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Self-Vulcanisable Rubber-Rubber Blends Based on Epoxidised Natural Rubber and Polychloroprene

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Mill mixed blends of polychloroprene (Neoprene AC) and epoxidised NR (ENR) have been found to be self-vulcanisable in the absence of any vulcanising agent. This is found to be a partially miscible system. Crosslink density and physical properties of the system depend on the blend ratio

Selbstvulkanisierbare Kautschuk/Kautschuk-Verschnitte auf Basis von epoxidiertem Naturkautschuk und Polychloropren

Auf der Walze hergestellte Verschnitte aus epoxidiertem NR (ENR) und Polychloropren (CR) (Neoprene AC) zeigten in Abwesenheit jeglichen Vulkanisationsmittels die Fähigkeit zur Selbstvulkanisation. Es wurde festgestellt, daß es sich um ein teilweise mischbares System handelt. Die Netzwerkdichte und die physikalischen Eigenschaften sind vom Verschnittverhältnis abhängig

troduction

De and co-workers have developed self-vulcanisable blends based on rubbers with reactive groups. Examples are blends based on Hypalon (CSM)-epoxidised NR (ENR) [1, 2], CSM-carboxylated nitrile rubber (XNBR) [3], XNBR-ENR [4,5] and polychloroprene (CR)-XNBR [6]. These rubbers get crosslinked during moulding in the absence of any vulcanising agent and can be reinforced with fillers like carbon black and silica. While making further investigations on blends based on ENR, we observed that CR (Neoprene AC)-ENR system gets vulcanised during moulding in the absence of any crosslinking agent. *Zakharov* and *Mairov* have reportet that Neoprene can be vulcanised by epoxy resin [7].

In the present communication we report the results of our preliminary studies on self-vulcanisable Neoprene AC-ENR blend. - According to preliminary studies other forms of CR also undergo similar reaction like Neoprene AC grade. But we have not studied details. This paper, therefore, deals with only Neoprene AC type.

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As polychloroprene type Neoprene AC was procured from Du Pont, U.S A., ENR used was ENR-50 with 50 mol % epoxidation, obtained from Malaysian Rubber Producers' Research Association (MRPRA), U.K. The Mooney viscosities of the samples ML (1 + 4) at 120 °C were 0 for Neoprene AC and 46 for ENR-50. The formulation of the blends re given in *Table 1*. Both CR and ENR-50 were masticated on a 14×6 in wo roll mixing mill to the same Mooney viscosity and were blended on he mill for about 6 min. Minimum Mooney viscosity and scorch time ere determined as per ASTM D 1646-1963 by using Negretti automaion Mooney shearing disc viscometer model MK III. Rheographs of the lends were taken at 180 °C on a Monsanto rheometer R-100. The lends were cured at 180 °C for 60 min. The following physical propers of the vulcanisates were determined according to standard test ethods: Tensile strength (Instron 1195 universal testing machine, STM D 412-75 method A), tear strength (Instron 1195 universal testing achine ASTM D 624-85) using an unnicked 90° angle specimen (Die Shore A hardness (ASTM D 2240-86), resilience (Dunlop tripsometer S 903 Part A 8.1963 method A), compression set (ASTM D 395-85 ethod B), where the specimens were subjected to 25 % compressive deformation at 70 °C for 22 h, heat build-up (Goodrich flexometer ASTM D 623-83) with a load of 24 lb. and stroke of 4.45 mm and ambient temperature of 50 °C, abrasion resistance expressed as abrasion loss which is the volume in cm³ abraded from a specified test specimen for 1000 revolutions of the abrasive wheel (Du Pont abrasion tester BS 903: Part A 9 – 1957 method A).

Table 1. Formulation and processing characteristics of the blend

	Blend designation	
	N-E 75 25	N-E 50 50
Neoprene AC	75	50
ENR	25	50
Minium Mooney viscosity at 120 °C	38	31
Mooney scorch time at 120 °C in min	38	132

Dynamic Mechanical Analysis (DMA) was done by Toyo Baldwin Rheovibron model DDV III EP at a strain amplitude of 0.0025 cm and frequency of 3.5 Hz. The procedure was to cool the sample to – 100 °C and to record the measurements during the warm up. The temperature rise was 1 °C min⁻¹.

Differential Scanning Calorimeter (DSC) studies were done on a Du Pont thermal analyser model 910 in nitrogen atmosphere. Glass transition temperature (T_g) of the sample was taken as the midpoint of the step in the scan run at a heating rate of 20 °C min⁻¹.

The volume fraction of rubber (V_r) in solvent swollen blend was calculated from equilibrium swelling data by the method reported by *Ellis* and *Welding* [8].

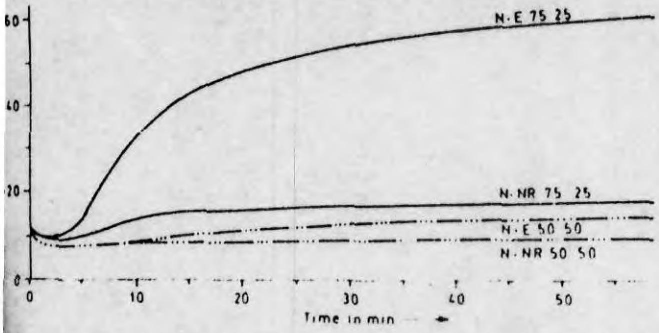
$$V_r = \frac{(D-FT)/\varrho_r}{(D-FT)/\varrho_r + A_0/\varrho_s}$$

T is the weight of the specimen. D is its deswollen weight. F is the weight fraction of insoluble components. A_0 is the weight of absorbed solvent corrected for swelling increment, and ϱ_r and ϱ_s are the densities of the rubber and solvent respectively. Chloroform was used as the solvent for the present study.

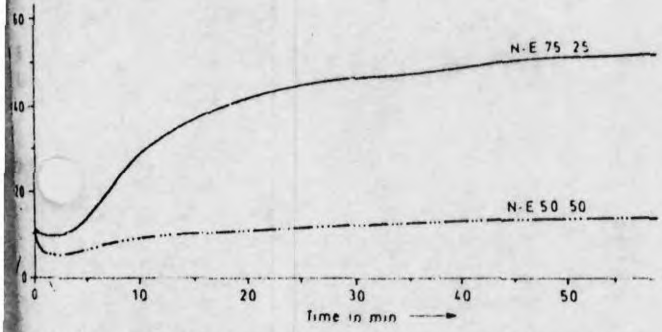
3 Results and discussion

The rheographs of the blends of Neoprene AC and ENR are shown in *Figure 1*. CR alone is reported to undergo thermovulcanisation [9]. It is not known whether thermovulcanisation of Neoprene AC will take place in the presence of functionally active rubbers like ENR. In a blend of Neoprene AC and a rubber which does not contain active functional groups (for example, NR), rise in rheometric torque, if any, in the blend, will be due to thermovulcanisation of Neoprene AC only. Accordingly, for comparison we have taken rheographs of blends of Neoprene AC and NR. The blend compositions of Neoprene AC-NR system were chosen to be the same as the Neoprene AC-ENR system. It is believed that in the same blend composition rheometric torque in the Neoprene AC-NR system corresponds to thermovulcanisation alone while in the case of the Neoprene AC-ENR system the torque rise corresponds to thermovulcanisation of Neoprene AC as well as self-vulcanisation between Neoprene AC and ENR. At a particular curing time the difference in the two torque values will correspond to the torque due to self-vulcanisation. The calculated rheographs thus obtained are shown in *Figure 2*. Although both ENR and Neoprene AC are soluble in chloroform, the moulded blend is insoluble in the same solvent showing thereby that each blend constituent gets crosslinked by the other during moulding. The weight loss after 48 h of immersion in chloroform is less than 15 % for the blends showing that during vulcanisation both ENR and Neoprene AC gets crosslinked to a large extent. This is also evident from V_r (volume fraction of rubber in the swollen vulcanisate), shown in *Table 2*. The crosslink density which can be regarded as proportional to V_r is high when the Neoprene AC content is high. A plausible mechanism of self-vulcanisation between Neoprene and ENR is shown in *Figure 3*.

The very long scorch time for the blends of Neoprene AC and ENR shows good processing safety. The processing characteristics are shown in Table 1.



igure 1. Rheographs of Neoprene AC-ENR and Neoprene AC-NR lends at 180 °C

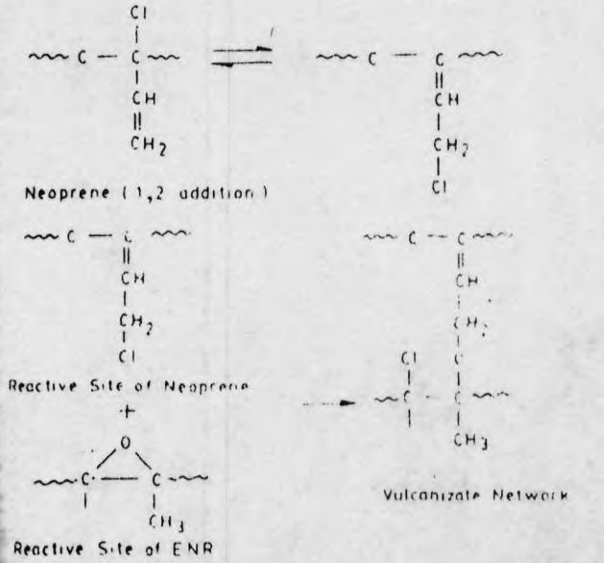


ure 2. Calculated rheographs of the self-vulcanisable Neoprene AC-R blends after deducting the effect due to thermovulcanisation of oprene AC

Table 2 **Physical properties of the blends moulded at 180 °C *for 60 min***

	Blend designation N-E 75:25	 N-E 50:50
Modulus 300 % in MPa	1.8	1.1
Tensile Strength in MPa	5.7	3.8
Elongation at break in %	460	570
Tear strength in kN/m	16.8	13.0
Hardness, Shore A	41.0	30.0
Resilience at 40 °C in %	55.0	55.0
Compression set at constant strain in %	4.0	11.0
Heat build-up by Goodrich flexometer		
(a) T in °C	14.0	*
Dynamic set after 25 min in %	1.0	*
on loss in cm³/1000 rev	1.1	4.8
e fraction, V_r	0.14	0.05

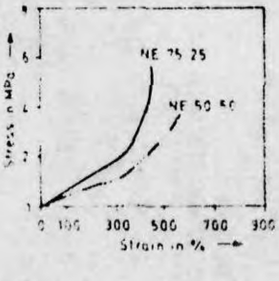
*Sample blown out in the 10th min



3 Crosslinking reaction between ENR and Neoprene AC in the

The physical properties of blends are shown in Table 2. Higher proportion of Neoprene AC in the blend results in improved physical properties. The stress-strain curves are shown in *Figure 4*. As the proportion of Neoprene AC in the blend increases, compression set, abrasion loss and heat build-up decreases. However, resilience values do not show any change.

Figure 4 (right). Stress-strain curves of blends of Neoprene AC and ENR



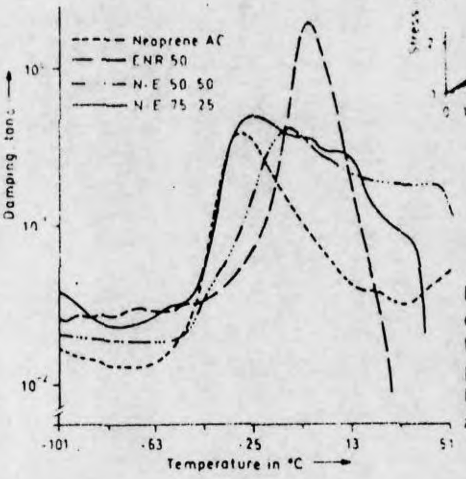
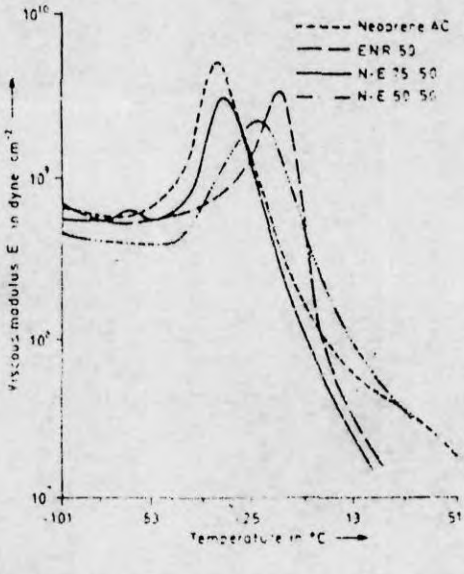


Figure 5. Plots of damping (tan δ) versus temperature for Neoprene AC, ENR and blends of Neoprene AC and ENR

Figure 6. Plots of viscous modulus versus temperature for Neoprene AC, ENR and blends of Neoprene AC and ENR



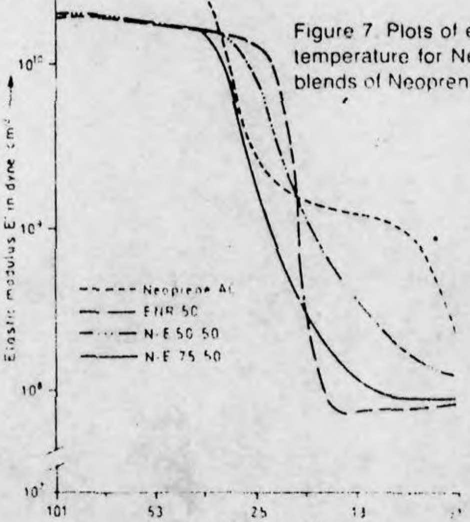


Figure 7. Plots of elastic modulus versus temperature for Neoprene AC, ENR and blends of Neoprene AC and ENR

Dynamic storage modulus or elastic modulus (E′), dynamic viscous modulus or loss modulus (E″) and damping (tan δ) at different compositions are shown in *Figures 5 to 7*. The temperatures corresponding to maximum damping and maximum viscous modulus, were as taken as T_gs. The T_gs of the samples thus obtained are shown in *Table 3*. Pure ENR shows a main relaxation at T_g and a relaxation corresponding to motion of side groups in the glassy region as seen from plots of viscous modulus and damping versus temperature [10]. Neoprene AC in the glassy region does not show any transition other than T_g. In the T_g region as a general trend loss modulus and damping increase until they attain their maxima and then fall with increase in temperature whereas the dynamic storage modulus falls rapidly to the level in the rubber elastic region. Pure ENR shows single transition in the T_g region. Pure Neoprene AC is observed to show two transitions in the rubbery region as reflected from plots of damping and elastic modulus. For Neoprene AC there is a sharp transition in elastic modulus around −46 °C and a slow s[illegible]d transition around −13 to +36 °C. In the plots of damping[illegible]ersus temperature the maximum damping occurs at −29 °C.

Table 3 T_g and width of T_g zone in Neoprene-ENR blends

	T_g in °C			Width of T_g zone in DSC thermogram ΔT in °C
	DMA		DSC	
	tan δ	E″		
Neoprene AC	−29	−37	−37	9
N-E 75:25	−27	−33	−36	17
N-E 50:50	−13	−22	−33	24
ENR-50	−6	−13	−15	12

In Neoprene AC the first sharp transition observed in damping and elastic modulus is due to transition from the glassy to the rubbery state, and the second transition is due to the melting of the crystallites in the polymer as it contains about 90 % trans 1,4 configuration of the chloroprene unit in CR [11]. Development of crystallinity at low temperatures for elastomers which are substantially amorphous at room temperature have been reported earlier [12, 13].

[illegible]elaxation shown by pure ENR is absent in the case of [illegible] of Neoprene AC and ENR. This shows that there is inter-ction between the blend components. Absence of secondary elaxation in blends, due to the interaction between blend components have been reported earlier [14, 15]. In blends of eoprene AC and ENR there is considerable broadening of the $_g$ zone. This shows that there is microlevel inhomogeniety i.e. artial miscibility for the blends. When the Neoprene AC content s increased the transition to rubbery region starts at a lower mperature. In Neoprene AC-ENR 75:25 blend the damping is gh in the region −27 to +9 °C. However, maximum damping s observed at −27 °C. In Neoprene AC-ENR 50:50 blend the aximum damping is observed at −13 °C and the damping is gh in the region −13 to +50 °C. The transition in elastic modlus occurs in a wider range of temperature, −43 to −6 °C for eoprene AC-ENR 75:25 blend and −38 to +50 °C for eoprene AC-ENR 50:50 blend. This wide temperature range transition in the T_g region is also observed in the loss modulus ots of the blends. Thus the blends show high damping over a de range of temperature depending on the blend ratio

SC thermograms as shown in *Figure 8* gives additional support the partial miscibility of ENR-Neoprene AC blends. Blends hibit a single T_g which is shifted to a higher temperature as R content decreases. As observed in the case of DMA results re also the T_g zone becomes broadened in the case of blends.

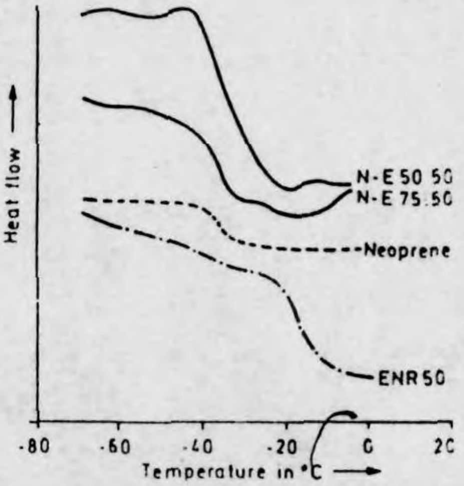


Figure 8. DSC thermograms of Neoprene AC, ENR and blends of Neoprene AC and ENR

This broadening shows partial miscibility of the components in the blend. *Vukovic* et al. [16] while studying compatibility of poly(2,6 dimethyl 1,4-phenylene oxide)/poly(fluorostyrene-co-chlorostyrene) have observed that there is increase in T_g width of DSC thermogram with blend composition till there is phase separation. In an immiscible system the T_g width of the DSC thermograms in the blends is the same as the T_g width of DSC thermograms of individual components. The magnitude of this broadening and the transition width temperature (ΔT) is shown in Table 3. The difference in transition temperature obtained from DMA and DSC results, is due to different nature of response in molecular segments of samples in the two techniques of analysis.

4 Conclusions

It is concluded that mill mixed blends of ENR and Neoprene AC form a self-vulcanisable system when moulded at 180 °C. These blends are partially miscible. The system shows high damping in a wide range of temperature depending on the blend ratio. The extent of self-vulcanisation also depends on the blend ratio. Higher proportion of Neoprene AC in the blend shows higher crosslink density and improved physical properties.

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