Self-vulcanizable and miscible ternary rubber blend system based on epoxidized natural rubber, carboxylated nitrile rubber and polychloroprene

Rosamma Alex, Prajna P. De and Sadhan K. De
Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721 302, India

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Incorporation of epoxidized natural rubber (ENR) into the immiscible blend of carboxylated nitrile rubber (XNBR) and polychloroprene rubber (Neoprene) results in a miscible ternary blend which is self-vulcanizable in the absence of any vulcanizing agent. The moulded blend registers properties similar to that of conventional rubber vulcanizates.

(Keywords: epoxidized natural rubber; carboxylated nitrile rubber; polychloroprene rubber; self-vulcanizable rubber blend; miscible rubber blend)

INTRODUCTION

Blends of carboxylated nitrile rubber (XNBR) and polychloroprene rubber (Neoprene) have been reported to be self-vulcanizable but immiscible[1]. However, epoxidized natural rubber (ENR) was found to form miscible self-vulcanizable binary blends with XNBR and with Neoprene[2,3]. Accordingly, it was thought that if ENR is blended with the XNBR–Neoprene binary system to form a ternary blend, it could result in a miscible ternary blend system which is self-crosslinkable in the absence of any vulcanizing agent. There are no published reports of self-vulcanizable and miscible ternary rubber blend systems. In the present communication, we report the results of our preliminary studies on the XNBR–ENR–Neoprene ternary blend.

EXPERIMENTAL

Neoprene AC was procured from Du Pont Limited, USA. The ENR used was ENR-50 (Malaysian Rubber Producers' Research Association, UK) with 50 mol% epoxidation. The XNBR used was Krynac-221 (Polysar Limited, Canada) containing high level of carboxylated monomer and medium high bound acrylonitrile level. Neoprene, ENR and XNBR were masticated in a 14 × 6 inch, two-roll mill for about 2 min each. Masticated samples of Neoprene and XNBR were blended in the mill for about 2 min. Masticated ENR was added to this blend and further mixed for about 4 min. A rheograph of the blend was taken at 150°C on a Monsanto Rheometer R-100. The scorch time was determined using Mooney shearing disc viscometer, model MK-III (Negretti Automation, UK) according to ASTM D1646-1963. The following physical properties of the vulcanizates were determined as per standard test methods: tensile strength (Instron 1195 universal testing machine, ASTM D 412-87 method A); tear resistance (Instron 1195 universal testing machine, ASTM D 624-86), using an unnicked 90° angle specimen (Die C); hardness (Shore A, ASTM D 2240-86); resilience (Dunlop Tripsometer BS: 903: Part A8: 1963-method A); compression set (ASTM D 395-85 method A and method B), where the samples were subjected to compressive deformation at 70°C for 22 h; heat build-up (Goodrich Flexometer, ASTM D 623-78) with a load of 10.9 kg and stroke of 4.45 mm; and abrasion resistance (Du Pont Abrasion Tester BS: 903: Part A9-1957 - method C) expressed as abrasion loss, which is the volume in cubic centimetres abraded from a specified test specimen for 1000 revolutions of the abrasive wheel. Volume fraction of the rubber in the solvent swollen vulcanizate was determined by equilibrium swelling in chloroform. The method is the same as that reported by Ellis and Welding[4].

Dynamic mechanical properties were measured using 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 record the measurements during the warm up. The temperature rise was 1°C min^{-1}.

Differential scanning calorimeter measurements were run on a Du Pont differential scanning calorimeter, model 910 in nitrogen atmosphere. The glass transition temperature (T_g) of the samples was taken as the midpoint of the step in the scan, run at a heating rate of 20°C min^{-1}.

RESULTS AND DISCUSSION

Formulation and processing characteristics are shown in *Table 1*. A rheograph of the blend is shown in *Figure 1*. The increase in rheometric torque with time indicates progressive crosslinking of the system. Although ENR, Neoprene and XNBR are soluble in chloroform, the vulcanized blend is insoluble in chloroform; this indicates that a crosslinking reaction has taken place. The volume fraction of the rubber in the swollen vulcanizate is 0.1. The stress–strain curve of the blend is shown in *Figure 2*. *Table 2* gives the physical properties of the blend. It registers poor physical properties like non-crystallizing rubbers.

Table 1 Formulation and processing characteristics of the ternary blend

ENR-50	100
Neoprene AC	100
XNBR (Krynac-221)	100
Minimum Mooney viscosity, at 120°C	29
Mooney score time at 120°C (min)	9.1

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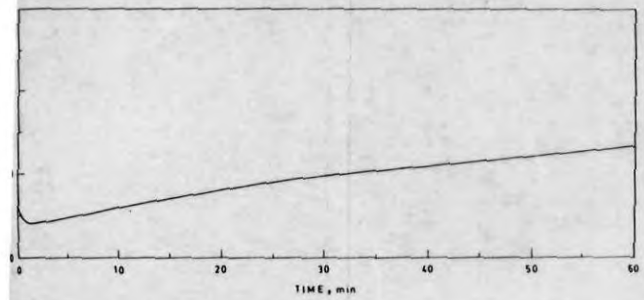

igure 1 Rheograph of ENR–XNBR–Neoprene ternary blend at 50°C

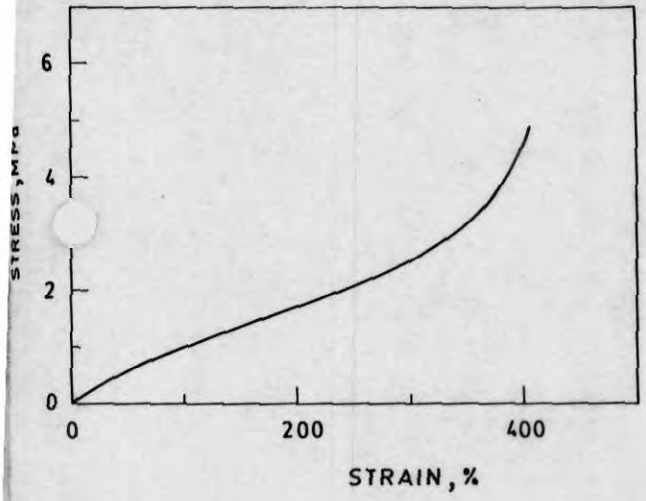

Figure 2 Stress–strain curve of ENR XNBR Neoprene blend

Table 2 Physical properties of ENR–XNBR–Neoprene ternary blend *moulded at 150°C for 60 min*

300% modulus (MPa)	2.9
Tensile strength (MPa)	4.6
Elongation at break (%)	400
Tear strength (kN m^{-1})	16.0
Compression set at constant stress (%)	19
Co[illegible]ion set at constant strain (%)	27
Ha[illegible], Shore A	55
Heat build-up (Goodrich Flexometer)	
ΔT at 50°C (°C)	29
Dynamic set after 25 min (%)	2.8
Abrasion loss (cc per 1000 rev)	5
Resilience at 40°C (%)	66
Volume fraction	0.10

Differential scanning calorimeter thermograms of Neoprene, XNBR, ENR and the ternary blend are shown in *Figure 3*. The blend shows a single T_g at a temperature of $-30°C$, indicating that the polymers are miscible. The results of dynamic mechanical studies (*Figures 4, 5* and *6*) further substantiate this observation. The glass transition temperatures as determined by d.s.c. and Rheovibron studies are summarized in *Table 3*. The occurrence of a single T_g does not correspond to the coexistence of two binary XNBR–ENR and ENR Neoprene phases because the binary phases do not have close T_g values[2,3]. Accordingly, it is believed that the three polymers in XNBR–ENR–Neoprene system form a homogeneous phase in the 100:100:100 blend composition studied.

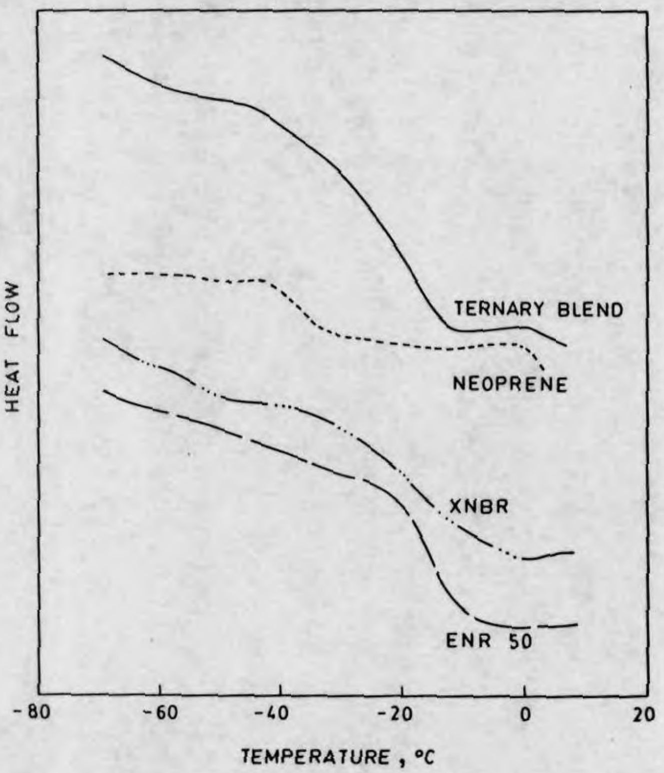

Figure 3 D.s.c. thermograms of Neoprene, ENR, XNBR and the ternary blend

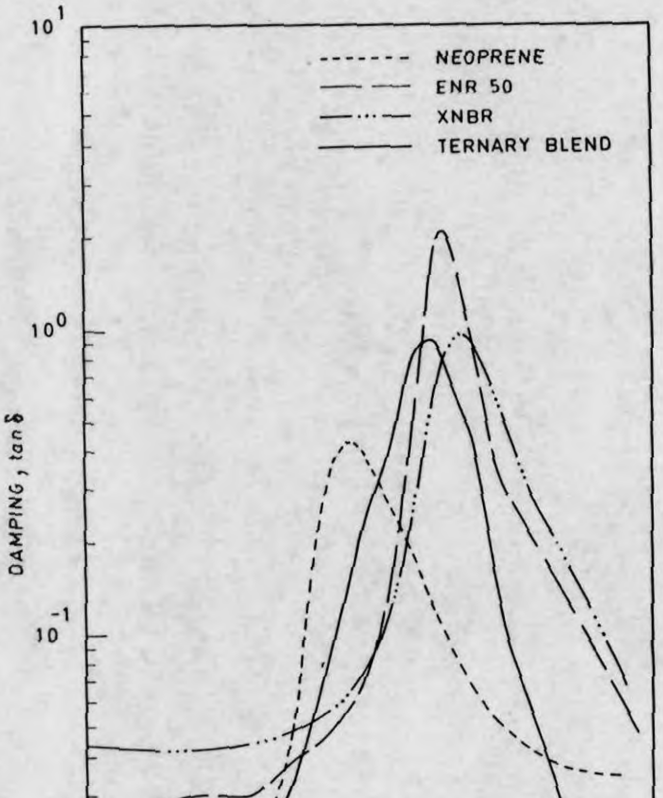

Figure 4 Damping (tan δ) plots of neoprene, ENR, XNBR and the ternary blend

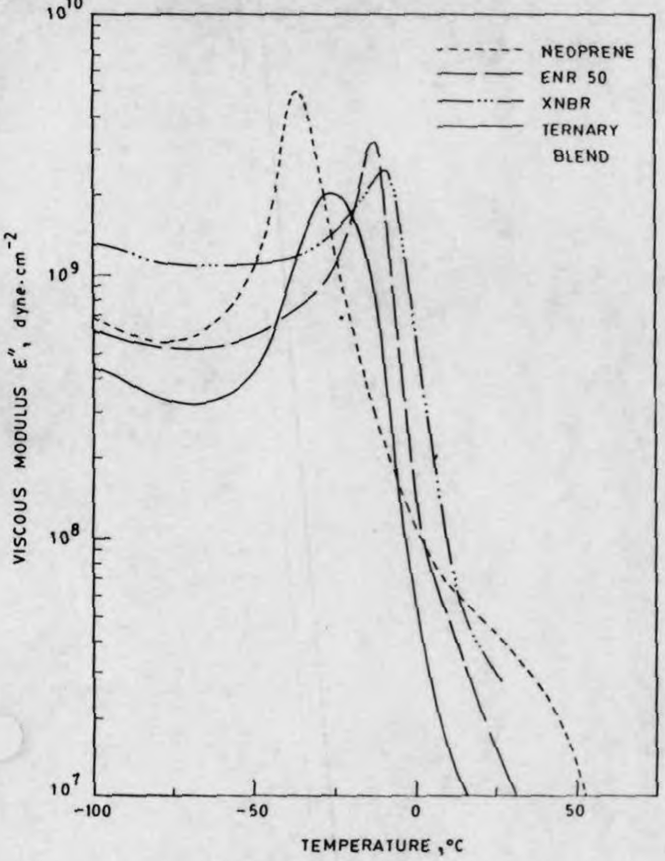

Figure 5 Loss modulus (E'') plots of Neoprene, ENR, XNBR and the ternary blend

Examination of the literature reveals recent interest in studies on the thermodynamic phase behaviour of ternary blends where two of the binary pairs, (A + B) and (A + C), are miscible, but the third binary (B + C) is not[5–9]. It is of interest to study how much of A is to be added to the immiscible blend B–C to create a miscible ternary blend A–B–C. The ternary system in the present investigation belongs to the same category. Moreover, the present system is self-crosslinkable in the absence of any vulcanizing agent. Further work on such novel ternary blends is in progress.

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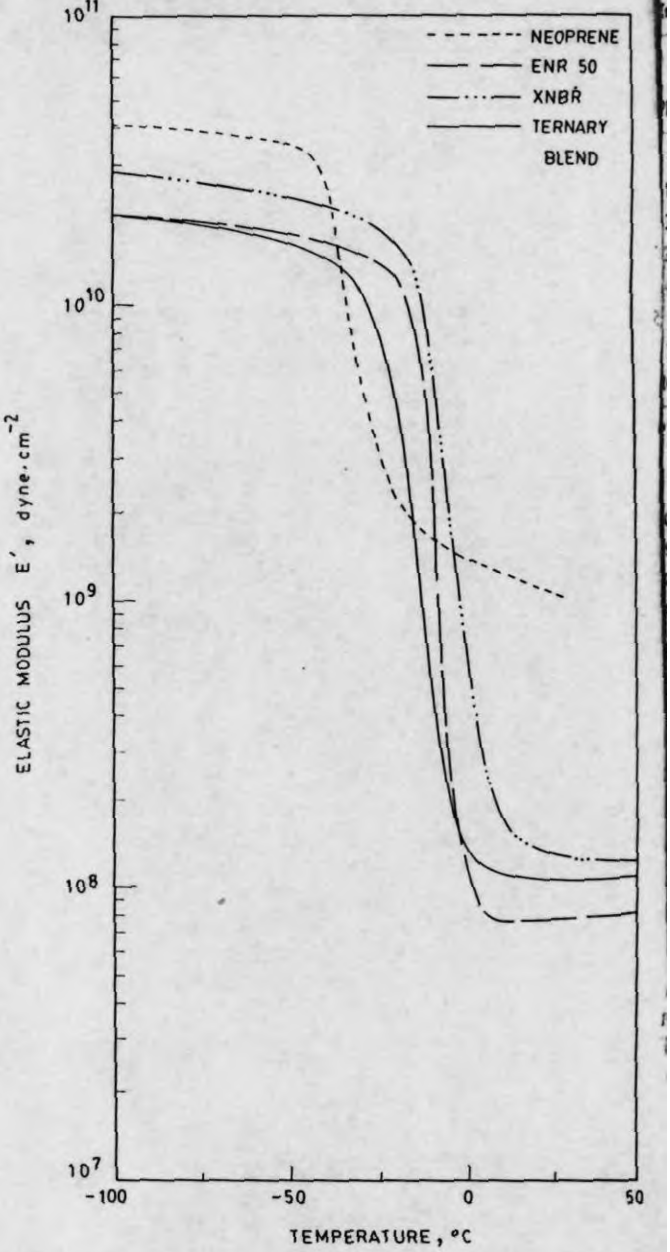

Figure 6 Elastic modulus (E'') plots of Neoprene, ENR, XNBR and the ternary blend

Table 3 Glass transition temperatures as obtained from differential scanning calorimeter and Rheovibron studies

	Glass transition temperature T_g (°C)		
		Dynamic mechanical analysis	
Sample	D.s.c.	Tan δ (max)	E'' (max)
XNBR	−25	0	−9
ENR-50	−15	−5	−13
Neoprene AC	−37	−29	−37
Ternary blend	−30	−9	−25

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