Development of elastomer blends for specific defence application[†]

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Abstract. Several aspects of butyl (CIIR)-polychloroprene (CR) rubber blends viz (i) phase morphology evolution with respect to varied blend ratios and the effect of compatibilizer, (ii) processing characteristics, (iii) vapour impermeability and flame retardancy, (iv) mechanical properties, (v) ageing characteristics and (vi) the effect of addition of fillers into these blends have been studied. Scanning electron microscopy (SEM) has been used as a tool to investigate the phase morphology and also the failure mechanism. Blends based on CR and CIIR are likely to be important to Defence services for developing several rubber products with the above properties and characteristics.

Keywords. Elastomer blend; phase morphology; compatibilization; impermeability; flame retardancy.

1. Introduction

Elastomer blends are widely used to produce vulcanized products and thermoplastic elastomers. However, most of the binary blends exhibit two phases and morphology is important to control the physical and rheological properties (Bauer 1977, 1982; Nelson *et al* 1977; Roland 1988). It was demonstrated by Walters and Keyte (1962), that elastomer blends are never truly homogenous, showing discrete areas of each elastomer varying from $\approx 0.5 \mu\text{m}$ upward, depending on methods of mixing, elastomer viscosity and crystallinity etc.

Structurally different polymers in polymer blends interact through secondary forces with no covalent bonding (Shen and Kawai 1978). The manifestation of superior properties depends upon compatibility or miscibility of homopolymers at molecular levels. Depending upon the degree of molecular mixing, the blends may be categorized as totally miscible (compatible blends), semimiscible (semicompatible), and immiscible (incompatible blends).

It has long been known that the introduction of small quantities of certain additives to blends of thermoplastic (Ide and Hasegawa 1974; Heikens *et al* 1978; Chen *et al* 1988; Yoshida *et al* 1990) or of thermoplastic elastomers (Coran *et al* 1980; Coran and Patel 1985) can lead to major changes in phase morphology and in mechanical behaviour. Such additives or compatibilizing agents are usually block or graft copolymers. There have been few similar investigations of blends of elastomer with other elastomers, until rather recently (Lohmar 1986; Setua and White 1991a, b).

In rubber compounding, in many instances, two or more rubbers are blended. The blends of relatively compatible rubbers like NR, BR and SBR are used on a large scale both in tyre and non-tyre applications. However, little use is made of less compatible rubbers, e.g. NR/NBR, NR/CR, NBR/EPDM and CIIR/CR etc, although these could

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Table 1. Formulation of the mixes A to E.

Ingredient	Content of mix (parts by weight)				
	A	B	C	D	E
Bromo butyl rubber	60	60	60	60	60
Polychloroprene rubber	40	40	40	40	40
Paraffin wax	5.0	5.0	5.0	5.0	5.0
PBNA	1.0	1.0	1.0	1.0	1.0
Sulphur	1.5	1.5	1.5	1.5	1.5
TMT	1.5	1.5	1.5	1.5	1.5
MBTS	1.5	1.5	1.5	1.5	1.5
Na-22	0.3	0.3	0.3	0.3	0.3
ZnO	5.0	5.0	5.0	5.0	5.0
MgO	4.0	4.0	4.0	4.0	4.0
Stearic acid	1.0	1.0	1.0	1.0	1.0
Sb ₂ O ₃	2.0	2.0	2.0	2.0	2.0
SRF	30	—	—	—	—
Ca(SiO ₃)	—	30	—	—	—
Mica	—	—	30	—	—
Chlorinated polyethylene	—	—	—	—	5

Bromo butyl rubber	: Polysar 301 grade;
Polychloroprene rubber	: WM-1, supplied by Bengal Water Proof Ltd., Panihati, Calcutta;
SRF	: N-785, Semi-reinforcing filler, supplied by M/s Philips Carbon Black Ltd., Calcutta;
Mica	: Powdered MUSOVITE Mica was used, particle size = 3 micron, supplied by Mica Trading Corpn. of India, Patna;
Chlorinated polyethylene	: (CM 0136) Supplied by DOW Chemical Corpn., USA;
PBNA	: Phenyl-beta-naphthylamine, supplied by M/s Bayer Farbenfabriken, West Germany;
TMT	: Tetra methyl thiurum disulphide, supplied by M/s Bayer Farbenfabriken, West Germany;
MBTS	: Mercapto-benzothiazyl disulphide, supplied by M/s Bayer Farbenfabriken, West Germany;
Na-22	: 2-Mercaptomidozoline, Supplied by E. I. Dupont, USA
Paraffin wax	: Supplied by BDH (India) Pvt. Ltd., Bombay.

also offer great benefits. Compatibilization, that is to say, modification of normally immiscible blends to give alloys with improved end-use performance is an important factor in almost all commercial blends. The achievement of compatibilization, whether by addition of third component or by inducing *in situ* chemical reactions between blend components (reactive blending), has played an important role in the development of polymer blends (Hofmann 1984).

2. Experimental

The formulation of mixes are given in table 1. Mixing was carried out in a conventional laboratory open mill (150 mm × 330 mm) at 30–40°C according to ASTM designation

Figure 1. Rheographs of different blends.

D 15–70. Butyl and neoprene rubbers were masticated separately and mixed together. Different ingredients were added by careful control of temperature, nip gap, time of mastication and uniform cutting operation. The compounding ingredients were added in the following order i.e. stearic acid, magnesium oxide, antioxidant, reinforcing agent, sulphur, zinc oxide and accelerators as per ASTM designation D 15–62 T. Optimum cure times at 160°C for the mixes were obtained by using Monsanto R-100 rheometer and the rheographs are shown in figure 1. Mixes were vulcanized to their respective optimum cure times at 160°C and 200 kg/cm² pressure in a hydraulic press having electrically heated platens. Specimens for tensile and tear testings were punched out along the grain direction from the vulcanized sheets. Tensile testing was done as per ASTM designation D 412–51 T, using dumb-bell specimens. This test also enables us to obtain elongation at break and modulus values of the vulcanizates. The tear strength was measured with an unnotched 90° angle test specimen according to ASTM method D 624–54. Both tensile and tear tests were carried out in a tensile testing machine having capacity of 50 kg, samples were stretched at a rate of 20 inch/min. Shore A hardness was measured according to ASTM D 676–52 T. Compression set at constant (25%) strain were measured according to ASTM method D 395–61. Abrasion loss of the vulcanizates was measured by using a Du Pont abrader as per ASTM D 394, method A. The specimens were abraded for 2 min and the abrasion loss was calculated in terms of volume loss per hour.

Volume fraction of the rubber in the swollen vulcanizate (V_r) was calculated using the method suggested by Ellis and Welding (Ellis and Welding 1964; Iden 1964), which takes into account the correction of swelling increment with duration of immersion after the equilibrium is attained. Equilibrium was obtained after 72 h of swelling in the mixture of toluene and isooctane (having the ratio 30:70) at 35°C.

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

where T the weight of the test specimens, D the deswollen weight of the test specimens, F the weight fraction of insoluble components, A_0 the weight of absorbent solvent corrected for the swelling increment and ρ_r and ρ_s are the densities of the rubber and

solvent, respectively. $\rho_r = 0.92 \text{ g/cm}^3$ for CIIR rubber, $\rho_s = 0.69 \text{ g/cm}^3$ for isooctane, $\rho_r = 1.23 \text{ g/cm}^3$ for CR rubber, $\rho_s = 0.867 \text{ g/cm}^3$ for toluene.

The tensile test specimens were aged for 7 days at 120°C in a heated oven to determine the retention of tensile strength, elongation at break, hardness, modulus and volume fraction after ageing. Morphological behaviour of rubber blends and tensile fractured surfaces of vulcanizates have been studied by SEM. The fracture surfaces were carefully cut from the failed test pieces without touching the surface. These specimens were stored in a dessicator to avoid contamination from dust particles and then sputter-coated with gold within 24 h of testing.

Figure 2 shows the shapes of the tensile, tear and abrasion test specimens and the corresponding fracture surfaces and scan areas.

3. Results and discussion

3.1 Phase morphology

Several blends in different blend ratios e.g. CIIR:CR::50:50, 60:40, 70:30, 80:20 were prepared. The raw polymers were first masticated in the mixing mill, for the same

Figure 2. Shapes of the tensile, tear and abrasion test specimens, corresponding fracture surfaces and scan areas.

Figure 3. a. Depicts morphology of 40/60 CIIR/CR rubber blend and b. depicts morphology of 40/60 CIIR/CR rubber blend with compatibilizer.

period of time as that of preparation of rubber compounds. The masticated polymers were then mixed together in proper proportions and dissolved in toluene by stirring till equilibrium. Subsequently, they were film casted on glass slides, dried in an oven and studied under SEM for morphological informations. All the blends showed discrete two-phase morphology. CR particles, up to a blend ratio of 40 parts, were found to be dispersed into the continuous CIIR phase. CIIR because of its saturated nature, lower viscosity and higher concentration compared to CR, acts as a continuous phase with CR particles scattered into it. Lack of adhesion was also observed due to immiscibility of CR and CIIR.

Distribution of CR globules inside CIIR improved and the dispersed phase size also reduced with increasing CR concentration in the blends. At 40 parts of CR, the scale of dispersed domains were calculated to be of the average size of $0.8 \mu\text{m}$. Beyond 40 parts of CR, the blends were co-continuous e.g. in the case of 50:50 blends. At least 20 particles were considered for calculation of average dispersed phase size.

Figure 4. Morphology of different blends.

Figure 5. DSC plot of uncompatibilized blend.

SEM photomicrograph of 40:60 blend of CR:CIIR is given in figure 3a and the plot of average dispersed phase size with respect to blend ratios is depicted in figure 4.

3.2 Effect of addition of compatibilizer

Little study has been made so far in exploring a suitable compatibilizing agent in immiscible rubber blends. In this paper we also wanted to seek a suitable compatibilizer for CIIR–CR blends. Setua *et al* (1991a, b, 1994) in their earlier publications have shown that chlorinated polyethylene (CM) can act as a suitable compatibilizing agent for NBR–EPDM and Nylon 6–HNBR system. As CM is a halogen containing elastomer (36% chlorine content) and polar, we expect polar–polar interaction between CM and CR and like wise NBR and PVC blends. Residual ethylene containing segments of CM may be miscible with CIIR due to similar carbon–hydrogen saturated structures.

CM, in 5 parts concentration with respect to total rubber concentration in the blend, was first mixed with CIIR in the mixing mill during mastication. Masterbatch of CIIR and CM, was subsequently used for blending with CR 40:60 blend of the above, was film casted on a glass plate and studied for phase morphology in SEM. It has been observed, due to addition of CM, the immiscible two-phase morphology, as observed earlier for the blend without CM (figure 3a), converted into a single phase morphology (figure 3b). CM due to its lower viscosity at the mixing temperature as well as higher segmental chain length, floats to the surface of CIIR and form a skin on top of CIIR. Thus, polar CM concentrates in the interface of CR particles and CIIR phase and makes the blend compatible due to polar–polar interaction of CR and CM.

Figure 6. DSC plot of compatibilized blend.

The DSC plots of both the uncompatibilized and compatibilized blends are given in figures 5 and 6. Two separate T_g peaks (at -40°C and at -60°C) which were obtained for uncompatibilized blends (figure 5) merged into a broad single peak with broad plateau in the intermediate T_g values for individual components (figure 6).

3.3 Impermeability values of the blends

Figure 7 shows the vapour impermeability values of the different blends. CIIR, always remains in the continuous phase with discrete CR globules inside it, excepting for 50:50 blend when the phase morphology is co-continuous. All these blends show, therefore, very high impermeability values and the extent of impermeability increases with decreasing concentration of CR. The passage of vapour through a rubbery material entails dissolution/adsorption of the gas into the rubber, molecular diffusion, and subsequent evaporation of the gas from the other side of the specimen. CIIR because of its more packing density as compared to CR, exerts less molecular diffusion for vapour through the bulk. Increasing concentration of CR into CIIR, therefore, imparts less impermeability values for the blends.

3.4 Flame retardancy

For some of our defence applications, we were looking into a suitable rubber composition containing CR and CIIR for developing a suitable dough to coat onto

Figure 7. Impermeability of different blends.

Table 2. Flammability characteristics of coated fabric.

Property	Observed values
1. Mass/sq. m of	
(a) Basic nylon fabric (g)	80
(b) Coated fabric (g)	350
2. Flame proofness	
(a) After flame (sec)	2
(b) After glow (sec)	Nil
(c) Char length (cm)	5.6

Table 3. % Retention of physical properties after ageing at 120°C for 7 days.

Property	D	E	A
Tensile strength (kg/cm ²)	88 (49.7)	54 (97.1)	72 (88.7)
Elongation at break (%)	37 (650)	15 (875)	31 (450)
Modulus at 100% elongation (kg/cm ²)	340 (6.72)	420 (9.71)	400 (16.40)
Hardness (shore A)	131 (38)	143 (44)	156 (48)
V _r	135 (0.026)	290 (0.019)	88 (0.046)

* Values in the parenthesis indicate actually measured properties before ageing.

both sides of the Nylon Fabric. These rubber coated fabrics are meant to be used for fabricating protective garments which require both high impermeability as well as flame retardancy in end-use requirements.

60:40 blends of CIIR and CR were made in toluene alongwith curatives and antioxidant etc (as given in table 1) and dough was prepared with 20% solid content. This dough was applied for coating onto both sides of Nylon fabric with add-on concentration of 270 g/sq meter. The coated fabric was subsequently cured in a heated oven and tested for their flame proofness properties, as per BS method 5438:1989. A small igniting flame of LPG burner with total flame height of 19 mm was applied to the bottom edge of a strip of coated fabric of length 190 mm and width 27 mm. The sample was ignited in the flame for 10 sec. The flame was then removed and the flammability of the fabric was determined as follows:

- (i) *After flame*: The length of time for which the material continues to flame, after the ignition source has been removed.
- (ii) *After glow*: Combustion of a material without flame but with the emission of light from the combustion zone. After glow time is the time for which a material continues to glow after cessation of flaming or after removal of ignition source.
- (iii) *Char length*: The maximum extent of the damaged/charred material is measured in the vertical direction. This parameter indicates the maximum extent of total damage of material ignoring any surface effect such as scorching or smoke deposition.

Table 2 mentions the flammability characteristics of coated nylon fabric. Very good flame retardancy was observed for this blend composition and the coated fabric was found suitable for utilization in Defence equipments.

Figure 8. Depicts SEM photograph of tensile fracture surface of uncompatibilized vulcanizate of mix D.

Table 4. Physical properties of different blends.

Property	A	B	C	D
Tensile strength (kg/cm ²)	88.7	53.1	36.0	44.7
Elongation at break (%)	450	470	600	650
Tear strength (kg/cm)	27.5	22.3	16.3	13.1
Abrasion loss (cc/h)	25.3	19.5	25.5	39.8
Hardness (shore A)	48	54	50	38
Modulus at 300% elongation (kg/cm ²)	56.6	33.9	19.8	13.2
Compression set (%)	20	18	25	16
V_r	0.046	0.051	0.051	0.026

3.5 Ageing properties

Table 3 shows the percentage retention of physical properties after ageing for seven days at 120°C of both compatibilized (mix E) and uncompatibilized (mix D) vulcanizates. Thermo oxidative ageing of rubber is believed to occur in two ways via main chain scission or crosslink scission. In compatibilized blend, interface deterioration due to ageing may also lead to degradation of physical properties. Increase in modulus, hardness and V_r values for both vulcanizates due to ageing indicate enhanced stiffness, cleavage of crosslinks and molecular chain scission, the extent of which is much more predominant in case of mix E than mix D. Another possibility is that during prolonged exposure to heat at elevated temperature, CM gets dissolved into CIIR phase and thereby, reducing its effective concentration in proximity to CR for interfacial coupling. We, therefore, observed a drastic fall (e.g. ~ 50%) drop in tensile properties of mix E due to ageing compared to only 20% drop of that of mix D.

SEM photograph (figure 8) of tensile fracture surface of uncompatibilized vulcanizate of mix D shows microductile type of fracture with slip lines and microcraters. Addition of CM into mix E, results in enhancement of physical properties (table 4). This

Figure 9. SEM photograph of tensile fracture surface of compatibilized vulcanizate of mix E.

Figure 10. SEM photograph of aged fracture surface of mix D.

is also reflected in SEM photograph (figure 9) of tensile fracture surface of mix E. Rough fracture surface, short fracture path and absence of any cavitation has been observed. Increase in hardness and modulus as well as the reduction of elongation at break and tensile strength leads to disappearance of slip lines, increased number of pits due to degradation of rubber in ageing the vulcanizate of mix D (figure 10). Extensive matrix deterioration, absence of fracture fronts and formation of holes and cracks in figure 11 signifies the deterioration of interface due to ageing and also sharper reduction of physical properties of mix E compared to those of mix D.

3.6 Processing characteristics of unfilled, filled (e.g. either carbon black/mica/silicate) and compatibilized blends

Rheograph (figure 1) of different vulcanizates were obtained at 160°C with $\pm 3^\circ$ arc of the rotor. It can be seen that the final torque is maximum in the case of mix B (silicate

Figure 11. SEM photograph of aged fracture surface of mix E.

Figure 12. SEM photograph of tensile fracture surface of mix C.

filled), followed by those of mixes A, C, D and E. Optimum cure time for different vulcanizates do not show significant changes either due to addition of different fillers or compatibilizer. All the mixes show sufficient scorch safety and acceptable cure rate and cure time.

3.7 *Physical properties of the vulcanizates*

Table 4 shows the physical properties of all the vulcanizates of mixes A, B, C and D. Carbon black filled vulcanizate of mix A has been found to provide best match between technical properties and ageing characteristics as given in table 3.

3.8 *SEM studies on tensile failure of filled vulcanizates*

The tensile strength of gum vulcanizate (mix D) is poor and addition of mica in mix C, further impairs this property. Marginal improvement in the strength occurs due to the

Figure 13. SEM photograph of tensile fracture surface of mix B.

Figure 14. SEM photograph of tensile fracture surface of mix A.

addition of silica (mix B). However, carbon black filled vulcanizate (mix A) shows maximum values.

Near the tip of a growing crack, stress dissipation by viscoelastic mechanism is essential for the development of high strength. The addition of filler registers additional mechanism through which stress dissipation occurs. Dispersed particles also serve to deflect or arrest growing crack, thereby giving further resistance to failure.

Figure 12 is a photograph of the mica-filled vulcanizate C. Detachment of mica flakes from polymer surfaces as well as formations of grooves and deep cracks are evident.

Figure 13 is the corresponding tensile failed surface for silica-filled vulcanizate B. Comparatively better polymer-filler interaction and bound rubber on silica aggregates resists the propagation of fracture. Silica filled vulcanizate, therefore, shows higher tensile strength as compared to mica filled vulcanizate.

Figure 14 is the SEM photograph of carbon black filled vulcanizate. Very good polymer-filler interaction in this case, causes formation of a coarse fracture surface.

Filler agglomerates are all very well dispersed and these also resist growth of fracture fronts. Low elongation properties for this vulcanizate cause catastrophic fracture of the vulcanizate.

4. Conclusions

- (1) Mixing of polychloroprene (CR: T_g , -40°C) and chlorinated isobutylene isoprene copolymer (CIIR: T_g , -60°C) can give rise to a high performance elastomer blend where the physical strength, chemical and solvent resistance as well as very good flame retardent properties of CR may be combined with low temperature flexibility and good impermeability of CIIR.
- (2) Due to dissimilarity in both the structural as well as solubility parameter of CR = 9.26, CIIR = 7.60, relative polarity value, CR and CIIR form immiscible blends and also produces a coarse phase morphology.
- (3) Chlorinated polyethylene (CM) has been seen to act as an efficient compatibilizer in these blends. Addition of CM causes a rapid reduction in the scale of dimensions of the dispersed domains as well as improved mechanical properties.
- (4) Addition of carbon black into these blends, leads to the development of a high performance rubber composite with balanced technical properties and ageing resistance.
- (5) SEM studies help to obtain a better insight into the phase morphology and mechanism of failure.

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