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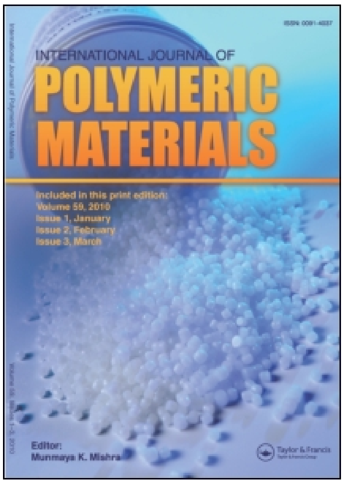

International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Polyblends of the Carboxylated Nitrile Rubber and Fluoroelastomers

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To cite this Article Roy, S. K. Singha and Das, C. K.(1995) 'Polyblends of the Carboxylated Nitrile Rubber and Fluoroelastomers', International Journal of Polymeric Materials, 27: 3, 209 — 222

To link to this Article: DOI: 10.1080/00914039508009670

URL: http://dx.doi.org/10.1080/00914039508009670

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Intern. J. Polymeric Mater., 1995, Vol. 27, pp. 209–222
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Polyblends of the Carboxylated Nitrile Rubber and Fluoroelastomers

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(Received July 24, 1994)

The blends of carboxylated nitrile rubber with two different grades of fluoroelastomers (Viton) has been studied using different blending techniques, but keeping all other parameters constant. The preblending technique gives better results because of the interpolymer reaction between XNBR and Viton. IR spectra suggests an interaction between the two functional groups of the polymers. Preheating of the preblends before adding curatives improves the properties of the blend, and retards degradation and weight loss. The preheating of the preblend also restricts the extraction of the XNBR phase in solvents.

KEY WORDS XNBR, Viton, interchain-crosslinking, phase morphology.

INTRODUCTION

Polymer blends have become an important area of research because these new materials with improved properties can be prepared from existing polymers to meet specific needs. One of the areas where special kinds of elastomers and their blends are required is in oil resistant applications. Carboxylated nitrile rubber (XNBR) is an important oil resistant elastomer, and its properties has been studies by Dunn.[1] Schwarz[2] reported that modulus and tensile strength of chlorosulphanated polyethylene (CSM) increases when blended with XNBR. XNBR improves the oil resistance of CSM. XNBR/Polyvinylchloride blends can be used where good oil and abrasion resistance are required.[3,4] Recently Das *et al.* have studied blends of polyacrylic rubber/fluoroelastomer[5] and triblends of nitrile/polyacrylic/fluoroelastomer.[6]

This study concerns the blends of XNBR and fluoroelastomer (Viton). The interest in fluorinated elastomers stems from their exceptional thermal, chemical and oxidative stability. This stability has been attributed to the superior strength of carbon-fluorine bond over carbon-carbon bond, to steric hindrance and to strong Van der walls forces.[7,8] This elastomer is very hard and costly, and cannot be easily processed. Blending will result in a cheaper, more easy processed high performance material. Two types of curative systems have been used to co-vulcanize the blends. In this paper, we report the effect of curatives and blending sequence on blend properties, as well as the effect of heat treatment on the properties of the blend.

EXPERIMENTAL

The carboxylated nitrile rubber used was Nipol N-34 grade manufactured by Nippon Zeon Co. Ltd., Japan, and the fluoroelastomers were Viton B-50 and Viton E 60-C from Dupont, USA. The blends of XNBR and Viton elastomers were prepared in an open two roll mixing mill at room temperature, uniform nip gap and speed. The cured sheet were prepared by compression molding at 170°C to optimum cure time (t_{90}). The continuous cure characteristics were studied in Monsanto Rheometer R-100 at 170°C. Physical properties were studied on a cured sheet both before and after aging. Aging was performed in an air oven at 140°C for 60 hours, and aging in oil was performed in ASTM Oil No. 3 at 140°C for 48 hours. The tensile properties were measured by the Universal Tensile Testing Machine. Compression set was measured at 120°C for 24 hours at 25% deflection. Solvent swelling was studied at ambient for 48 hours in the Methyl ethyl ketone (MEK) and chloroform ($CHCl_3$). Infrared spectra were taken of pure XNBR and Viton B, and cured film of blended polymer using a Perkin Elmer Model 837. Phase morphology was studied for extracted samples in chloroform with the help of SEM (Camscan Series 2 and E5200 Auto Sputter Coater). Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were conducted using a Shimadzu Thermal analyzer (DT-40) in air at a rate 10°C per minute within the temperature range 25°C to 500°C. Differential Scanning Calorimetry (DSC) studies were carried out using the Stanton Redcroft Thermal Analyzer STA-625 in a nitrogen atmosphere to determine the T_g and heat of vulcanization.

Two types of blending techniques were followed.

(a) Preblending technique: The two elastomers, Viton and XNBR, were first blended in the entire composition range and then in the curatives. Fillers were incorporated into the preblended stock.

(b) Masterbatch technique: The curatives and fillers were first incorporated into each elastomer separately. These two masterbatches were then blended in the entire composition range.

RESULTS AND DISCUSSION

1. Blends of Viton B-50 and XNBR (Diak 3 as curative)

1.1 Physical properties. The compounding formulations and properties are given in Table IA and IB, respectively.

In the masterbatch technique, the state of cure ($\tau_{max} - \tau_{min}$) hardness and modulus gradually increases as XNBR is successively replaced by Viton. The tensile strength increases and is maximum at 50/50 blend ratio, while the elongation at break and compression set gradually decreases as XNBR is replaced by Viton in the blend. On aging deterioration of the physical properties occurs but the percentage loss in the properties are less in the Viton-rich blends. The percentage volume swell in oil decreases gradually as the XNBR is replaced by the Viton in the blend. The properties improve as Viton B-50 is incorporated in the blend.

TABLE IA

Compounding formulation (based on 100 phr rubber)

	A	B	C	D	E	F	G
XNBR Master batch (MB_1- MB_2)	100	80	60	50	40	20	0
Viton B-50 Master Batch/ Viton E60-C Master Batch	0	20	40	50	60	80	100

Viton B-50 Master Batch - Viton B-50 - 100 gms. ; Diak No. 3 - 2 gms.; Carbon Black - 20 gms.; XNBR (MB_1) - 100 gms.; Diak No. 3 - 2 gms.; Carbon Black - 20 gms.; Viton E-60 C Master Batch - Viton E-60C - 100 gms.; CaO - 5 gms.; MgO - 4 gms.; Carbon Black - 20 gms.; XNBR Master Batch (MB_2) XNBR - 100 gms.;CaO - 5 gms.; MgO - 4 gms.;Carbon Black -20 gms

TABLE IB

Physical properties (blend of XNBR Masterbatch MB_1 and Viton B-50 Masterbatch)

	A	B	C	D	E	F	G
Hardness (°A)	62	73	77	79	83	87	88
Modulus 200% (kg/cm^2)	8.5	21.8	37	49	59	99	76
Tensile strength.(kg/cm^2)	79	105	120	132	124	120	112
Elongation at break (%)	1500	650	600	550	450	250	240
Abrasion loss (cc/1000)	5×10^{-3}	8×10^{-3}	10×10^{-3}	12×10^{-3}	20×10^{-3}	56×10^{-3}	72×10^{-3}
Compression set (%)	82	91	86	84	76	71	60
Υ_{max}- Υ_{min} (dNm)	10.5	15	17	19.5	17.5	19	30
% Vol. Swell in oil	25.4	18	14.6	11.7	8.3	4.1	3.2
After aging (% change in physical properties) at 140°C, 60 hrs.							
Hardness	24	18	15	13	10	4	3
Tensile strength	-47	-58	-58	-58	-52	-32	-13
Elongation at Break (%)	-99	-89	-96	-96	-95	-64	-20

Solvent swelling[9] was carried out to study the phase adhesion between the XNBR and Viton B-50. The swelling coefficient of the blend was well below the additive average line, suggesting swelling restriction, which is further confirmed by the negative slope of the Kraus plot in Figure 1.

1.2 Effect of heat treatment on the properties of the blends. Two different techniques were chosen, the compounding formulations and properties of which are given in Tables IIIA, IIIB and IIIC, respectively.

(a) The Viton elastomers are very tough compared to the XNBR, which causes a difference in the viscosity between the two phases. In this part, the difference in the viscosity between the two masterbatches was reduced by curing the XNBR masterbatch: (i) up to 20%, and then blending it with the Viton masterbatch (set D′) and (ii) up to 60%, and then blending it with the Viton masterbatch (set D″). The properties of the D′ and D″ was compared with that of set D, which had not been precured.

The hardness and modulas increases in both the compounds D′ and D″. The tensile strength increases in D′ but decreases in D″, the elongation at break decreases in both D′ and D″. The properties of D are better than those of D and D″

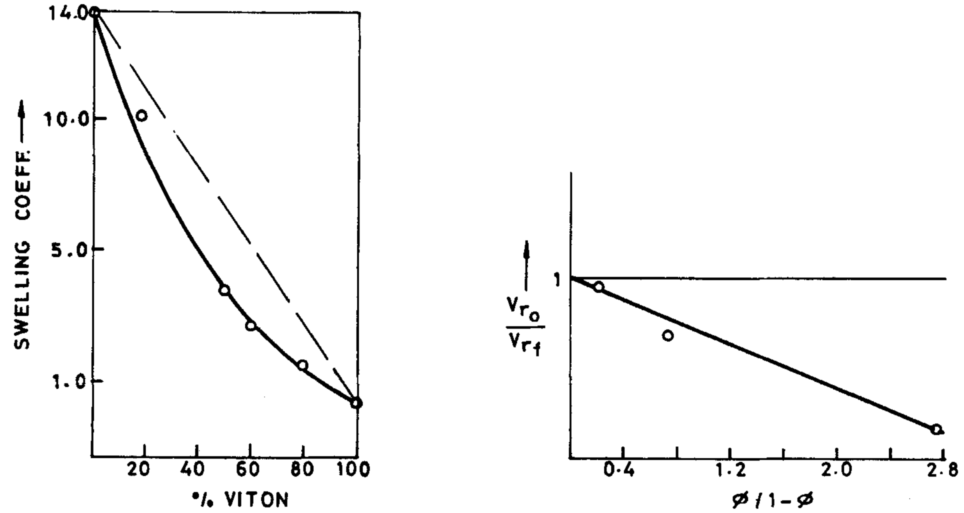


FIGURE 1 Plot of swelling coefficient against Viton and the Kraus Plot V_{ro}/V_{rf} against $\phi/(1 - \phi)$ for XNBR-Viton B-50 system.

TABLE IIIA

Compounding formulations

D	50/50 blend of uncured Viton B-50 masterbatch with uncured XNBR masterbatch MB_1
D′	50/50 blend of uncured Viton B-50 masterbatch with 20% cured XNBR masterbatch MB_1
D″	50/50 blend of uncured Viton B-50 masterbatch with 60% cured XNBR masterbatch MB

TABLE IIIB

Compounding formulations

	Adding curatives to the preblends of gum polymers		Heating the preblends, before adding curatives	
	P	Q	P	Q
XNBR	70	70	70	70
Viton B-50	30	-	30	-
Viton E-60C	-	30	-	30
Diak No.3	2	-	2	-
CaO	-	5	-	5
MgO	-	4	-	4

TABLE IIIC

Physical properties

	D	D′	D″	P	P	Q	Q
Hardness (Shore A)	79	83	83	34	36	60	74
Modulus (200%) (kg/cm^2)	49	68	77	11	11	31	28
Tensile strength (kg/cm^2)	132	156	89	26	29	77	190
Elongation at Break (%)	550	525	275	2500	2400	700	900
$\tau_{max} - \tau_{min}$ (dN-m)	19.5	14.5	17	-	-	-	-
% vol.swell in oil	12	14	9	20	21	18	19
After aging (% change in physical properties) at 140°C, 60 hrs.							
Hardness	13	12	14	35	35	20	14
Tensile strength	-58	-47	+2	-95	-95	-24	-95
Elongation at Break (%)	-96	-95	-81	-95	-95	-57	-88

In compound D, the viscosity of the XNBR phase is less and hence the Viton probably remains clustered in the continuous phase of the XNBR. As a result the blending does not result in uniform dispersion. In the D″, the blending is not uniform because the XNBR masterbatch precured up to 60% becomes too hard for blending. Whereas in the case of D′, the XNBR phase hardens slightly but, sufficiently to match the hardness of Viton masterbatch. These changes brought the relative viscosities of the masterbatches closer together and produced a considerably more homogeneous blend, which is in line with the work of Avgeropoulos *et al.*,[10] and thus results in better properties.

(b) The Viton polymers (XNBR and Viton) were blended and then heated at 170°C for 30 minutes, followed by the addition of curatives. It has been observed that, on heating, the physical properties improve to a small extent. The hardness and tensile strength of the blend vulcanizates increases, the modulus (at 200% elongation) remains same, but the elongation at break decreases to a very small extent. However, the after aging properties, in both the cases, remain the same. The swelling coefficient in $CHCl_3$ improves, but is poor in oil and MEK. As a whole, the heat treatment of the preblended compound does not have any remarkable effect on the blend properties.

2. Blends of Viton E-60 and XNBR (Metal oxide curatives)

2.1 Physical properties. The compounding formulations and properties XNBR-Viton E-60C made by the masterbatch technique are given in Tables IA & IC, respectively, and the compounding formulations of XNBR-Viton E-60C blends prepared by preblending technique is given in Tables IIA & IIB, respectively.

TABLE IC

Physical properties (XNBR Master Batch (MB_2)—Viton E60-C Master Batch)

	A	B	C	D	E	F	G
Hardness (Shore A)	84	85	86	86	88	88	92
Tensile strength (kg/cm^2)	240	48	40	30	65	100	150
Elongation at Break (%)	550	175	170	175	200	200	300
$\tau_{max} - \tau_{min}$ (dN-m)	30	24	19	11	30	63	90
Compression set	61	42	45	48	34	25	20
% vol.swell in oil	30	24	15	11	8	4	3
After aging (% change in physical properties) at 140°C, 60 hrs.							
Hardness	6	7	7	6	6	6	4
Tensile strength	-58	+20	-48	-73	+30	-23	-6
Elongation at Break (%)	-71	-48	-51	-42	-42	-40	-10

TABLE IIA

Compounding formulations

	H	I	J	K	L	M	N
XNBR	100	80	60	50	40	20	0
Viton E-60 C	0	20	40	50	60	80	100
CaO	5	5	5	5	5	5	5
MgO	4	4	4	4	4	4	4
Carbon Black	20	20	20	20	20	20	20

TABLE IIB

Physical properties

	H	I	J	K	L	M	N
Hardness (Shore A)	84	82	86	90	90	91	92
Modulus 200% (kg/cm^2)	120	60	72	80	104	140	110
Tensile strength (kg/cm^2)	240	70	80	88	132	170	150
Elongation at Break (%)	550	375	350	325	400	425	300
$\tau_{max} - \tau_{min}$ (dN-m)	30	8	10	10	27	47	90
Compression set	61	46	50	52	39	30	20
After aging (% change in physical properties) at 140°C, 60 hrs.							
Hardness	6	6	5	5	4	4	4
Tensile strength	-58	-18	- 6	+ 4	-10	-25	-6
Elongation at Break (%)	-71	-80	-76	-69	-70	-66	-10

In the masterbatch technique, the state of cure ($\tau_{max} - \tau_{min}$) and tensile strength decreases and is minimum at 50:50 blend ratio. Hardness and elongation at break gradually increases as XNBR is successively replaced by Viton, whereas, in case of the preblending technique, the state of cure, hardness and tensile strength gradually increases as XNBR is replaced by Viton. The elongation at break is minimum at 50:50 blend composition. It has been observed that the properties in the preblending technique are better than those of the masterbatch technique. This is because, in the masterbatch technique, the curatives and carbon black are added to the individual polymers and then the masterbatches are blended. The interpolymer reaction, therefore, does not occur to the same extent as in the case of preblending technique, where individual polymers are first blended and then the curatives and carbon blacks are added. Aging improves the tensile strength for the masterbatch techniques. Elongation at break, however, decreases in both the cases on aging, although it decrease more in the case of preblending. The percentage volume swell in oil decreases gradually in both cases as the XNBR is replaced by Viton in the blend. Solvent swelling was studied to determine the phase adhesion between the XNBR and Viton. It was observed that in the case of the blend prepared by the preblending technique the swelling restriction takes place and the swelling coefficient of the blend is below the additive average value and thus the phase adhesion is established. This is further confirmed by the negative slope of the Kraus plot in Figure 2. In case of the masterbatch technique, the swelling coefficient is above additive average up to 60% Viton and then the value is less than the additive average. This is also supported by the corresponding Kraus plot. Hence covulcanization seems to take place in the Viton rich blends.

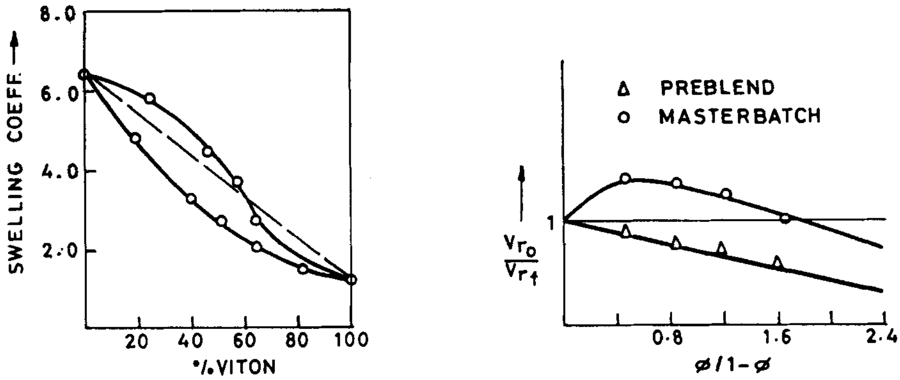


FIGURE 2 Plot of swelling coefficient against Viton and the Kraus plot of V_{ro}/V_{rf} against $\phi/(1 - \phi)$ for XNBR-Viton E-60C system.

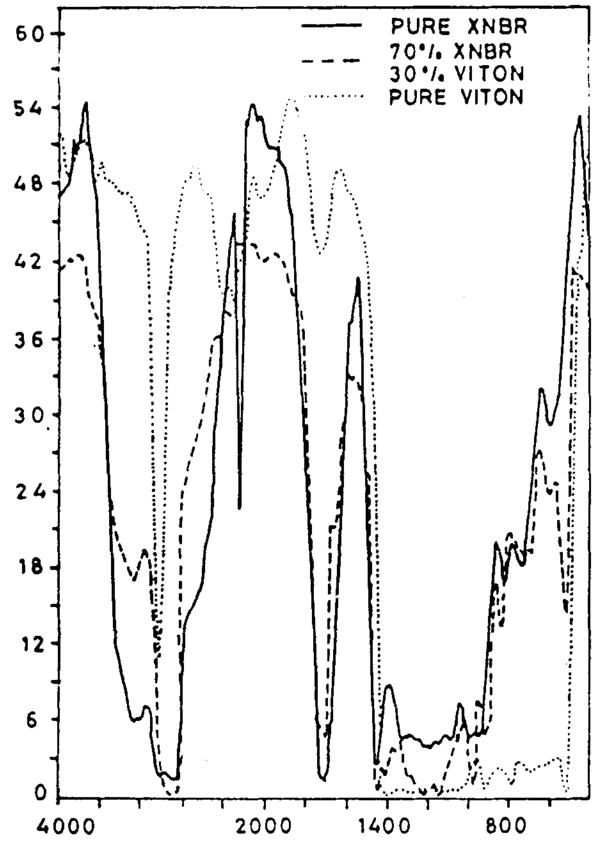


FIGURE 3 IR spectra of the pure XNBR; pure Viton and a blend (70:30 ≈ XNBR:Viton) without curatives.

2.2 Effect of heat treatment on the properties of the blends. In order to find out the effect of heat, the virgin polymers were blended and then heated at 170°C for 30 minutes, followed by the addition of curatives. The compounding formulations and properties are given in Tables IIIB & IIIC, respectively. It was found that, on heating, the physical properties of the blend were improved. The after aging properties of the blend and the percentage volume swell in oil, MEK and $CHCl_3$, however, were not good compared to the blend which had not undergone any heat treatment. This is because, in the first heating, a partial intermolecular reaction occurs and, at the same time, some of the curing sites are destroyed by this high temperature. Therefore, during the curing, the interaction between the two polymers is decreased. The properties of the blend after aging deteriorated because the blend was heated at 170°C twice.

3. IR Spectra Analysis

Figure 3 shows the IR spectra of the pure XNBR, Viton and a blend of 70% XNBR and 30% Viton, heated at 170°C for optimum cure time. There is a peak at 1700 cm^{-1} for —COOH group and a peak at 2241 cm^{-1} for —C≡N group in the pure XNBR.[11] In the IR spectra of the blend, the intensity of the —COOH group is reduced and a new peak at 1730 cm^{-1} appears because of the formation of the ester[12] linkage between the XNBR and Viton. This suggests an interaction between XNBR and Viton occurs at high temperature in the absence of any curative. The probable mechanism for the interaction between the polymers is given below and is in line with curing of Viton with curatives containing functional groups.[13]

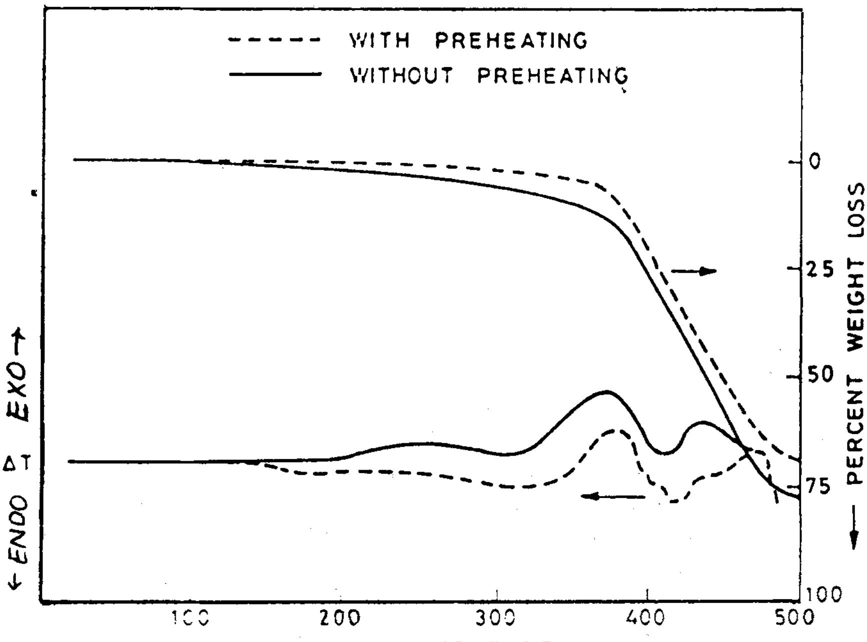
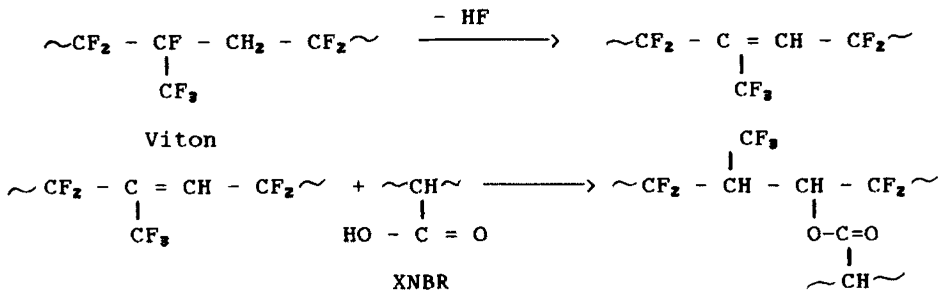
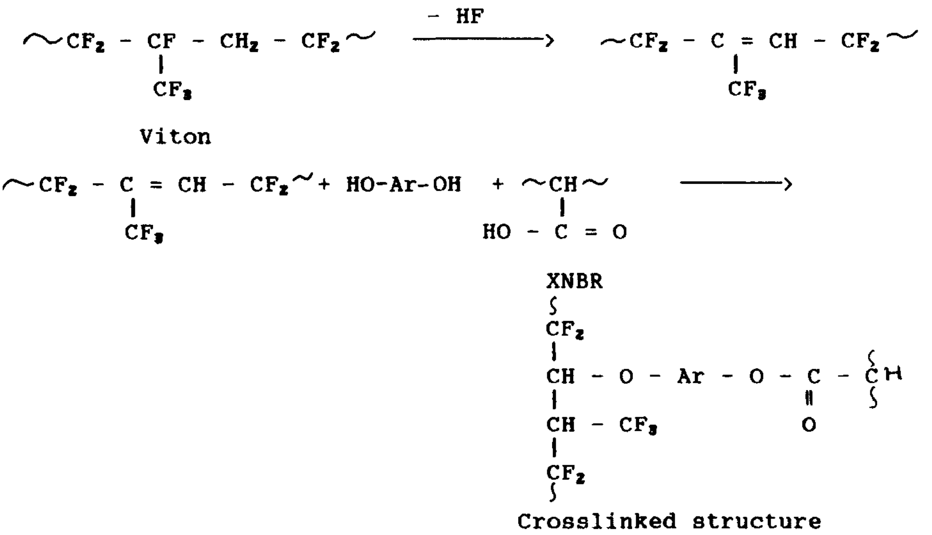


FIGURE 4 DTA and TGA plots of the blend (XNBR:Viton B-50).



In the XNBR/Viton E-60C system, the Viton E-60 contains dihydroxy compound as a curative, already incorporated in the gum polymer.[14] So, in this particular system, the crosslinking between the XNBR and Viton E-60 may take place through the dihydroxy compound on heating the blend, and may be caused by the reaction given below[15]:



4. Thermal Analysis

The DTA/TGA plots are shown in Figures 4 and 5 for XNBR/Viton B-50 and XNBR/Viton E 60-C, respectively, with special reference to the effect of heating. As observed from Figure 4, early degradation occurs in the polyblends system with loss in weight without heating. However, when the blends are preheated the degradation is delayed considerably and there is much less weight loss. This degradation is characterized by exothermic peaks. Figure 5 shows the suppression of the early degradation caused by heating the preblends of XNBR/Viton E 60-C. Note that the degradation starts at higher temperature for XNBR/Viton B-50 blends and lower weight loss than found with XNBR/Viton E 60-C blends.

Heat of vulcanization has been studied for XNBR/Viton B-50 blends. The heat of reaction and onset temperature of the interchain crosslinking reaction are shown in Table IV. Exotherms are observed within this temperature range in each of the

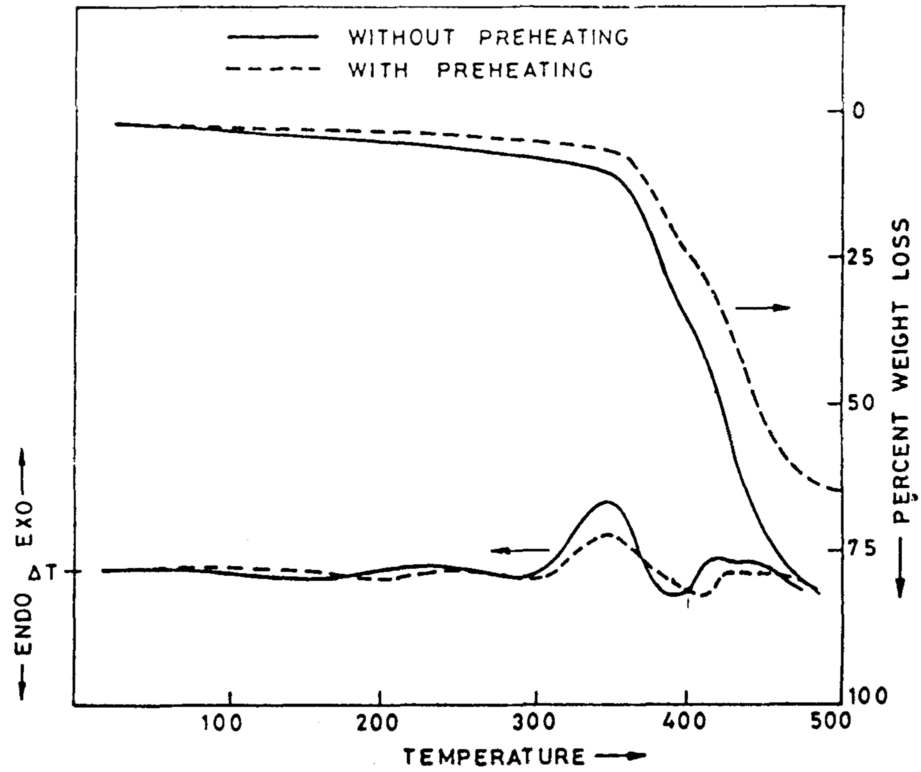


FIGURE 5 DTA and TGA plots of the blend (XNBR:Viton E-60C).

TABLE IV

Sl No.	Blend Ratio XNBR:Viton B-50	Onset temperature of curing (°C)	Heat of vulcanization (exothermic) mcal/mg
1	50:50	126.45	0.94
2	90:10	104.81	0.22
3	70:30	97.00	0.35
4	70:30 (with pre-heating of preblend)	119.00	0.54

four blends, depending on the blend ratio. As the Viton B-50 content in the blends increases, the heat of vulcanizate increases. However, the onset temperature of curing shows a minimum value at its 70:30 ratio. Preheating of the same blends increases both the onset temperature of curing and heat of the vulcanization. This study clearly reveals that there is an interaction between the two type of polymers and the extent of the interaction depends on the blend ratio.

The low temperature DSC plot of the XNBR-Viton E 60-C blend, with and without preheating, is shown in Figure 6. As observed from Figure 6, there is only one T_g for the blend sample. In the case of the preheated sample, there is no

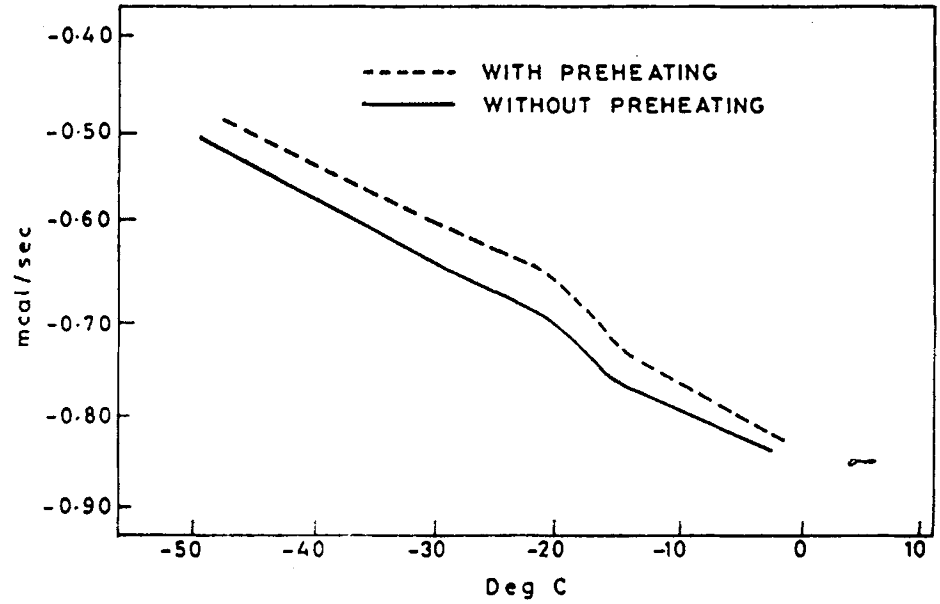


FIGURE 6 Plot of T_g curves of the blend (XNBR:Viton E-60C) with and without preheating of the preblend.

FIGURE 7 SEM photograph of solvent (CH_3Cl) extracted sample of D.

remarkable change in the nature and position of the T_g. As observed, the T_g has been found in the vicinity of $-21°C$. The T_g's of the two elastomers XNBR[12] and Viton[16] are very close and are reported to be at $-23°C$ and $-20°C$, respectively. Hence, it is difficult to conclude on compatibility from this study.

5. SEM Studies

Phase morphology of the blends was studied using a scanning electron microscope of the samples after differential solvent extraction process for the blends D, D′, shown in Figures 7 and 8, respectively. Blends were extracted with $CHCl_3$ where the XNBR phase dissolves out. Figure 6 suggests the presence of larger domains of Vitons, probably because of the inherent viscosity difference between the two components. The domain size of Viton decreases and more uniformly disperses as

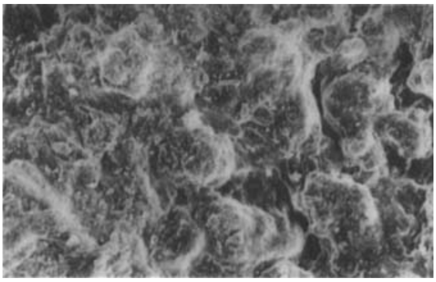


FIGURE 8 SEM photograph of solvent (CH_3Cl) extracted sample of D′

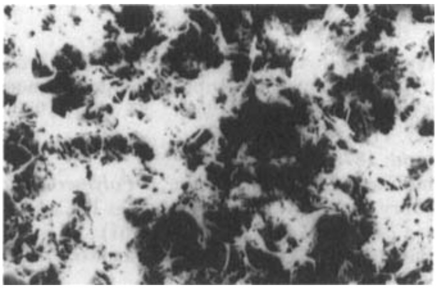


FIGURE 9 SEM photograph of solvent (CH_3Cl) extracted sample of (XNBR:Viton E-60C = 40:60) without preheating.

FIGURE 10 SEM photograph of solvent (CH_3Cl) extracted sample of (XNBR:Viton E-60C = 40:60) with preheating.

the XNBR phase is slightly precured and then blended (Figure 7). In the latter case, both phases seem to be continuous.

Effect of heating on the blend morphology are shown in Figures 9 & 10 for the blends XNBR/Viton-E 60 C 40/60. Figure 9 suggests the easy extraction of XNBR phase. The restricted extraction while heating the blends at high temperature (Figure 10) may be caused by interchain crosslinking between the two phases, as suggested in the earlier sections.

CONCLUSION

Carboxylated nitrile rubber reduces the viscosity and enhances the processibility of the fluoroelastomer. The incorporation of Viton improves the properties of the blend. In the case of XNBR/Viton B-50 blend, slight curing of the XNBR masterbatch improves the properties of the blend. In the case of XNBR/Viton E-60 C blend, the preblending technique gives better properties than the masterbatch technique. Heat treatment of the blend before adding the curatives enhances the phase adhesion due to interchain crosslinking, and improves the properties of the blend. The degradation of the preheated blend system is delayed and the weight loss is also retarded, as compared to the blend with no preheating. Preheating is most effective in the case of Viton E-60-C/XNBR blends than Viton B-50/XNBR blends.

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