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THERMAL ANALYSIS ON INFLUENCE OF COMPATIBILIZING AGENTS
Effect of vulcanization of incompatible elastomer blend

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Abstract

Studies have been made on differential scanning calorimetry (DSC), thermogravimetric analysis (TG) and dynamic mechanical analysis (DMA) of binary blends of isobutylene-isoprene (IIR) copolymer and polychloroprene (CR) elastomers. Blends of IIR and CR are incompatible and showed separate T_g peaks in DSC curves similar to Tanδ peaks. However, addition of chlorinated polyethylene (CM) elastomer, as compatibilizer, imparts miscibility between IIR and CR which could be judged both through DSC as well as by dynamic loss measurements (Loss modulus E'' and Tanδ). The storage modulus (E') showed variation of stiffness due to structural changes associated with the addition of compatibilizer. TG plots for these blends showed improvement of thermal stability both by addition of a suitable compatibilizer as well as due to formation of crosslinked structures associated with the vulcanization of the blends by standard curative package.

Keywords: compatibilization, elastomer blend, phase morphology, thermal analysis, ultrasonic velocity

Introduction

Elastomer blends have become very popular in recent years. This is because of the ease with which material possessing the desirable properties can be developed from the known polymers. However, most of the elastomer blends are immiscible and incompatible. Reasons stand in the way of homogeneity are high interfacial tension and poor interphase adhesion. It is reported that the compatibility of immiscible polymers can be enhanced by addition of a small quantity of graft or block copolymers termed as compatibilizer [1–3].

Many experimental and theoretical methods have been used to investigate the polymer compatibility. Flow visualization of mixing and homogenization of several elastomer blends and effect of addition of compatibilizer on rate of mixing as well as final phase morphology have been reported by Setua and White [4–6]. Subsequently, Setua *et al.* have also reported their studies on evaluation of compatibility of elastomer–elastomer and elastomer–plastic blends through infrared spectros-

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copy, scanning electron microscopy and rheological techniques [7]. Determination of mechanical and ageing properties and the effect of addition of fillers and compatibilizer have also been reported in these studies. Dynamic mechanical analysis and transmission electron microscopy techniques have been utilized by Mazich *et al.* [8] to investigate the structure and morphology which lead to better physical properties for ternary blends of natural rubber (NR), butyl rubber (IIR) and polyisobutylene. Dynamic mechanical properties over a wide temperature range for blends of NR, IIR, styrene-butadiene rubber (SBR) and polybutadiene rubber (BR) have been evaluated by Bauer [9]. The extent of compatibilization as well as the effects of vulcanization which promotes interaction between heterogeneous phases on Tanδ values have been investigated in these studies. The effect of different compatibilizers on the physical properties ageing behaviour, thermal stability and dynamic mechanical properties of blends of silicone and ethylene propylene diene (EPDM) rubbers have been reported by Kole *et al.* [10]. Morphology, thermal behaviour, mechanical and dynamic mechanical properties of polypropylene (PP) blended with different amounts of EPDM have also been appeared [11]. Dutta *et al.* [12] have examined the influence of reinforcing carbon black on dynamic mechanical properties of IIR. Dynamic mechanical and Impact properties in case of blends of PP with butadiene-styrene block co-polymer have been studied by Saroop *et al.* [13].

Elastomer blends based on IIR and CR are expected to be attractive to polymer technologists due to the inherent characteristics of individual components e.g., low temperature flexibility and gas impermeability of IIR which may be combined with

Table 1 Formulation of rubber mixes

Ingredients	Mix Nos.			
	A	B	C	D
Butyl rubber (IIR)$^{+}$	100	–	50	50
Polychloroprene rubber (CR)$^{++}$	–	100	50	50
Chlorinated polyethylene elastomer (CM)$^{+++}$	–	–	–	5
Paraffin wax	5	5	5	5
Stearic acid	1	1	1	1
PBNA	1	1	1	1
MgO	4	4	4	4
ZnO	5	5	5	5
S	1.5	1.5	1.5	1.5
MBTS	1.5	1.5	1.5	1.5
NA-22	0.3	0.3	0.3	0.3
TMTD	1.5	1.5	1.5	1.5

$^{+}$ Polysar's bromo butyl rubber (X2)

$^{++}$ DuPont's neoprene WM-1 grade

$^{+++}$ Dow chemical's Tyrin® (CM 0136).

the flame proofness, chemical resistance and superior strength properties of CR. However, no useful blend with these elastomers has appeared, at least in the published literature. Setua *et al.* have reported, only recently, their studies on flame retardancy and gas impermeability [14], ultrasonic velocity measurements [15] and the failure mechanism of IIR-CR blends [16].

In the present paper, we report our results on the influences of compatibilizing agents and the effect of vulcanization on thermal properties of IIR-CR blends.

Experimental

The formulations of the mixes are given in Table 1. Mixing of the elastomers in a laboratory open mill, determination of physical properties and ageing characteristics of the vulcanizates were done as per ASTM procedures. A JEOL 35 CF Scanning Electron Microscope was used for morphological studies. DuPont 910 DSC module was used to determine the T_s's of the blends (heating rate 10°C min^{-1} in N_2). TGA 2950 HI-Res Thermogravimetric analyser of TA instruments was used for TG measurements of samples at scan rate of 50°C min^{-1} and DuPont 983 DMA (dynamic mechanical analyser) with a LNCA was used for visco-elastic property measurements from −150 to 60°C. The ultrasonic velocity measurements were performed in solutions by ultrasonic interferometric technique at frequency of 5 MHz.

Results and discussions

Phase morphology

The raw polymers, IIR and CR, were first masticated in the mixing mill, for the same period of time as that of preparation of rubber compounds. The masticated polymers were then dissolved in toluene in 50:50 blend ratio by stirring till equilibrium. The solution was then film casted on glass slides, dried in an oven and studied under SEM for morphological informations. The blend showed discrete two-phase morphology with CR particles of average particle size of 0.8 μm dispersed into the continuous IIR phase.

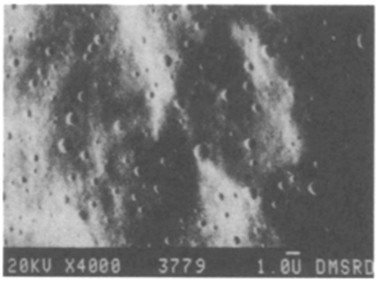

Fig. 1 SEM Photomicrograph depicts phase morphology of 50/50 IIR/CR rubber blend

In another experiment, CM in 5 parts concentration with respect to total rubber content in the blend was first mixed with IIR in the mixing mill during mastication. Masterbatch of IIR and CM was mixed with CR in 50:50 blend ratio and dissolved in toluene. Subsequently, the solution was film casted and studied under SEM. It has been observed, due to addition of CM, the immiscible two-phase morphology, as observed earlier (Fig. 1), converted into a single phase morphology (Fig. 2). CM due to its lower viscosity at the mixing temperature as well as higher segmental chain length, floats to the surface of IIR and forms a skin on top of IIR. As a result, the blend becomes compatible due to polar–polar interaction of CR and CM.

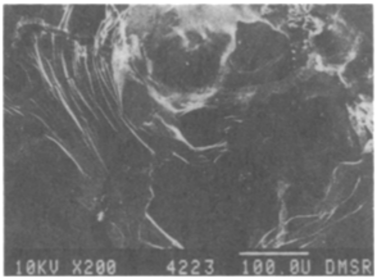

Fig. 2 SEM Photomicrograph depicts phase morphology of 50/50 IIR/CR rubber blend with compatibilizer

Ultrasonic velocity measurements

Figure 3 shows the variation of ultrasonic velocity of the blend without CM in varied blend ratios in toluene. The curve shows deviation from linearity and an S-shaped nature of the plot signifies incompatibility between IIR and CR. Appearance of the S-type shape depicts sudden increase or decrease in the ultrasonic velocity in the phase inversion region which may be attributed to the association of dispersed polymer domains in polymer–polymer–solvent system.

In contrast to blends without any compatibilizer, addition of CM results in a marked increase in ultrasonic velocity values for all blend composition (Fig. 4).

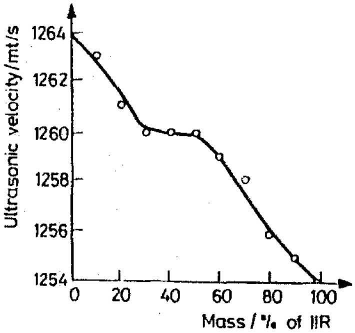

Fig. 3 Ultrasonic velocity of IIR/CR blend without compatibilizer

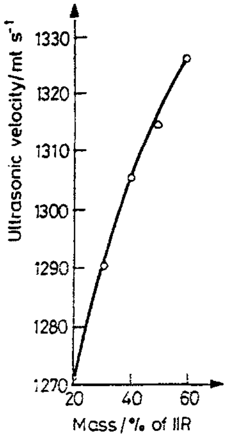

Fig. 4 Ultrasonic velocity of IIR/CR blend with compatibilizer

Linear variation of ultrasonic velocity values for blends containing CM signifies compatibility between component phases.

Physical properties and ageing characteristics

Table 2 shows the physical properties as well as the extent of retention of these properties after ageing of the vulcanizates of Mixes A to D for 10 days at 120°C in a heated oven. Mechanical properties of the gum vulcanizate of butyl rubber (mix A) are very poor in comparison to those of the polychloroprene vulcanizate (Mix B). Polychloroprene because of its strain crystallizing nature showed much better technical properties than IIR. Because of incompatibility, blending of IIR and CR resulted in inferior technical properties as observed in case of vulcanizate of

Table 2 Physical properties of the vulcanizates and property retention after ageing

Property	Vulcanizate Nos.			
	A	B	C	D
Hardness, Shore A	30	40	36	41
Tensile strength/kg cm^{-2}	12.5	172.0	79.5	88.0
Elongation at break/ %	600	950	700	700
Tear strength/kg cm^{-1}	1.3	20.5	11.2	13.5
Percent retention of property after ageing at 120°C for 10 days				
A. Hardness	100	180	175	150
B. Tensile strength	50	20	45	55
C. Elongation at break	90	20	25	30

* Mixes were cured for 30 min at 160°C in a hydraulic press under 200 kg cm^{-2} pressure.

Mix C. However, addition of CM imparts adhesion between CR and IIR thereby generated improvement in technical properties for vulcanizate of Mix D.

Under normal ageing conditions as prescribed in ASTM procedures i.e., heat ageing either at 70 or 100°C for 72 h, all the vulcanizates showed only marginal fall in technical properties. We have, therefore, chosen a drastic ageing condition i.e., at 120°C for 10 days to obtain considerable fall in technical properties. Butyl rubber, because of its saturated structure showed better retention of properties after ageing compared to polychloroprene. In case of uncompatibilized vulcanizate of Mix C, polychloroprene is mostly responsible for drastic reduction of technical properties. Addition of CM, however, resist oxidative degradation and vulcanizate of Mix D showed better retention of technical properties compared to those of Mix C.

DSC studies

Figures 5A and 5B show the DSC curves of the raw polymers of IIR and CR respectively. IIR shows glass transition temperature (T_g) at –60°C and CR at –40°C. The DSC plots of both the uncompatibilized (50:50 IIR and CR) and compatibilized

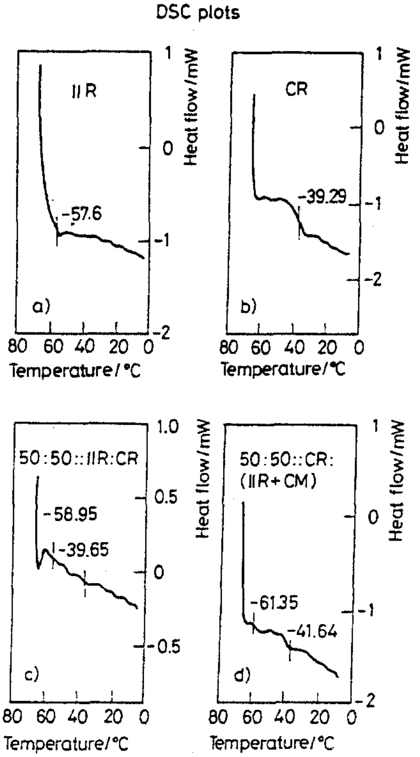

Fig. 5 **A** DSC plot of raw butyl rubber; **B** DSC plot of raw polychloroprene rubber; **C** DSC plot of raw IIR/CR rubber blend without compatibilizer; **D** DSC plot of raw IIR/CR rubber blend with compatibilizer

[50:50 blend of CR and (IIR+CM) masterbatch] polymer blends are given in Figs 5C and 5D respectively. Two separate T_g peaks, one at –40°C (due to CR) and another at –60°C (due to IIR) which were obtained for uncompatibilized blend (Fig. 5C) merged into a broad single peak with broad plateau in the intermediate T_g values for individual components (Fig. 5D).

Dynamic mechanical analysis

In measurements of dynamic mechanical properties over a temperature range of –150°C to +60°C, the appearance of intermediate loss peaks and the concomitant decrease of the loss peaks of the individual phase components of the blend is a useful criterion of blend compatibility.

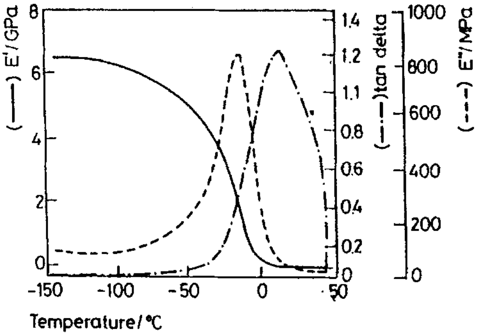

Fig. 6 DMA plots of butyl rubber vulcanizate of Mix A

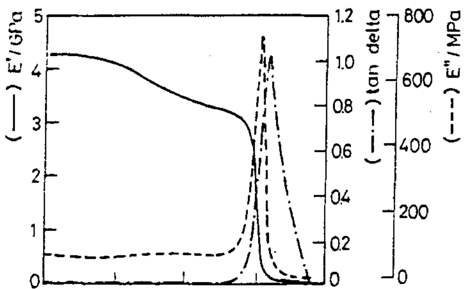

Fig. 7 DMA plots of polychloroprene rubber vulcanizate of Mix B

Figure 6 shows the combination of storage modulus (E'), loss modulus (E'') and Tanδ plots for Mix A and those of Mix B are depicted in Fig. 7. In contrast to polychloroprene compound (Mix B) which showed sharp peaks, butyl compound of Mix A showed formation of a broad shoulder for both E'' and Tanδ in the region of glass transition temperature. Compared to T_g data obtained from DSC studies of raw polymers, DMA plots showed uniform T_g shifts which is due to presence of compounding ingredients in Mixes A and B (Table 1). The storage modulus (E') values for individual polymers resemble stiffness properties of gum compounds and also showed significant changes in the glass transition regions.

Visco-elastic properties showed little changes while the two incompatible polymers of IIR and CR are simply mixed without any compatibilizer as in the case of Mix C (Fig. 8). However, when the same blend is vulcanized for 30 min at 160°C, a distinctly different dynamic spectrum is obtained with the formation of an intermediate loss peak. These results are shown in Fig. 9. To conclude on IIR and CR blends without any compatibilizer, it can be said that while blends showed little evidence of mutual solubility, formation of broad intermediate loss peak in the T_g region due to vulcanization of the same incompatible blend signifies the generation of a crosslinked structure during curing between the heterogeneous rubber phases.

Addition of a chemical compatibilizer (CM) and subsequent vulcanization which was carried out in the case of the vulcanizate of Mix D, improves the level of miscibility between individual polymers compared to the vulcanizate of Mix C and thereby, showed further enhancement of dynamic mechanical properties (Fig. 10).

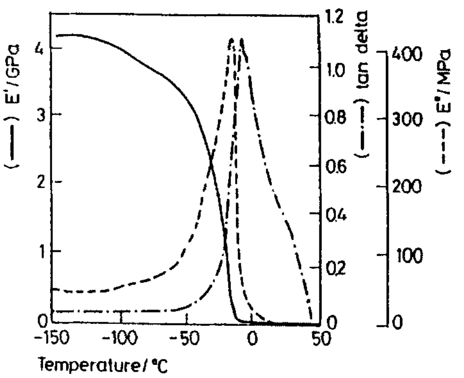

Fig. 8 DMA plots of uncured and uncompatibilized IIR/CR rubber blend of Mix C

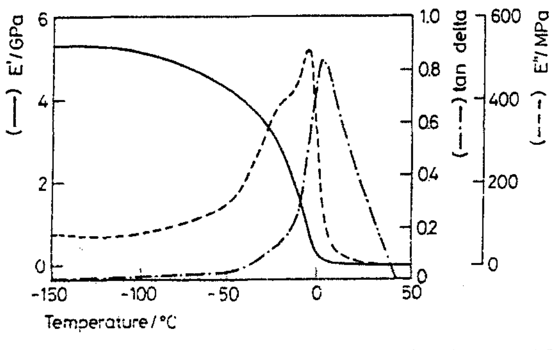

Fig. 9 DMA plots of uncompatibilized IIR/CR vulcanizate of Mix C

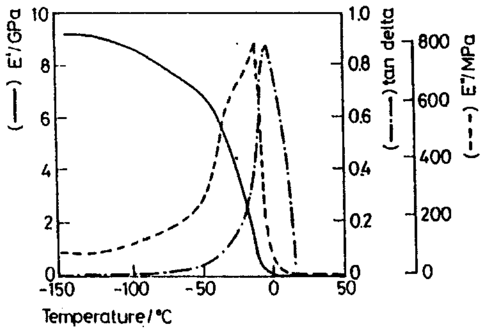

Fig. 10 DMA plots of compatibilized IIR/CR vulcanizate of Mix D

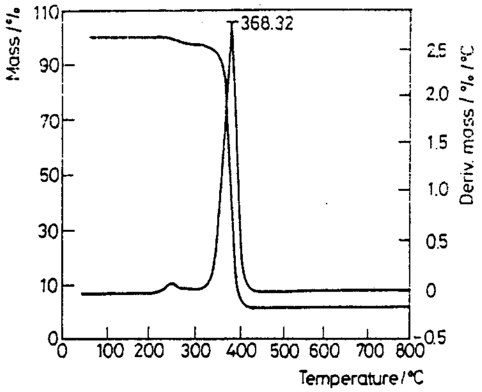

Fig. 11 TG plot of raw butyl rubber

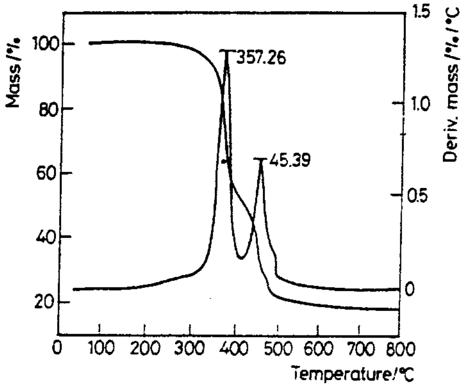

Fig. 12 TG plot of raw polychloroprene rubber

Thermogravimetric analysis

Figures 11 and 12 show the TG plots of the raw polymers of IIR and CR respectively. IIR, due to its saturated structure shows better heat resistance properties compared to CR. In contrast to one single sharp derivative mass loss peak at 368°C for IIR, we observed two peak maxima one at 357°C and another at 445°C for CR. The peak at 445°C for CR may be due to elimination of small molecules like $\mathrm{Cl_2}$, HCl, etc. from rubber chain prior to complete chain degradation.

TG plot of uncured compound of Mix C, (Fig. 13) shows intermediate thermal stability of those of individual polymers. However, addition of CM in Mix D resulted marked increase in thermal stability (Fig. 14).

Smart changes occurred in the thermal stability parameters with the vulcanization of both the Mixes C (Fig. 15) and D (Fig. 16). Formation of crosslinked structure restricts matrix flow and chain scission, thereby, improves thermal stability for vulcanizates compared to corresponding unvulcanized gum compounds. As ex-

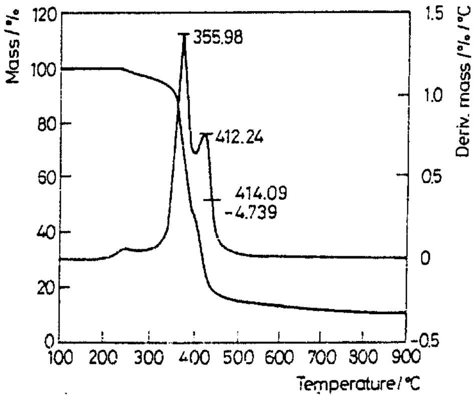

Fig. 13 TG plot of uncured and uncompatibilized IIR/CR blend of Mix C

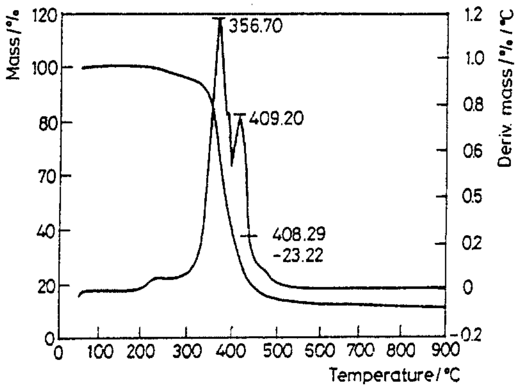

Fig. 14 TG plot of uncured and compatibilized IIR/CR blend of Mix D

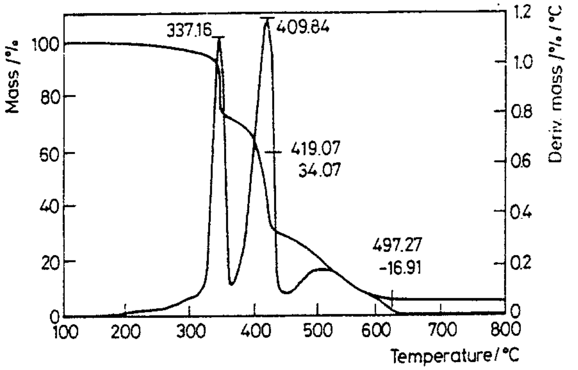

Fig. 15 TG plot of uncompatibilized vulcanizate of Mix C

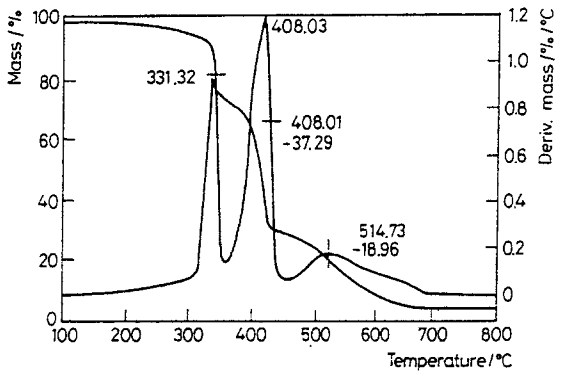

Fig. 16 TG plot of compatibilized vulcanizate of Mix D

pected, compatibilized vulcanizate of Mix D, showed best thermal properties due to improvement in level of adhesion between phase components which is in line with percent retention of physical properties due to ageing.

Conclusions

1. Binary blends of polychloroprene and butyl rubbers are incompatible. SEM studies on phase morphology, ultrasonic, DSC and DMA studies on binary blends confirm the above.
2. Chlorinated polyethylene elastomer (chlorine content ≈36 mol percent) acts as a phase emulsifier and also interphase modifier which imparts compatibility between CR and IIR phases.
3. Physical properties and retention of physical properties after ageing improves due to addition of CM into CR and IIR blends. Compatibilized blends, therefore, expected to find wide usages in civil as well as Defence sectors.

4. SEM, ultrasonic velocity measurements, DSC, DMA and TG techniques are useful tools to measure the extent of compatibility in elastomer blends where the component phases vary in levels of relative polarity.

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