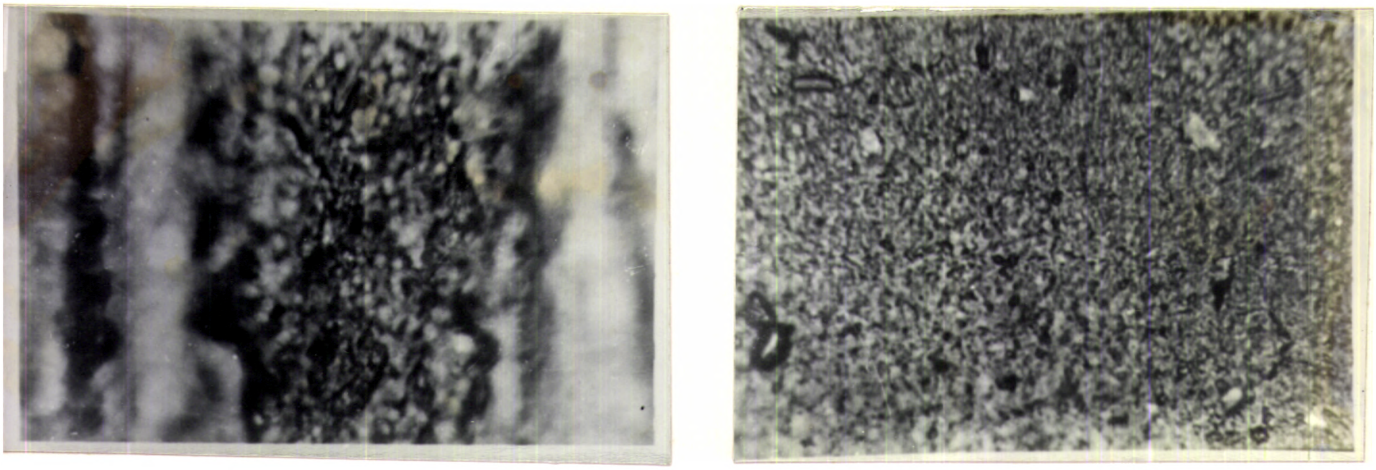
(a) Conventional (b) Modified

Fig.5.8 Optical micrograph of 90/10 NBR/Butyl blend.



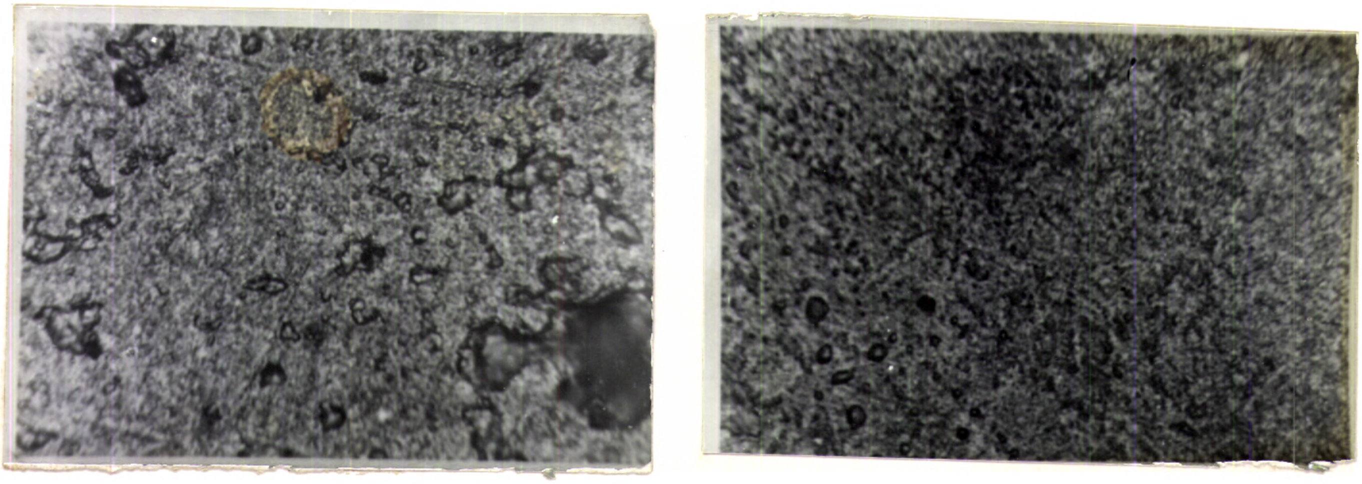
(a) Conventional (b) Modified

Fig.5.9 Optical micrograph of 70/30 NBR/Butyl blend.



(a) Conventional (b) Modified

Fig.5.10 Optical micrograph of 50/50 NBR/Butyl blend.



(a) Conventional (b) Modified

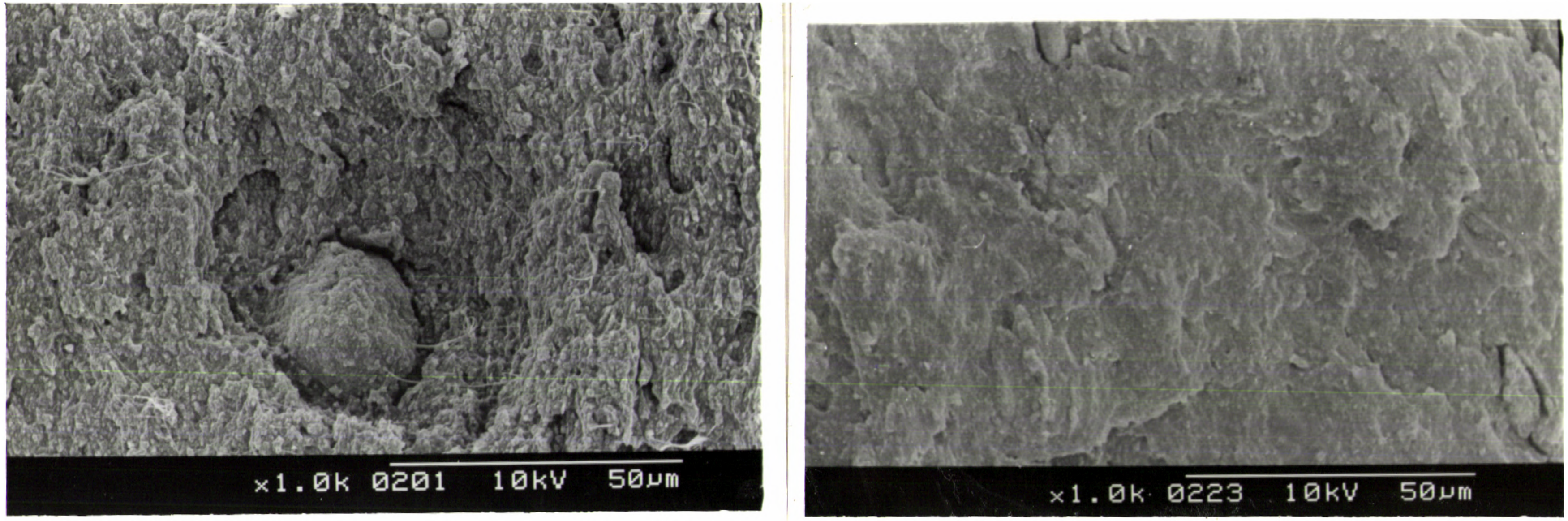
Fig.5.11 Optical micrograph of 50/50 NR/Butyl blend.

Photographs 5.11a and b show 50/50 NR/butyl conventional and modified blends respectively. Modified blend shows better compatibility compared to the conventional blend. Smaller average disperse area in the modified blends indicates homogenity of blends. This behaviour is similar to the NBR/butyl blends.

b) Scanning electron microscopic studies

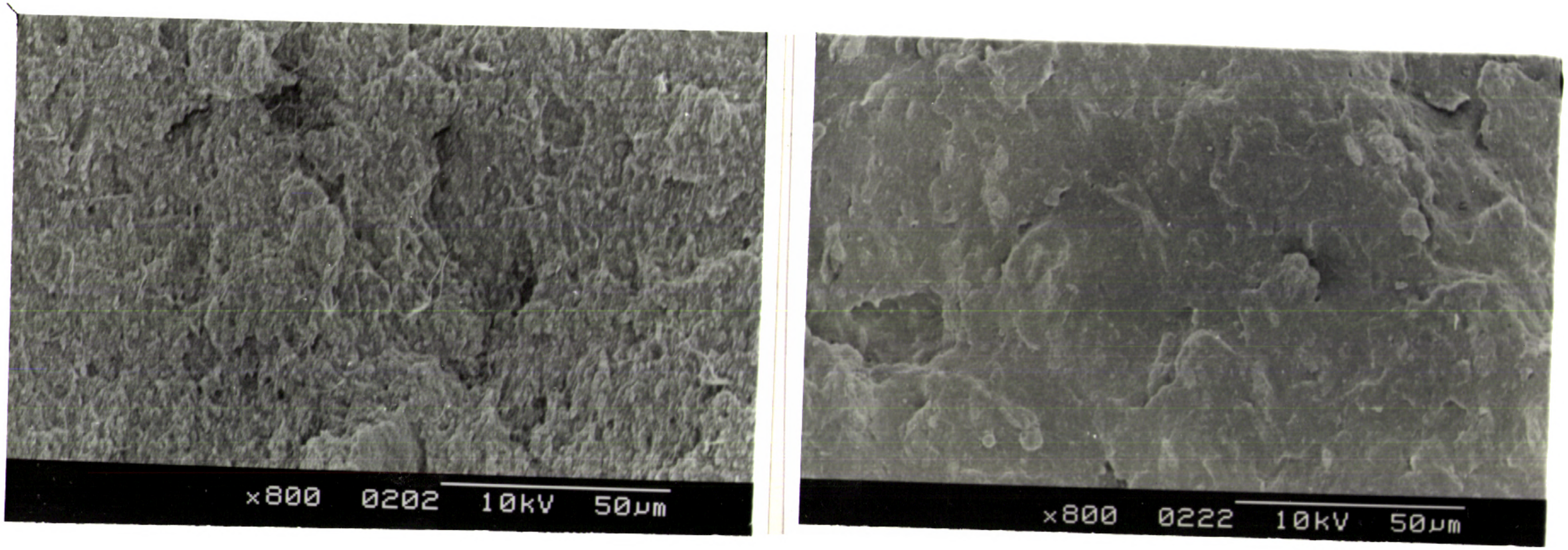
Photographs 5.12a and b show the tensile fracture surface of 50/50 NBR/butyl conventional and modified blends respectively. 'Crater' formation at the fracture surface of the conventional blends shows poor adhesion between the phases in conventional blends and this may be the reason for the low tensile strength. For modified blends uniform curing within the phases and at the interphase results in better adhesion between the phases. A different region of the same fracture surface with 800 magnification also shows similar appearance (Photographs 5.13a and b).

Photograph of 50/50 NR/butyl blend is shown in Figs.5.14a (conventional) and b (modified). Severe distortion and separations are seen on the fracture surface of the conventional blend which are obviously due to the inhomogenity in the blend. These observations are in



(a) Conventional (b) Modified

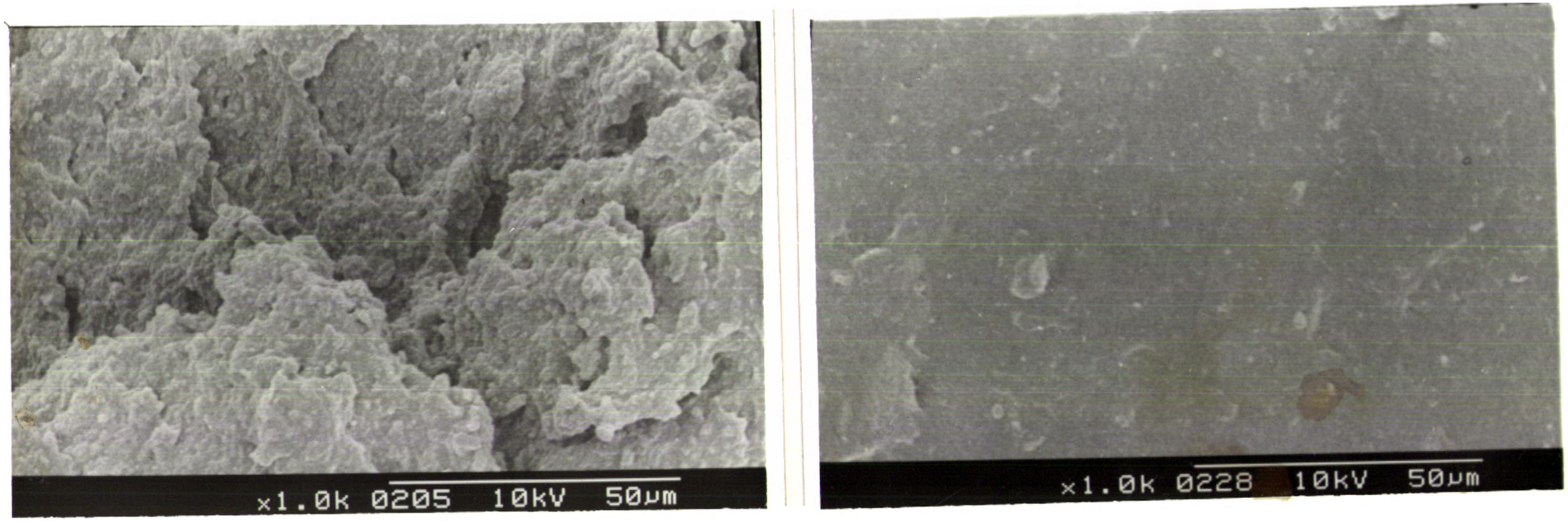
Fig.5.12 SEM photograph of 50/50 NBR/Butyl tensile fracture surface.



(a) Conventional

(b) Modified

Fig.5.13 SEM photograph of 50/50 NBR/Butyl tensile fracture surface at 800 magnification.



(a) Conventional

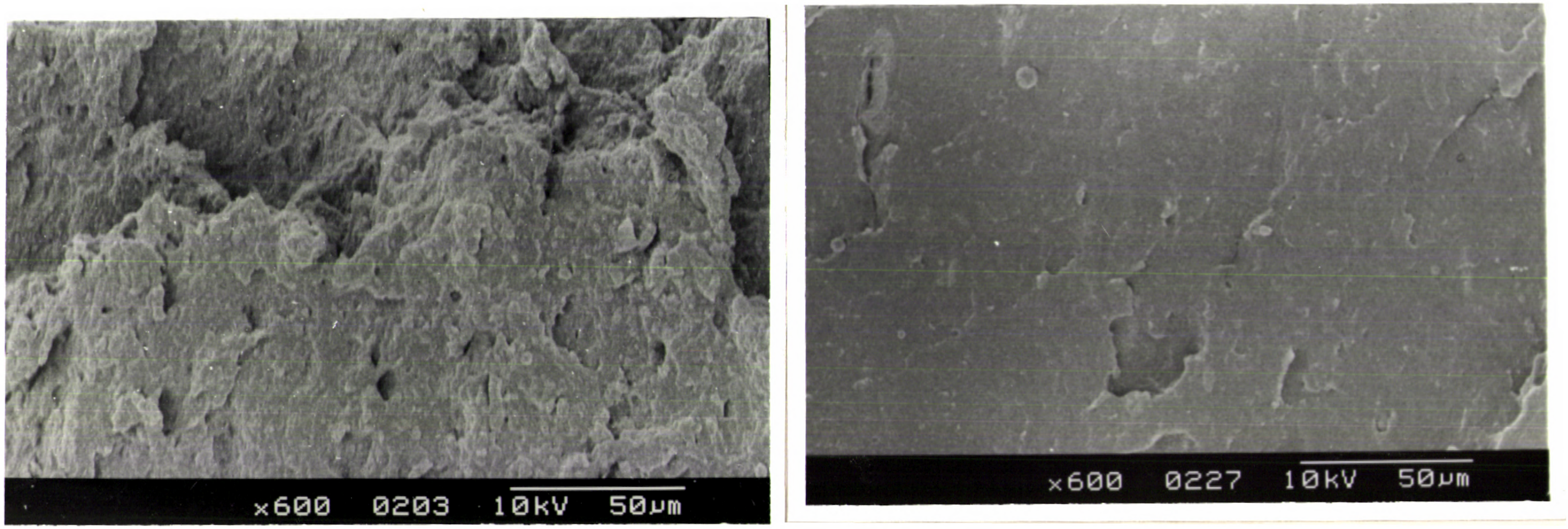
(b) Modified

Fig.5.14 SEM photograph of 50/50 NR/Butyl tensile fracture surface.

accordance with the tensile properties. But in the modified blends uniform curing of the blend results in good adhesion between the phases and better tensile properties. The photograph of another region with 600 magnification is shown in Figs. 5.15a and b. This also shows similar pattern showing uniformity of the mix.

Photographs 5.16a and b show the fracture surfaces of 30/70 NR/butyl conventional and modified blend respectively. Several imperfections can be seen on the fracture surface for conventional blend while for the modified blend, due to the excellent interphase crosslinks and adhesion between the phases, failure occurs by severe twisting and stretching of the specimen. The same behaviour is also shown in another region of the same fracture surface (Figs.5.17a and b).

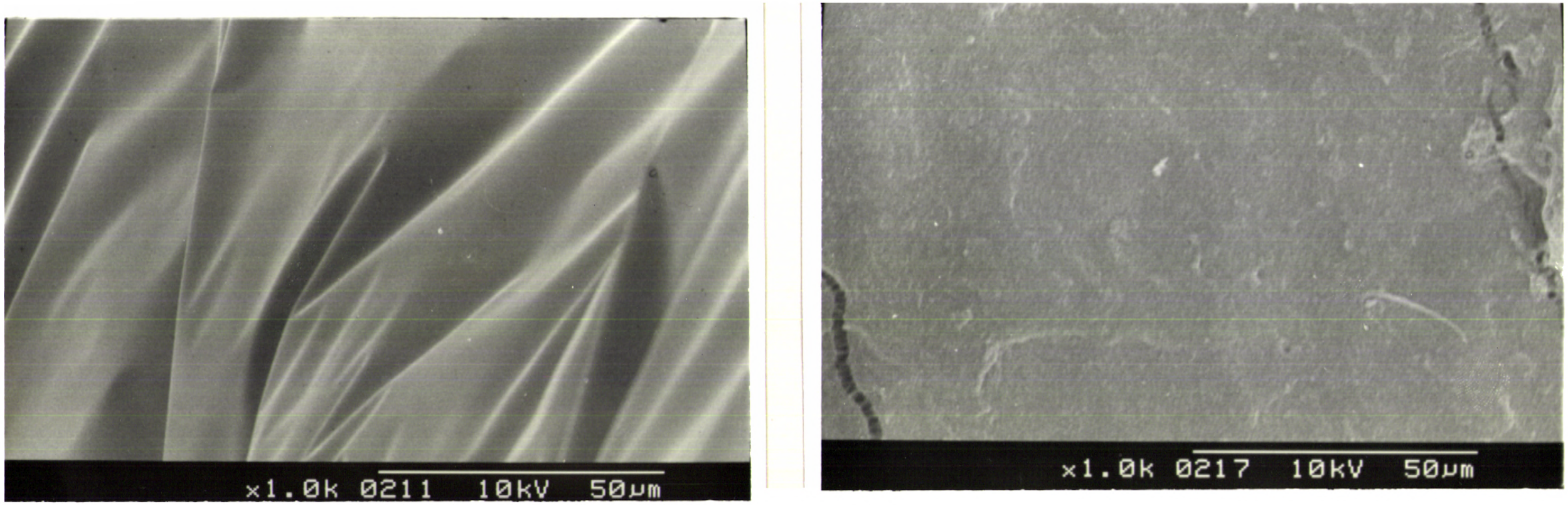
Photographs 5.18a and b show the fracture surfaces of 70/30 NR/butyl conventional and modified blend respectively. Severe imperfections and folded structures of the fracture surface of conventional blends indicate that failure has resulted due to phase separation. But the modified blend has a very smooth appearance showing homogenity of blend. Fissures and cracks observed for modified blends



(a) Conventional

(b) Modified

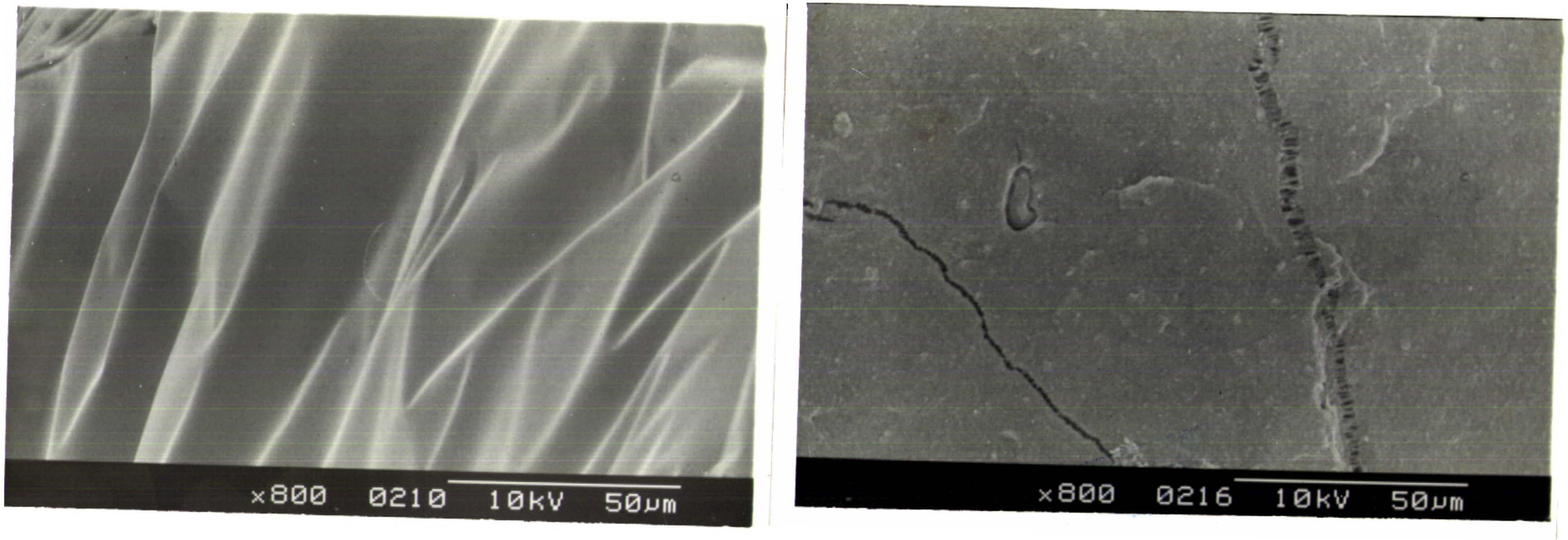
Fig.5.15 SEM photograph of 50/50 NR/Butyl tensile fracture surface at 600 magnification



(a) Conventional

(b) Modified

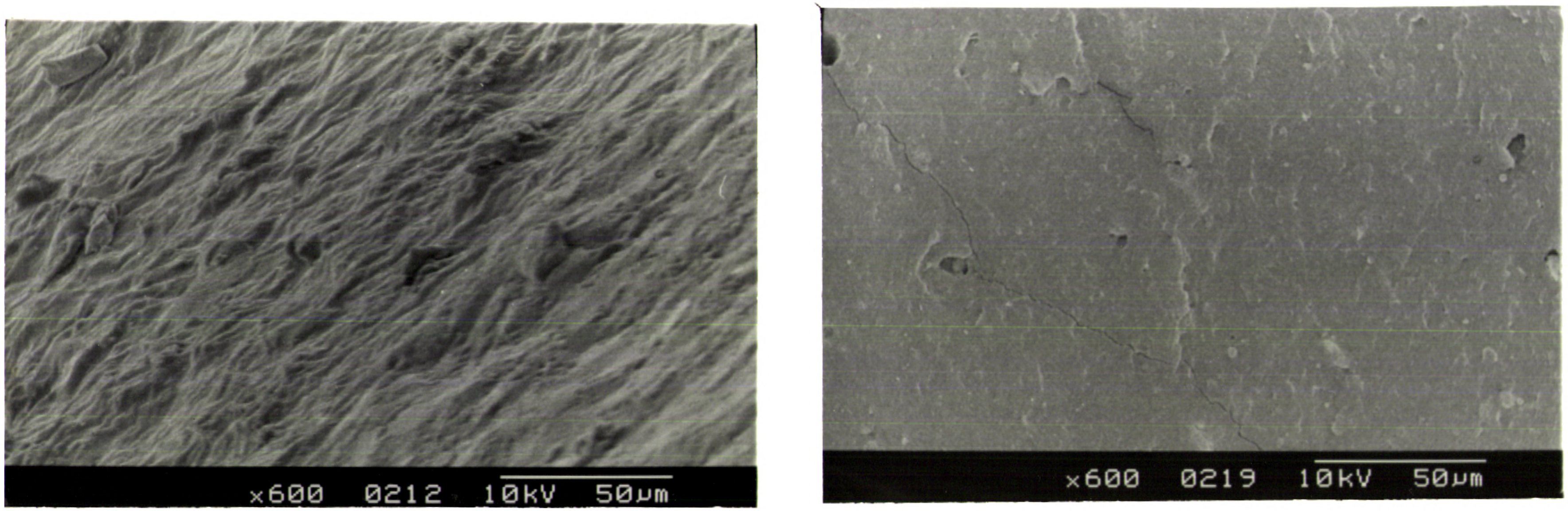
Fig.5.16 SEM photograph of 30/70 NR/Butyl tensile fracture surface.



(a) Conventional

(b) Modified

Fig.5.17 SEM photograph of 30/70 NR/Butyl tensile fracture surface at 800 magnification.



(a) Conventional

(b) Modified

Fig.5.18 SEM photograph of 70/30 NR/Butyl tensile fracture surface.

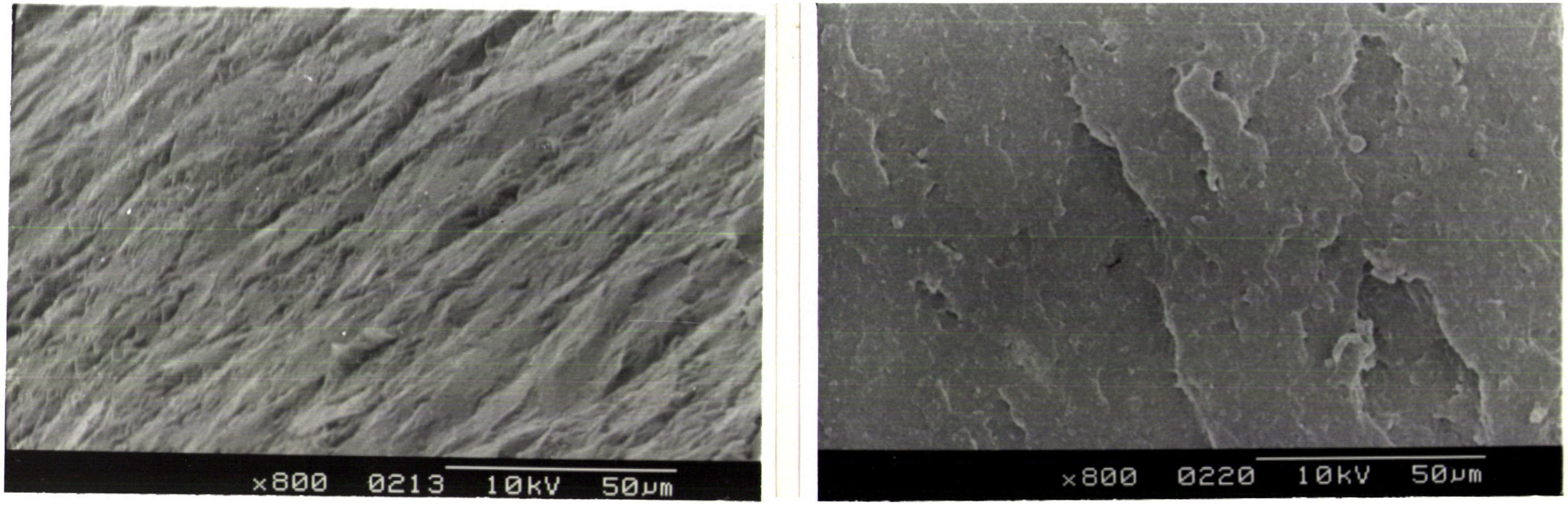
at a higher magnification are shown in photographs 5.19a and b.

Photographs 5.20a which shows the fracture surface of 50/50 NBR/EPDM conventional blends displays severe folded structure due to poor adhesion between the phases and nonuniform distribution of curatives resulting in the early failure of the tensile specimen. The modified blend shows good adhesion and homogenity of phases as seen in the photograph 5.20b. Similar patterns are seen at higher magnification (Figs.5.21a and b and Figs.5.22a and b) for conventional and modified blends respectively.

c) Dispersion studies

Photomicrographs 5.23a and b show 30/70 medium NBR/butyl conventional and modified blends respectively. Since butyl is the continuous phase a good degree of dispersion is achieved for both conventional and modified blends. Similar behaviour is observed when NBR is the continuous phase as in photographs 5.24a and b for 70/30 medium NBR/butyl conventional and modified blend.

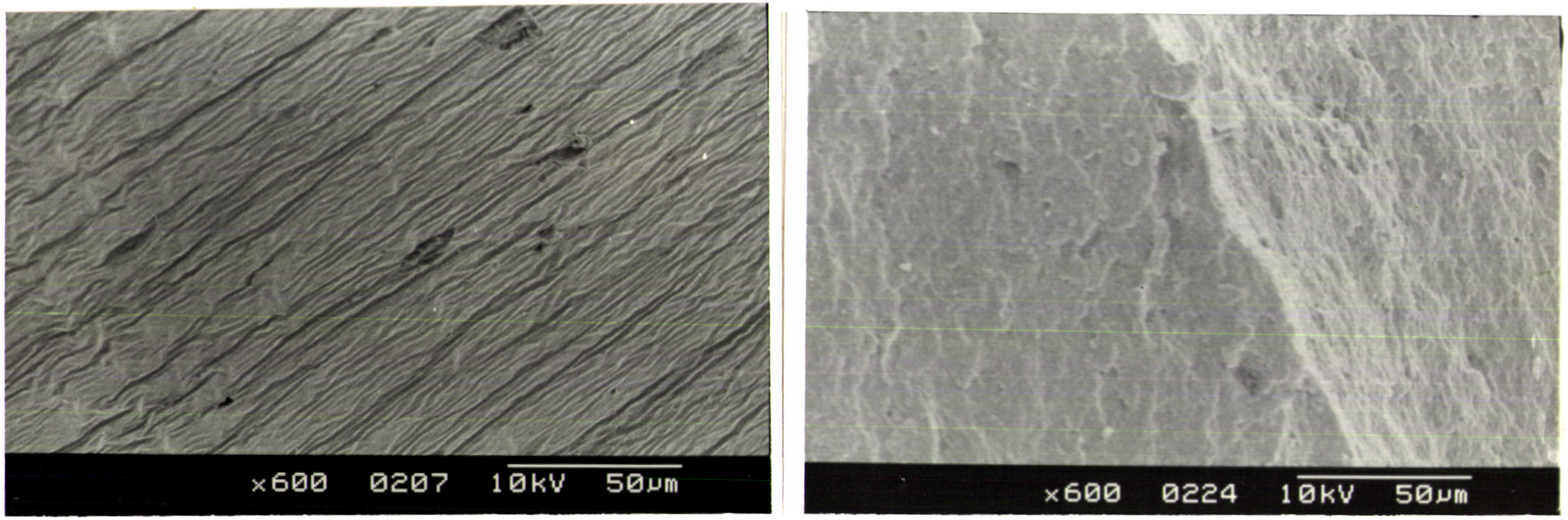
Photographs 5.25a and b show the surface 50/50 medium NBR/butyl blends, conventional and modified respectively. Modified blend shows much better dispersion compared to



(a) Conventional

(b) Modified

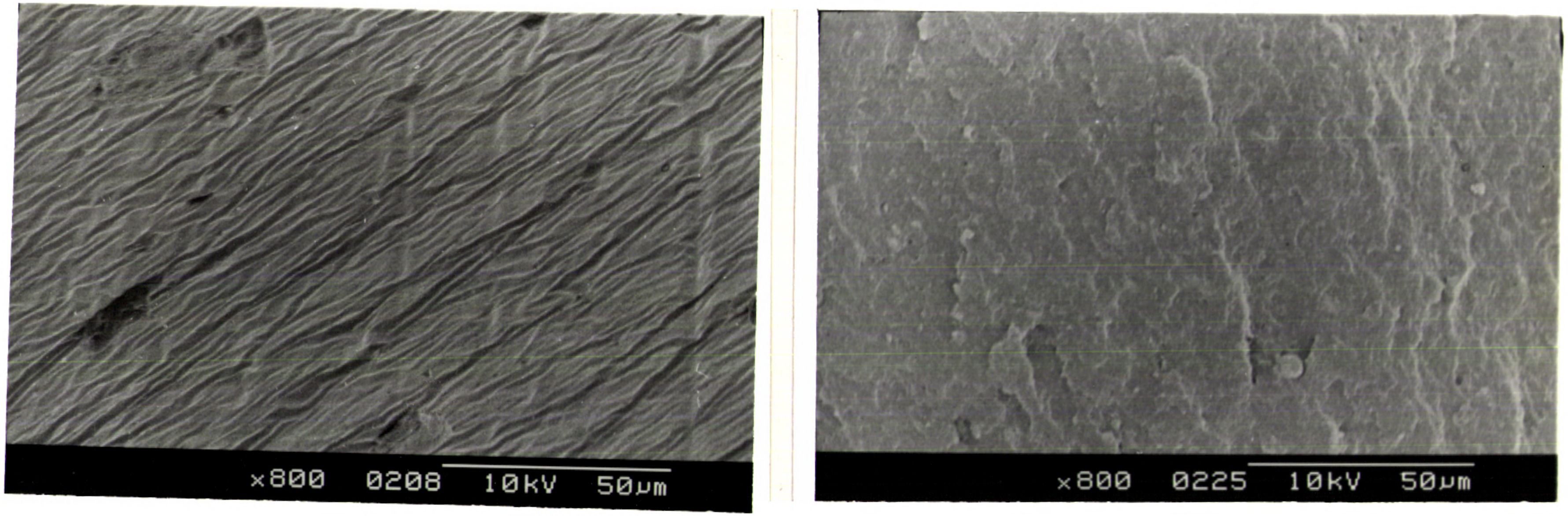
Fig.5.19 SEM photograph of 70/30 NR/Butyl tensile fracture surface at 800 magnification.



(a) Conventional

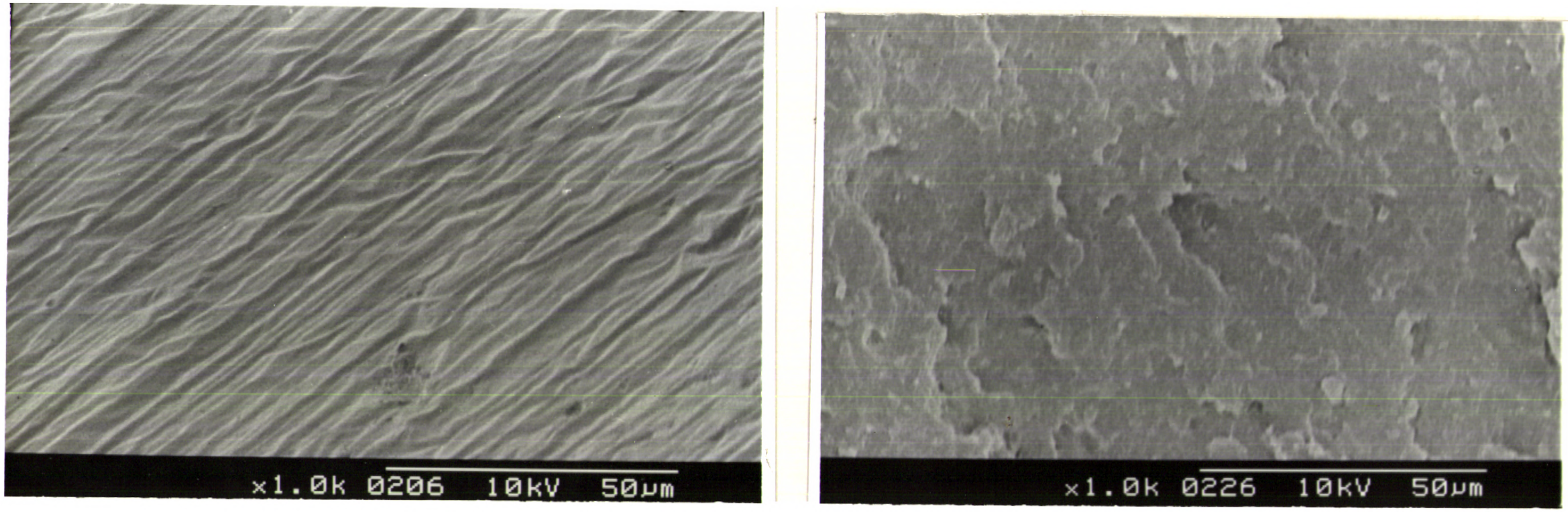
(b) Modified

Fig.5.20 SEM photograph of 50/50 NBR/EPDM tensile fracture surface.



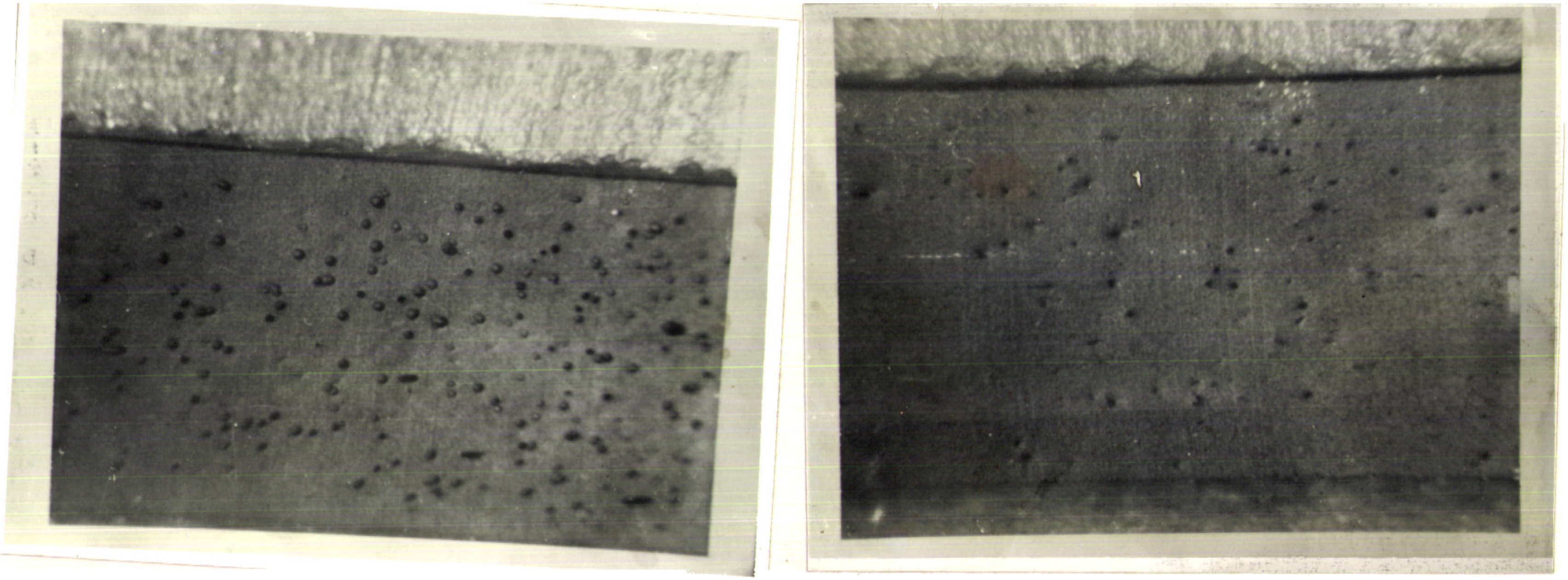
(a) Conventional (b) Modified

Fig.5.21 SEM photograph of 50/50 NBR/EPDM tensile fracture surface at 800 magnification.



(a) Conventional (b) Modified

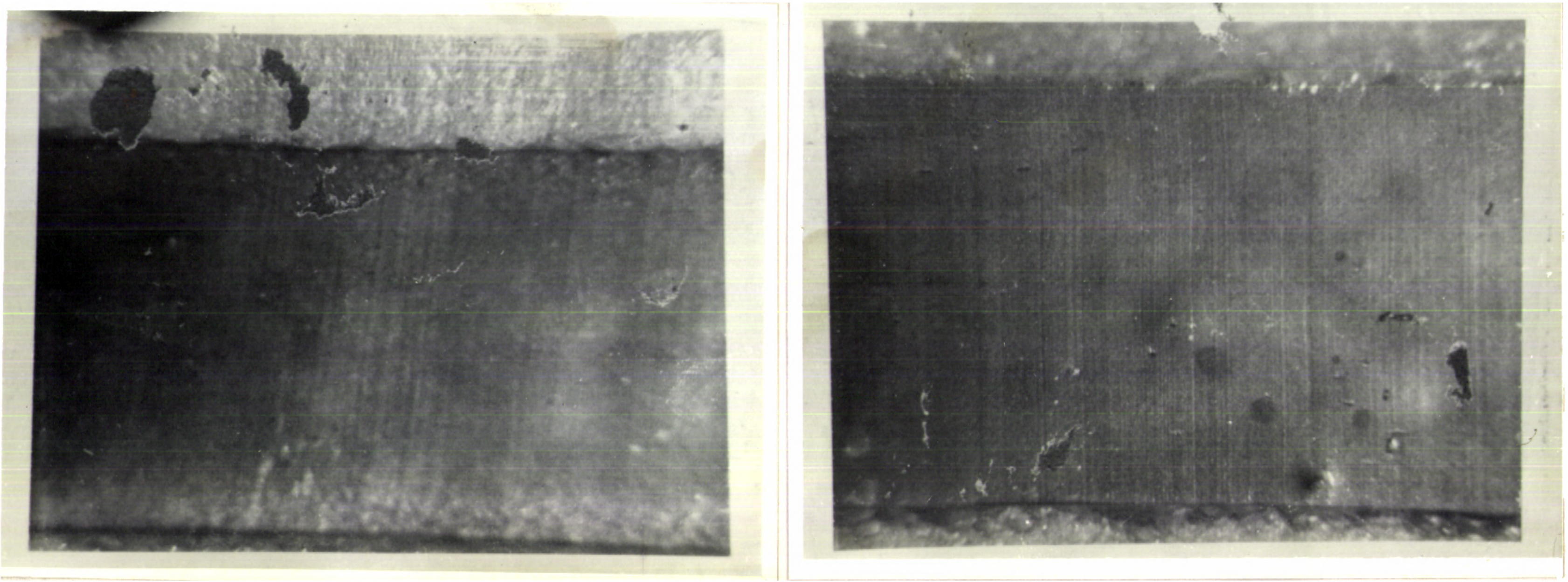
Fig.5.22 SEM photograph of 50/50 NBR/EPDM tensile fracture surface at 1000 magnification.



(a) Conventional

(b) Modified

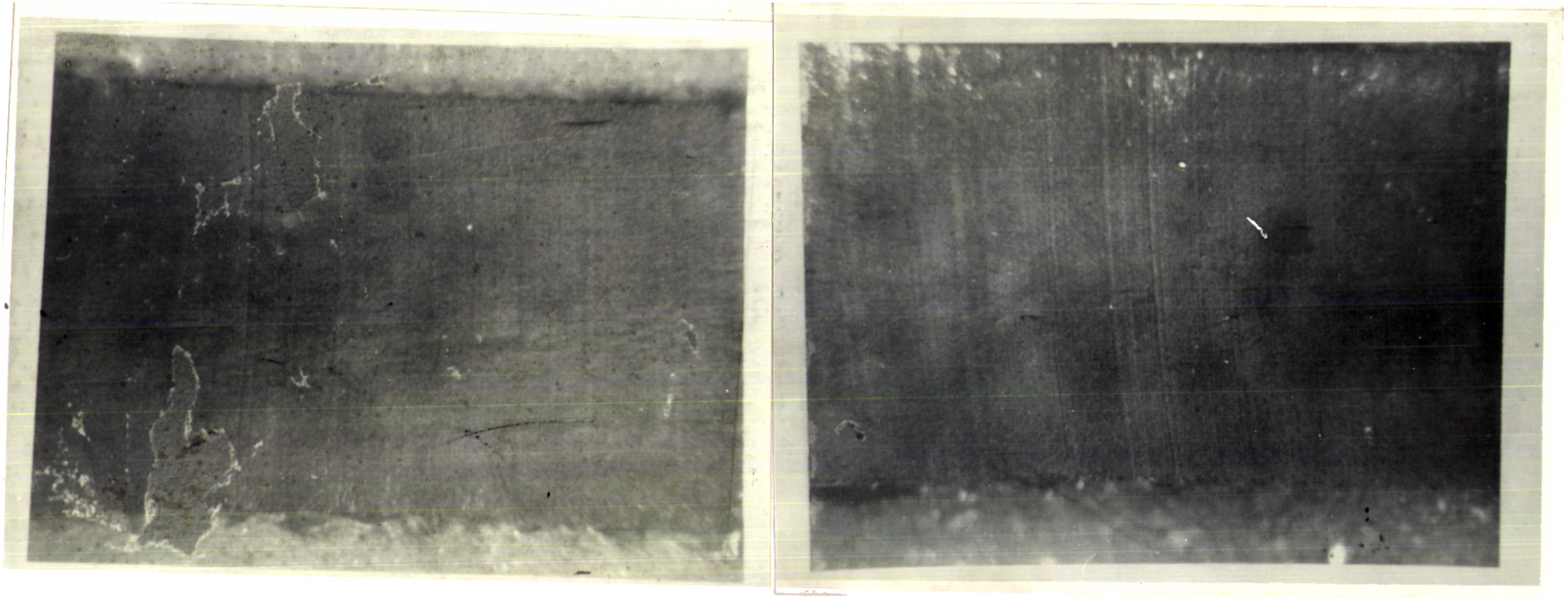
Fig.5.23 Photomicrograph of 30/70 medium NBR/Butyl blends.



(a) Conventional

(b) Modified

Fig.5.24 Photomicrograph of 70/30 medium NBR/Butyl blends.



(a) Conventional

(b) Modified

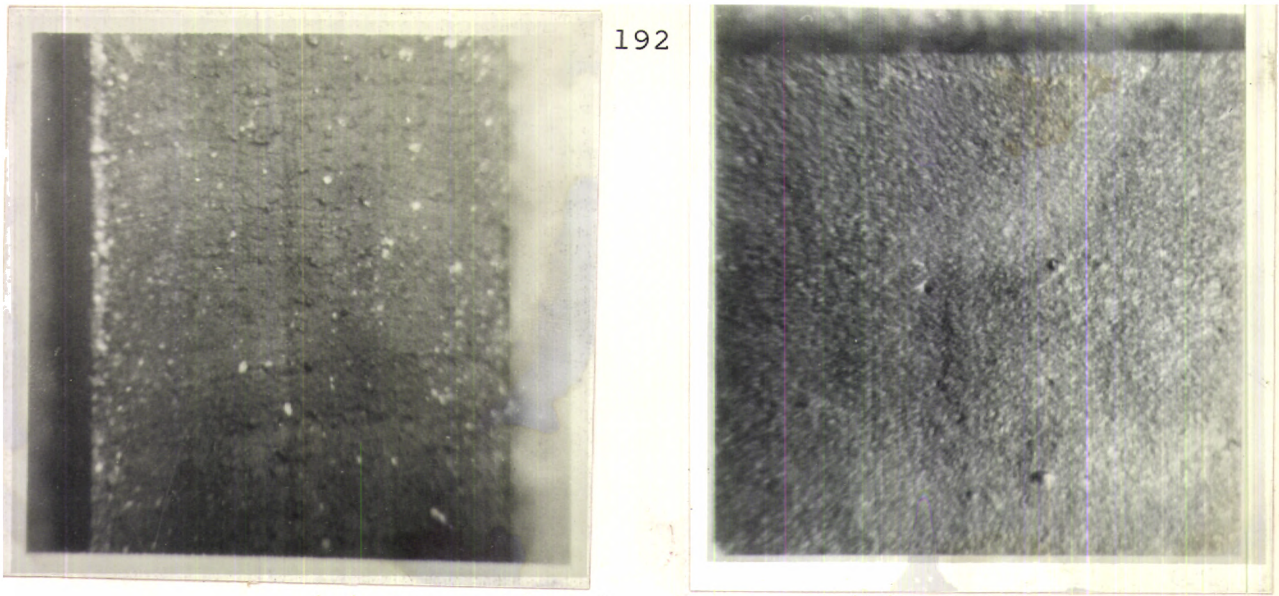
Fig.5.25 Photomicrograph of 50/50 medium NBR/Butyl blends.

conventional blend. The 70/30 high NBR/butyl blend also shows the same trend of dispersion as shown in photomicrograph 5.26a and b for conventional and modified blends respectively.

Photo micrographs 5.27a and b show the surface of 30/70 high NBR/butyl blend where butyl is the continuous phase. Very low dispersion is observed for conventional blend and this problem has been overcome in modified blend by way of precuring the butyl phase. Conventional and modified blends of 50/50 high NBR/butyl blends (Figs 5.28a and b) do not show appreciable difference in the degree of dispersion.

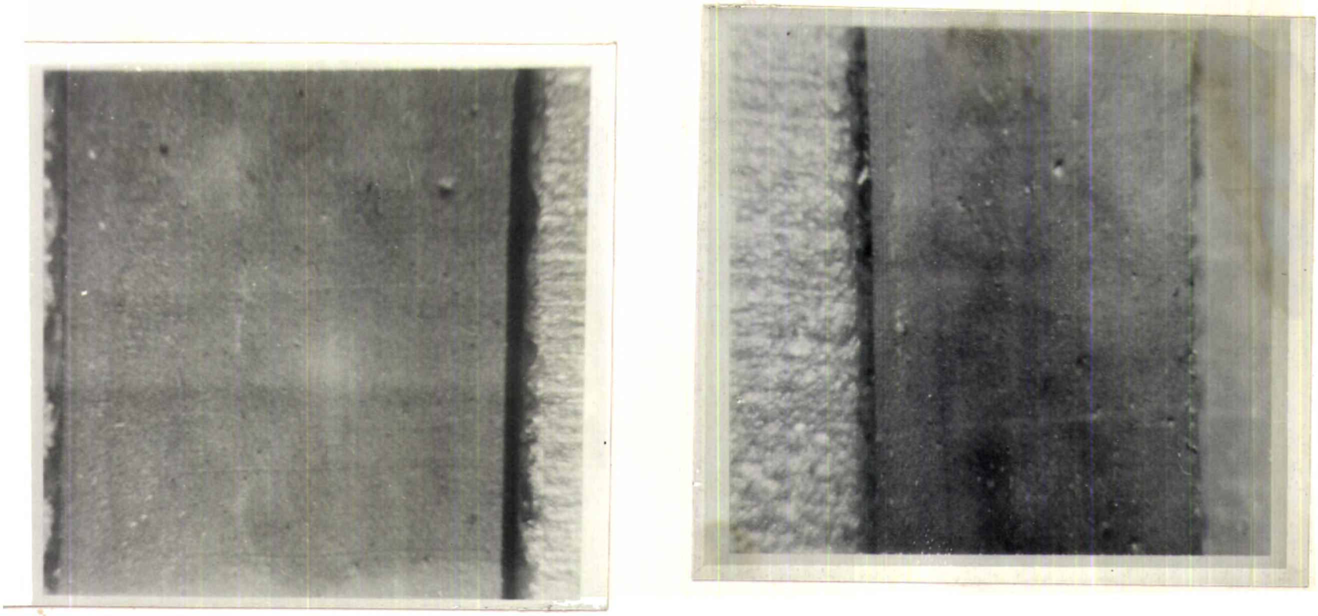
Due to the viscosity mismatch only poor dispersion occurs in the conventional blends of 70/30 NR/butyl as shown in photomicrographs 5.29a and b. By way of precuring dispersion improved for modified blend (photograph 5.29b). Similar behaviour is also shown by 30/70 NR/butyl blends as in photo micrograph 5.30a for conventional blend and 5.30b for modified blend.

Good dispersion has also been achieved in the modified blends of 50/50 NR/butyl blends as shown in photographs 5.31a and b for conventional and modified blends respectively.



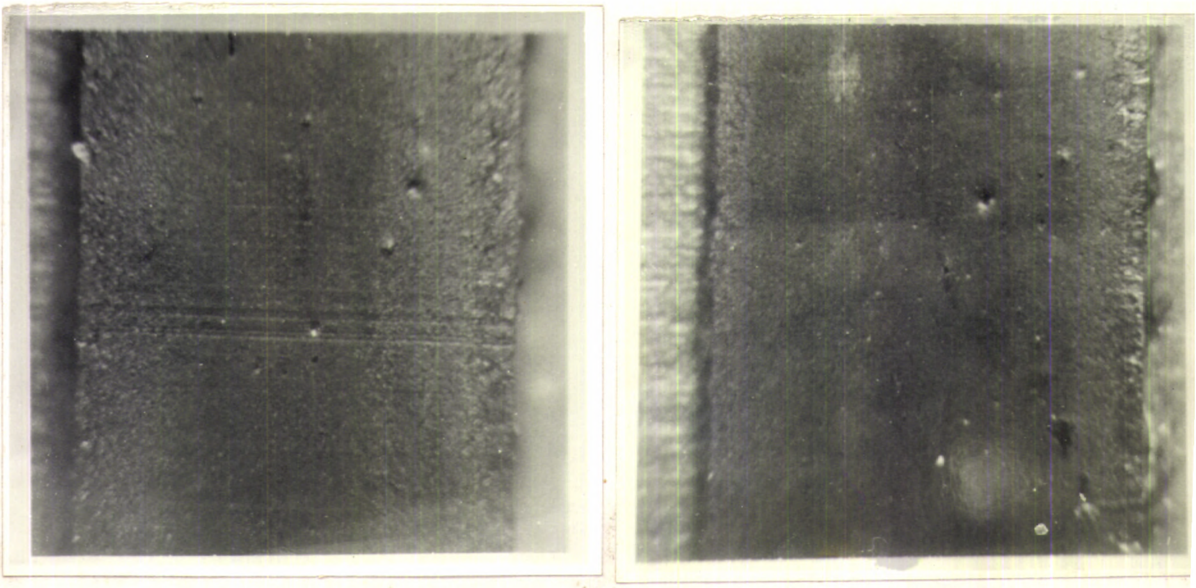
(a) Conventional (b) Modified

Fig.5.26 Photomicrograph of 70/30 high NBR/Butyl blends.



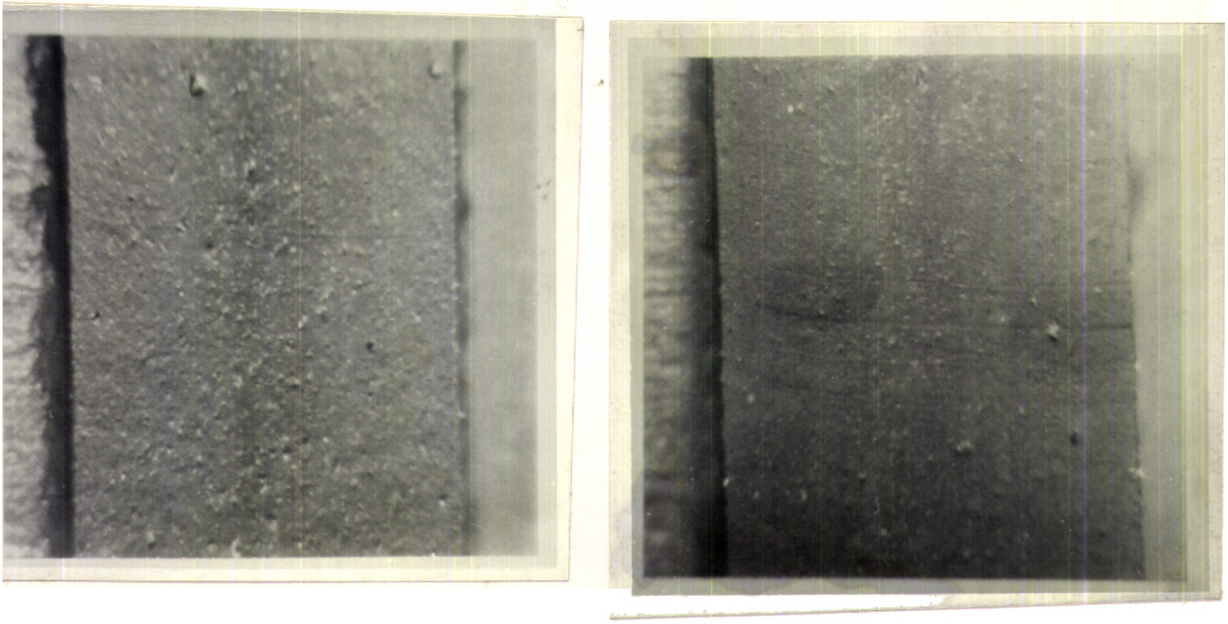
(a) Conventional (b) Modified

Fig.5.27 Photomicrograph of 30/70 high NBR/Butyl blends.



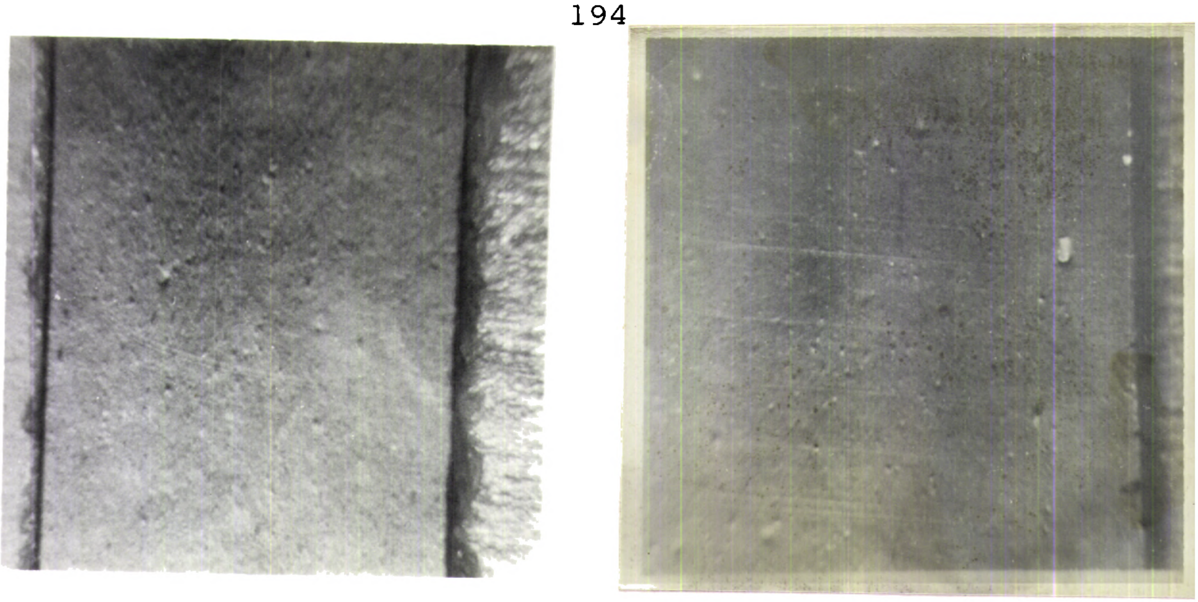
(a) Conventional (b) Modified

Fig.5.28 Photomicrograph of 50/50 high NBR/Butyl blends.



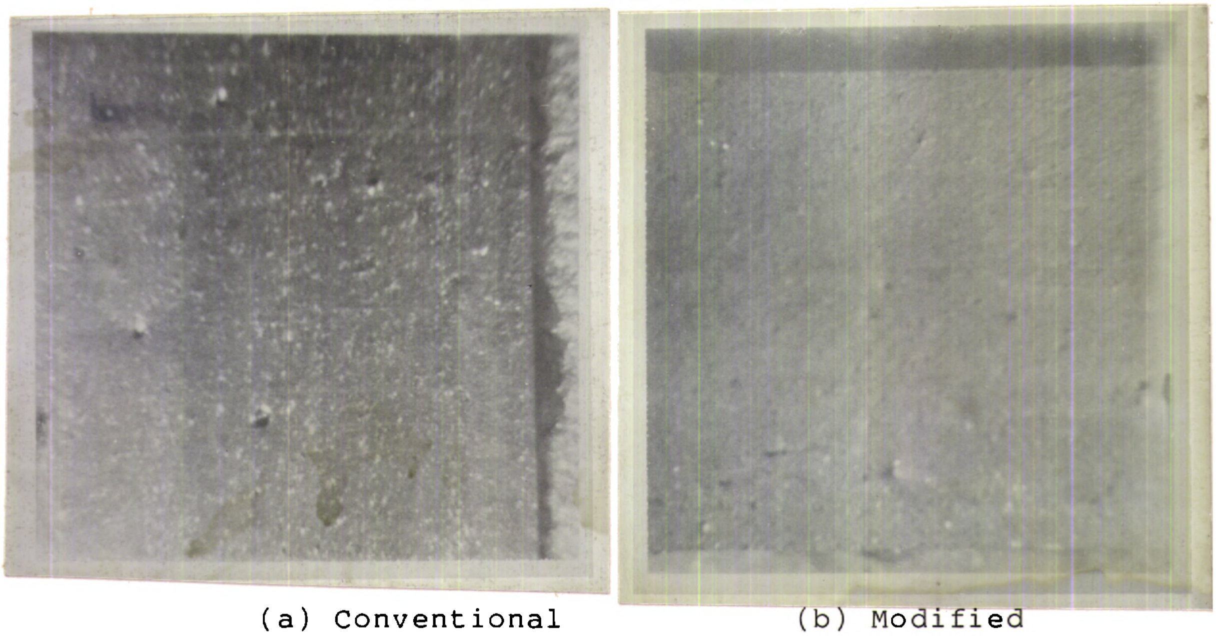
(a) Conventional (b) Modified

Fig.5.29 Photomicrograph of 70/30 NR/Butyl blends.



(a) Conventional (b) Modified

Fig.5.30 Photomicrograph of 30/70 NR/Butyl blends.



(a) Conventional (b) Modified

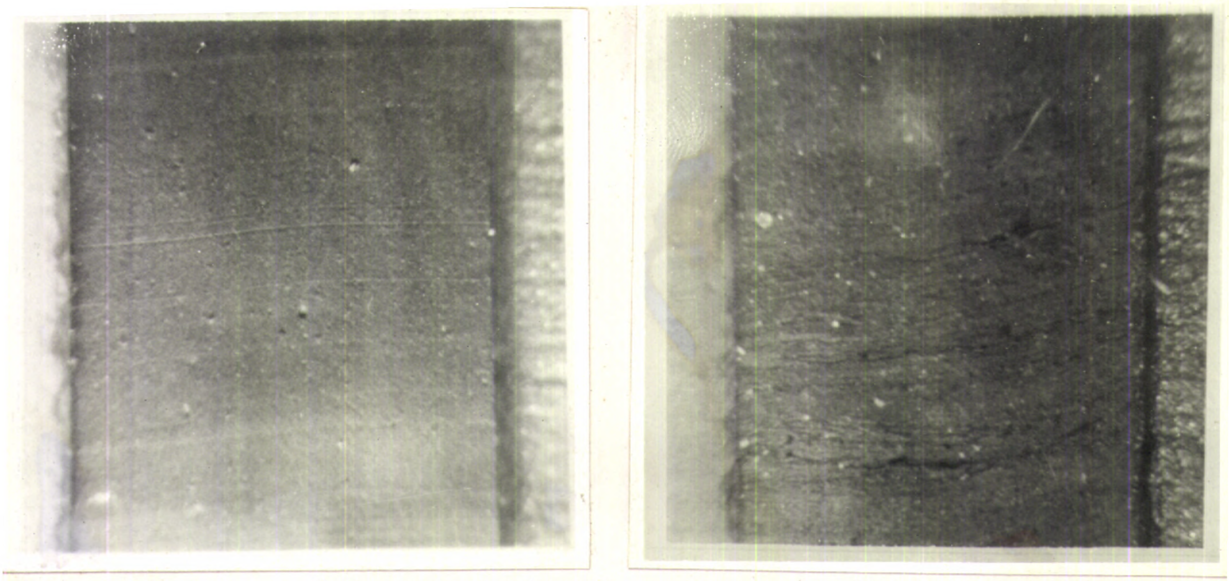
Fig.5.31 Photomicrograph of 50/50 NR/Butyl blends.

Photo micrographs 5.32a and b show the surfaces of 30/70 NBR/EPDM. Much difference is not seen in the dispersion of conventional and modified blends since EPDM forms the continuous phase. Similarly when NBR forms the continuous phase (5.33a and b) there is not much difference for conventional and modified 70/30 NBR/EPDM blends.

Viscosity mismatch in the blend of 50/50 NBR/EPDM blend is very less and hence the degree of dispersion is almost the same in photo micrographs 5.34a and b for conventional and modified blends respectively.

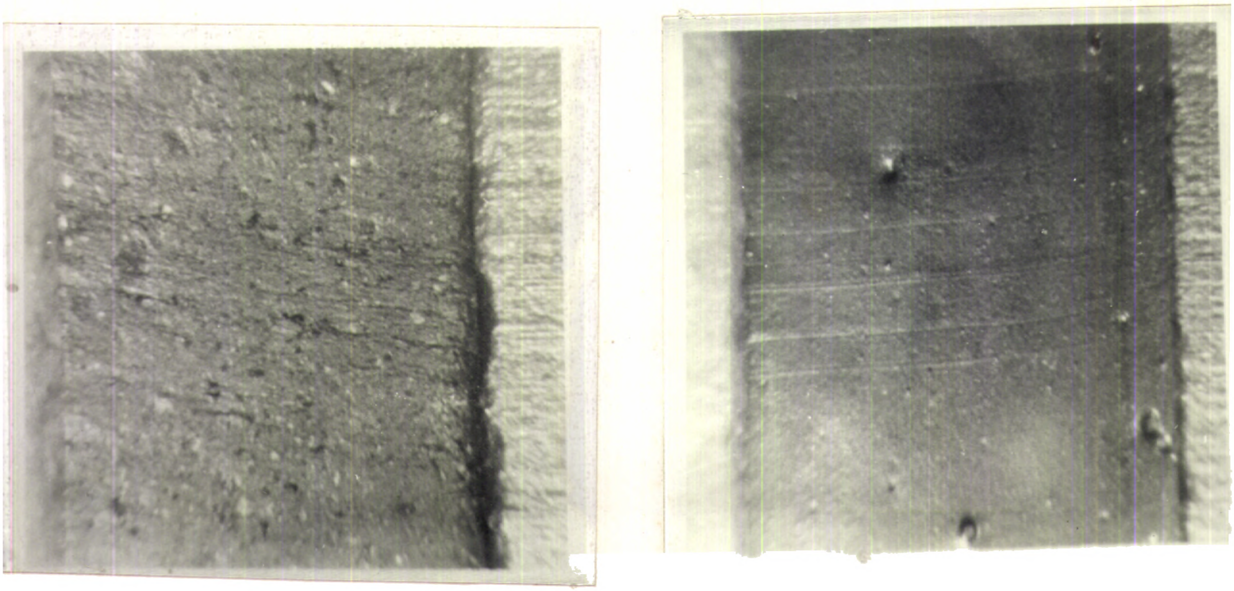
d) Crosslink density

Crosslink densities of the blends are shown in the Table 5.9. Values are as expected from the dispersion studies. First set of values for 30/70 NBR/butyl blends show that in conventional blends due to curative migration towards NBR phase it gets overcured and the values obtained are mostly those of NBR phase alone. But, by modifying the blends equal distribution of crosslinks occurs resulting in lower crosslink density values. Similar behaviour is observed when NBR becomes the continuous phase in 70/30 NBR/butyl blend values (second set of conventional blend show higher values and modified blends show lower values).



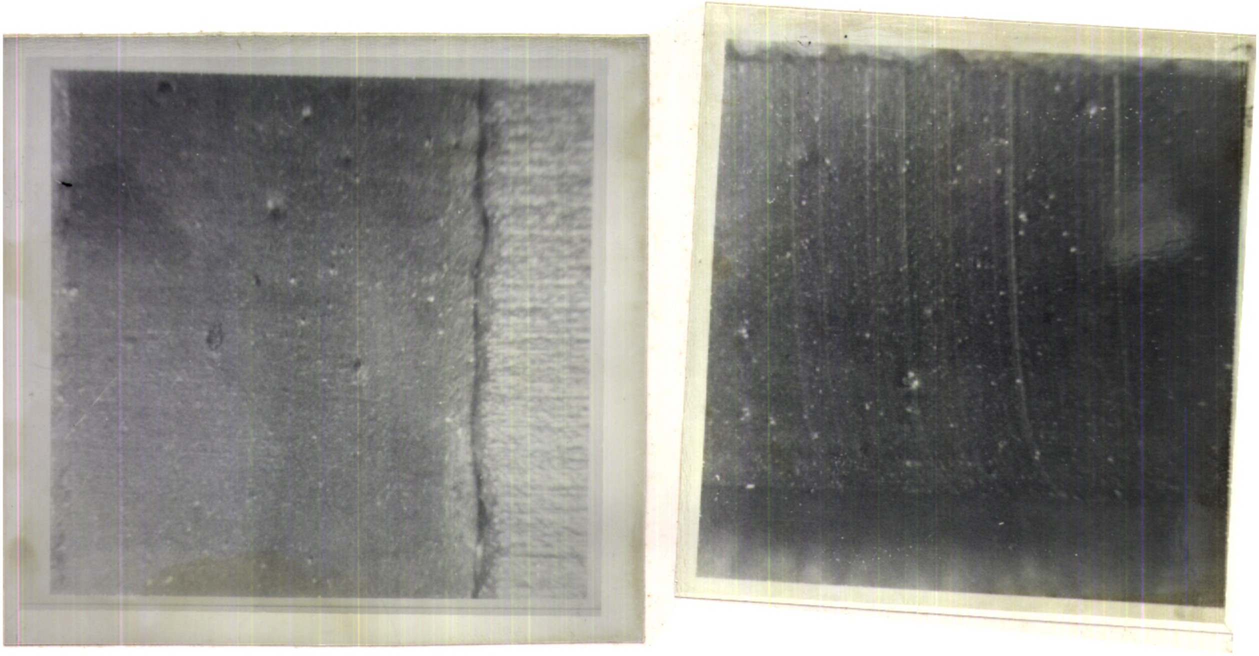
(a) Conventional (b) Modified

Fig.5.32 Photomicrograph of 30/70 NBR/EPDM blends.



(a) Conventional (b) Modified

Fig.5.33 Photomicrograph of 70/30 NBR/EPDM blends.



(a) Conventional (b) Modified

Fig.5.34 Photomicrograph of 50/50 NBR/EPDM blends.

TABLE 5.9

1/2Mc VALUES FOR VARIOUS BLENDS

BLEND	CONVENTIONAL x10^{-6} gm /cc	MODIFIED x10^{-6} gm/cc
30NBR/70 IIR	3.480	2.686
70NBR/ 30 IIR	3.541	3.186
50 NBR /50 IIR	1.175	4.085
30NR / 70 IIR	0.182	3.017
70NR / 30 IIR	1.384	5.495
50NR / 50 IIR	4.113	4.60
70 NBR / 30 EPDM	2.073	0.635
30 NBR / 70 EPDM	1.503	1.28
50 NBR / 50 EPDM	0.700	0.997

In 50/50 NBR/butyl blend, NBR gets over cured as in other cases. So the crosslink density value is lower for conventional blends compared to modified blends.

In 30/70 NR/butyl conventional blend, major component is butyl and crosslink density shown is largely that of butyl which is low due to curative migration. But on modification equal distribution of crosslinks takes place. In 70/30 NR/butyl blend crosslink density value reflects the crosslink density in the NR phase for conventional blend since it is the major component. But on modification both rubbers get equal distribution of crosslinks. In 50/50 NR/butyl blend eventhough NR phase gets a higher share of curatives, butyl phase also gets slightly cured in conventional blend. On modification both phases get equal share of curatives and hence higher values of crosslink density.

Higher crosslink density values for 70/30 NBR/EPDM conventional blend is due to the higher amount of crosslinking in NBR phase due to curative migration which gets reduced on modification due to equal distribution of crosslinks.

In 30/70 NBR/EPDM blend, since EPDM is the continuous phase, it gets more crosslinks, but on modification both the phases became equally crosslinked.

In 50/50 NBR/EPDM blend, since equal distribution of crosslinks occurs in both phases, due to reduced curative migration higher values are obtained for modified blends.

Permeability studies

Permeability values for 50/50 blends are shown in Table 5.10. There is only a marginal difference in the permeability values for modified and conventional blends since permeability is largely a property of the elastomer and is not much changed by the crosslink density distribution or homogenity of the blend.

Conductivity studies

In elastomers semiconductivity is usually achieved from the addition of carbon black. Table 5.11 shows the conductivity values of conventional and modified blends. In conventional blends, carbon black tends to get distributed in the low viscosity phase. Because of this nonuniform distribution conductivity values are higher for conventional

TABLE 5.10

PERMEABILITY VALUES FOR VARIOUS BLENDS

BLEND	CONVENTIONAL $cm^2 atm^{-1} sec^{-1} x 10^{-8}$	MODIFIED $cm^2 atm^{-1} sec^{-1} x 10^{-8}$
50NBR/50 IIR	3.5	3.1
50 NR/50 IIR	6.5	9.7
50 NBR/ 50 EPDM	7.7	10.4

TABLE 5.11

CONDUCTIVITY VALUES FOR VARIOUS BLENDS ($ohm^{-1} cm^{-1}$)

BLEND	CONVENTIONAL	MODIFIED
50/50 NBR / IIR	$1.085 X 10^{-3}$	$7.378 X 10^{-8}$
50/50 NR / IIR	$1.186 X 10^{-4}$	$1.259 X 10^{-7}$
50/50 NBR /EPDM	$1.686 X 10^{-5}$	$2.955 X 10^{-7}$

blends. But for modified blends viscosity mismatch is reduced and uniform dispersion of carbon black occurs which lowers the conductivity values.

CONCLUSIONS

The study shows that carbon black distribution in elastomer blends can be observed from the optical microscopy of the vulcanizate surfaces. A more accurate picture of the dispersion can be obtained from the photo micrographs of the microtromed vulcanizate samples. Scanning electron microscopic studies of the fracture surfaces of the vulcanizates of the elastomer blends is a powerful tool for studying the morphology of the blends. These studies in respect of the blends viz., NBR/IIR, NR/IIR and NBR/EPDM showed the superiority of the modified blends compared to the conventional blends. A uniform distribution of carbon black can also be observed from the lower electrical conductivities and the more uniform distribution of crosslinks from the lower crosslink densities of the modified blend compared to their conventional counterparts. Resistance to permeability of air is more or less the same for both conventional and modified blends since permeability is mere a property of the elastomer concerned rather than that of the crosslink densities of the rubber phases and the interphases.

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Chapter VI

SUMMARY AND CONCLUSIONS

The distribution of curing agents and fillers in the constituents of an elastomer blend is an important factor which determines the curing behaviour and vulcanizate properties of the blend. The distribution of curatives and fillers largely depends on the nature of elastomers. The curatives tend to migrate preferentially to the rubber of higher unsaturation and/or higher polarity, and reinforcing fillers tend to get distributed in the low viscosity phase, resulting in inferior mechanical properties of the blends.

The thesis suggests several methods for improving mechanical properties of blends like NBR/butyl, NR/butyl, NBR/EPDM and NR/NBR. The most promising method outlined is the partial precrosslinking of the slow curing phase either by static or dynamic crosslinking.

In the NBR/butyl and NBR/EPDM blends the slow curing butyl or EPDM phase was compounded first and then they were subjected to a partial precrosslinking at an optimum temperature for an optimum time. The partially precrosslinked compounds were then blended with NBR along with the compounding ingredients for NBR thus minimising the curative migration. This novel compounding sequence and partial precrosslinking of the slow curing rubbers resulted in significant improvements in the physical properties, ozone resistance etc. of the blends. The fillers are found to be more uniformly distributed from the Polaroid photo micrograph studies. The lower electrical conductivity of the modified blends also confirms the more uniform distribution of carbon black. Scanning electron microscopic studies of the fracture surface show stronger adhesion between the two rubber phases in the modified blends.

In the NR/butyl blend butyl was compounded first and then it was subjected to a partial dynamic precrosslinking in an internal mixer (Brabender Plasticorder) for an optimum time at a selected temperature and rpm. The partially precrosslinked butyl compound was then blended with NR along with the compounding ingredients for NR thus reducing the curative migration. As in the case of static precuring, dynamic precuring also resulted in significant improvement in the physical properties, ozone resistance etc. of the blends. The Polaroid microscopic studies revealed better filler distribution in this case also and the conductivity of modified blends further confirmed this. Scanning electron microscopic studies revealed better dispersion of ingredients.

Other methods outlined for improving mechanical properties of elastomer blends are

1) NBR/EPDM blends

a) Carboxylation of EPDM before blending with NBR

Carboxylation of EPDM gave only marginal improvements in the mechanical properties of NBR/EPDM over the conventional blends due to the poor thermal stability of ionic crosslinks.

b) Selecting ultra accelerators for the slow curing phase and slow curing accelerators for the fast curing phase

Selecting proper accelerators was found to be a promising technique for improving the mechanical properties of the blends.

2) NR/NBR blends

a) Use of a compatibiliser

Using amine terminated liquid natural rubber (ATNR) as a compatibiliser in NR/NBR blends improved the mechanical properties of the blends. Further it was observed that in NR/NBR blends containing silica filler ATNR could reduce the retarding effect of silica.

LIST OF PUBLICATIONS FROM THIS WORK

1. **K.A.Job,** R.Joseph and D.J.Francis, "Studies on NR/butyl **blends: Effect of partial dynamic curing of butyl before** blending", presented at the 16th National Rubber Conference of Indian Rubber Manufacturers Research Association (IRMRA), Bombay, March 1993. This paper won the **M.R.F. AWARD** for the best paper at the Conference. Proc. 16th Rubber Conference, IRMRA, p.27 (1993).

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