

Self-Crosslinkable Plastic–Rubber Blend System Based on Poly(vinyl Chloride) and Acrylonitrile-co-Butadiene Rubber

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SYNOPSIS

That the melt-mixed blend of poly(vinyl chloride) and acrylonitrile-co-butadiene rubber becomes crosslinked during high-temperature molding is evident from Monsanto rheometric, solvent swelling, and infrared spectroscopic studies. Dynamic mechanical analysis shows that such a self-crosslinkable plastic–rubber blend is miscible in different blend ratios. The degree of crosslinking depends on the blend ratios and the molding conditions. The crosslinking reaction involves the allylic chlorine sites in poly(vinyl chloride) and the $\text{—C}\equiv\text{N}$ group in the nitrile rubber. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

While studying the Brabender-mixed blend of poly(vinyl chloride) (PVC) and acrylonitrile-co-butadiene rubber (nitrile rubber or NBR), we observed that the blend gets crosslinked during molding at temperatures above 150°C, even in the absence of any crosslinking agents. This type of polymer mixtures has been designated as self-crosslinkable plastic–rubber blends.¹ Recently Ramesh and De^{1–4} have developed novel self-crosslinkable plastic–rubber blend systems based on polymers containing reactive functional groups that interact and crosslink between themselves during molding. Examples of such blends include PVC-epoxidized natural rubber,¹ PVC-carboxylated nitrile rubber,² polyacrylic acid-polychloroprene,³ and chlorinated rubber-carboxylated nitrile rubber.⁴

The blends of PVC and nitrile rubber have been commercialised since 1940. This blend is still of definite commercial utility. Technically the system has been described as miscible, partially miscible, and even heterogeneous based on the polymer charac-

teristics and mixing conditions.⁵ In a few examples, dynamic mechanical analysis indicates miscibility⁶ whereas microscopic⁷ and calorimetric⁸ studies show the presence of distinct phases. In general, with a range of 23–45% acrylonitrile copolymer content, the blend with PVC has been designated miscible.⁹

We report the results of our studies on the self-crosslinkable, melt-mixed blend of PVC and NBR.

EXPERIMENTAL

Details of the materials used are given in Table I. The blends were prepared in a Brabender Plastimeter (model PLE-330) at 180°C with a rotor speed of 60 rpm. First PVC was allowed to soften for 2 min and then the masticated nitrile rubber was added. The total mixing time was 6 min. Whenever a stabilizer was used, it was thoroughly mixed with PVC in the mixing chamber. The mixed blend was sheeted out in a tight-nipped two-roll mill immediately after being taken out of the plasticorder.

A solution mixed blend was also prepared using a common solvent (tetrahydrofuran, THF). First, PVC and NBR were dissolved in the solvent in separate containers, after which the solutions were mixed and stirred with a mechanical stirrer for 5 h. The solution was then taken in a petri dish and the

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Table I Details of the Materials

Materials	Characteristics	Source
Poly(vinyl chloride) (PVC)	Suspension polymerised PVC(NOCIL PVC S 67-311) K value 66-69	National Organic Chemical Industries Ltd., Bombay, India
Nitrile rubber (NBR)	Krynac 34.50, cold emulsion polymerised Bound ACN: 34% ML-4 (100): 50	Polysar Ltd., Sarnia, Canada
Nitrile rubber (NBR)	Paracryl AJLT Bound ACN: 25.8-29% ML 1+4 (100): 35-50	Uniroyal Chemical Company Inc., CT 06770
<i>cis</i> -1,4-polybutadiene rubber (BR)	Cisamer <i>cis</i> -1,4 content: 96% ML 1+4 (100): 42	Indian Petrochemicals Ltd., Baroda, India
Tribasic lead sulfate (TBLS)	Lead based stabilizer sp. gr.: 6.5	Waldies Ltd., Calcutta, India

solvent was allowed to evaporate in a vacuum oven at 75°C for 12 h.

Rheographs of the blends were taken in a Monsanto Rheometer R 100 at different temperatures. The minimum Mooney viscosity and scorch time were measured using a Negretti Mooney shearing disc viscometer, model MK-III, at 120°C.

The blends were vulcanized at 180°C in a hydraulic press and were cooled to room temperature by running water before being taken out of the press after the molding. The stress-strain and tear properties were measured by Zwick 1445, according to ASTM D 412-87 and D 624-86, respectively. The resilience was measured using a Dunlop Tripsometer and the hardness by a Shore D hardness testing machine, according to BS 903 Part A8 1963, method A and ASTM 2240-86, respectively.

The dynamic mechanical properties were measured in a Rheovibron DDV-III-EP dynamic viscoelastometer at a double strain amplitude of 0.25% and a frequency of 3.5 Hz. The measurements were recorded from -100°C to 150°C at a heating rate of 2°C/min in liquid nitrogen.

Differential scanning calorimetric (DSC) studies were carried out in Dupont 910 machine in nitrogen atmosphere, at a heating rate of 20°C/min. Glass-transition temperature (T_g) was taken as the midpoint of the inflection step in the scan.

Infrared spectroscopic studies were done in a Perkin Elmer IR spectrophotometer (model 843), using either a thin film or a film cast on a Potassium Bromide (KBR) disc. Thin films were made by pressing the sample between aluminium foils at the required temperature (120°C or 180°C).

RESULTS AND DISCUSSION

Mooney Viscometric Studies

Mooney scorch times of the 25/75 and 50/50 PVC/NBR blends are more than 120 min in each case, showing extraordinarily high processing safety of the blends. The minimum Mooney viscosity of the blends increases with increasing PVC fraction as expected (e.g., minimum viscosity of 25/75 and 50/50 PVC/NBR blends are 40 and 90, respectively). The viscosity of the 75/25 PVC/NBR blend was too high to be determined in the Mooney viscometer.

Rheometric Studies

The Monsanto rheographs of the 1 : 1 blend (50/50 PVC/NBR) at 180°C are shown in Figure 1. The rheograph records a gradual increase in torque with time, indicating the formation of a crosslinked network. Though PVC shows a marginal increase in torque with time, NBR does not show such an increase, which eliminates the possibility of thermovulcanization of the individual components in the blend. Figure 1 also shows the rheograph of the 1 : 1 blend of PVC and polybutadiene rubber (BR), which does not register any significant rise in torque. This observation indicates that the acrylonitrile group in NBR copolymer rubber is responsible for the crosslinking reaction with PVC. It is also seen that as the acrylonitrile content in the copolymer decreases, the rise in rheometric torque also decreases. Furthermore, in the presence of a PVC sta-

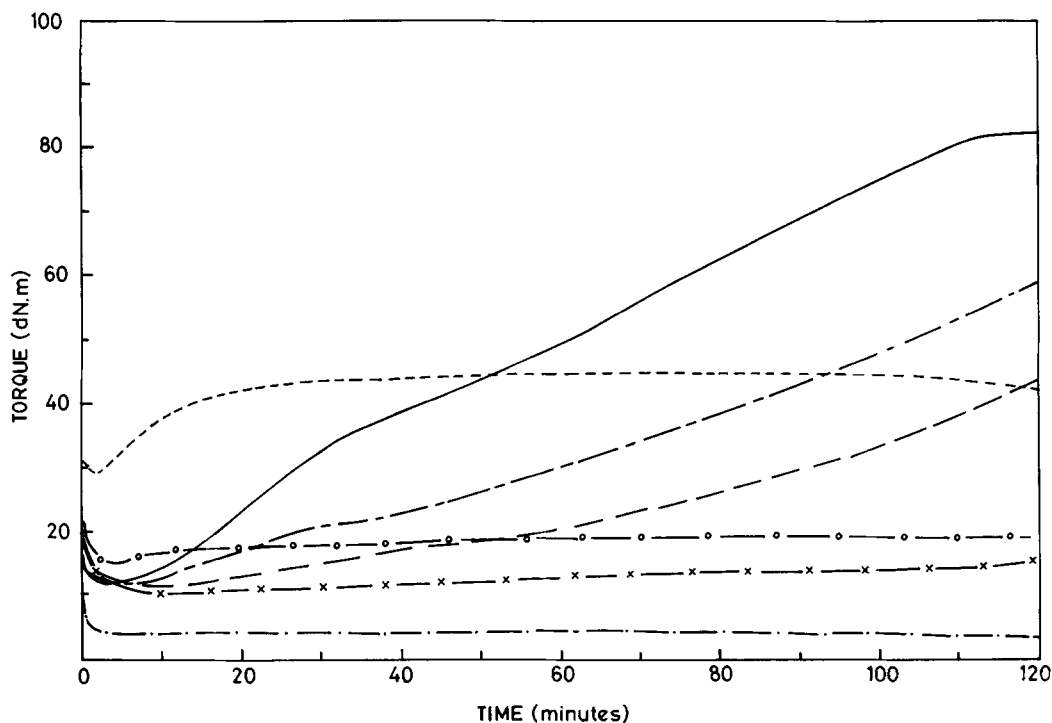


Figure 1 Rheographs at 180°C of PVC (---); NBR (- · - · -); solution-mixed 1 : 1 blend of PVC-NBR (· · · ·); melt-mixed 1 : 1 blends of PVC-NBR (—); stabilized PVC-NBR (- × -); PVC-BR (- ○ -); and PVC-NBR (- ○ -).

bilizer such as tribasic lead sulphate (TBLS), the rise in the torque was drastically reduced indicating that the stabilizer can prevent the crosslinking reaction between PVC and NBR.

Figure 2 shows the rheographs of the system at various blend ratios. It is evident that the 50/50 PVC/NBR blend registers the highest torque rise (72 units), compared to 25/75 PVC/NBR (63 units) and 75/25 PVC/NBR (42 units). This behaviour can be explained on the basis of the stoichiometry of the functional groups required for the chemical interaction. In the case of 25/75 PVC/NBR, the amount of PVC is insufficient to react with the nitrile groups, whereas in 75/25 PVC/NBR the percent of acrylonitrile is far less than sufficient to undergo a reaction to attain a higher degree of crosslinking. Where the functional groups are sufficient to interact with each other to attain the highest degree of crosslinking, 50/50 PVC/NBR forms the optimized blend.

The effect of temperature on the degree of crosslinking is shown in Figure 3. The rheographs are taken for the 50/50 PVC/NBR blend at 150°, 160°, 170°, 180°, and 190°C. It can be seen that as the temperature increases, the extent of crosslinking

increases systematically as indicated by the regular increase in the torque rise from six units at 150°C to 86 units at 190°C in a span of 1 h.

Swelling Studies

Both PVC and NBR are soluble in THF. Although the Brabender-mixed blend, before molding, is soluble in THF, the molded blend swells only to a limited extent, showing the presence of chemical crosslinks. The fact that the extent of swelling depends on the degree of crosslinking is clear from the observation that the percent swelling follows the order 50/50 PVC/NBR < 25/75 PVC/NBR < 75/25 PVC/NBR (Table II). This is expected since 50/50 PVC/NBR shows the highest and 75/25 PVC/NBR the lowest rise in rheometric torque, which can be considered as proportional to the degree of crosslinking.

Mechanism of Crosslinking

On the basis of the Monsanto rheometric studies and infrared spectroscopic studies, discussed below,

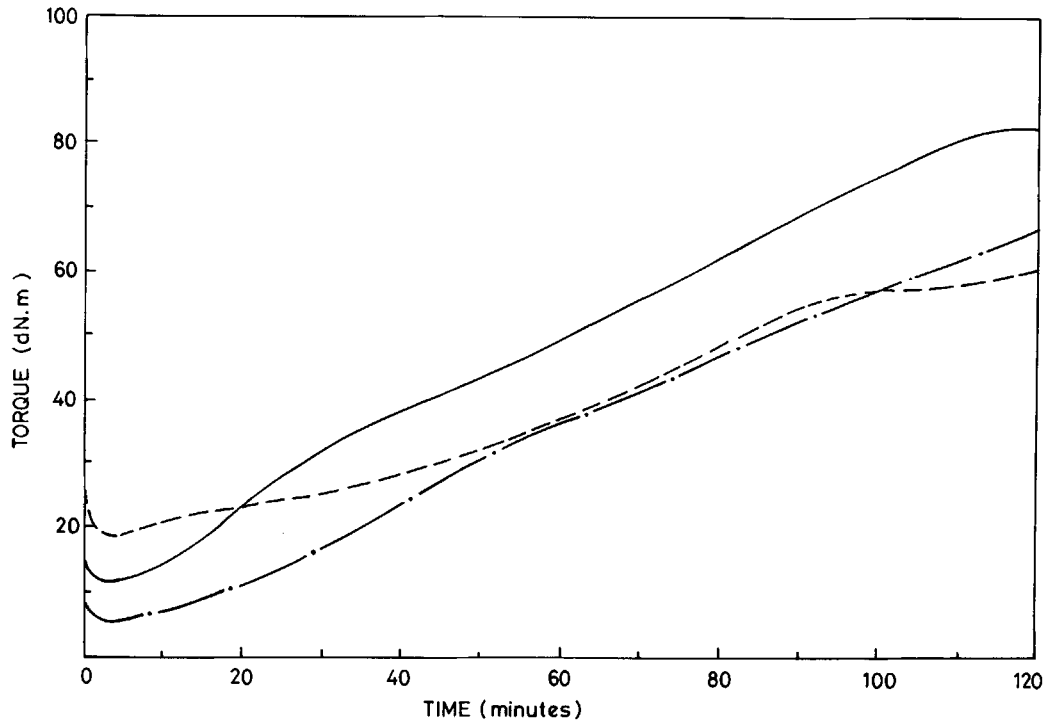


Figure 2 Rheograms at 180°C of PVC-NBR blends for varying blend ratios. 25/75 PVC/NBR (- · -); 50/50 PVC/NBR (—); and 75/25 PVC/NBR (- - -).

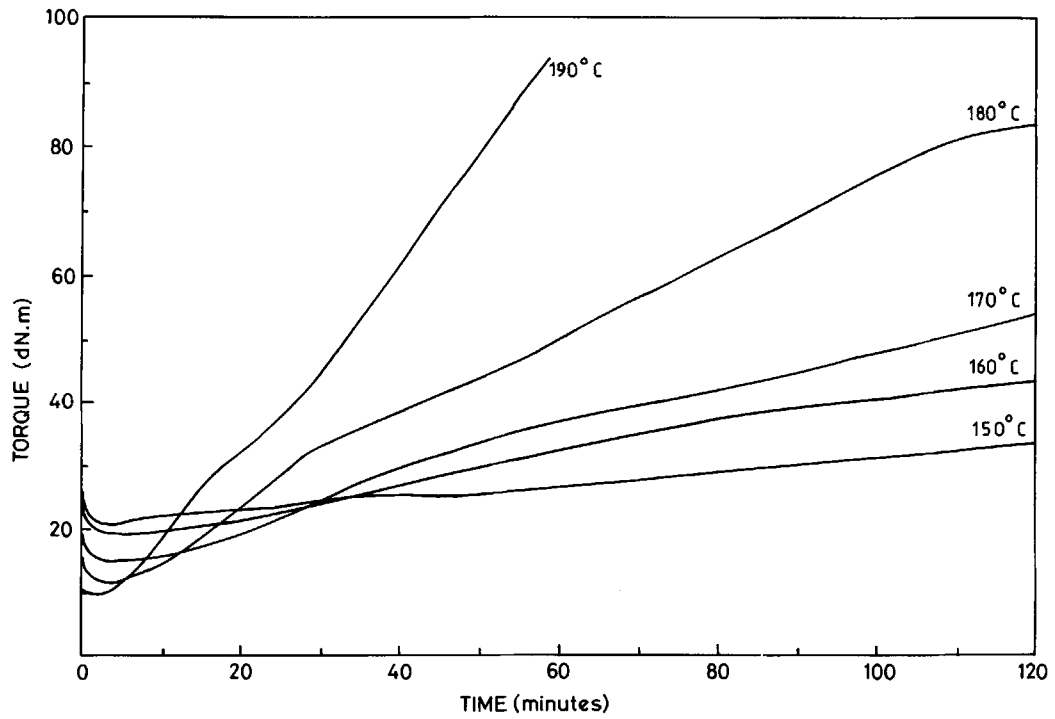


Figure 3 Rheographs of 50/50 PVC/NBR blend at different temperatures.

Table II Physical Properties of the Molded Blends

Properties	25/75 PVC/NBR	50/50 ^a PVC/NBR	50/50 PVC/NBR	75/25 PVC/NBR
100% Modulus (MPa)	1.8	10.2	10.5	24.7
Tensile strength (MPa)	5.8	11.5	14.1	32.0
Elongation at break (%)	450	200	229	100
Tear strength (kN/m)	54	71	82	175
Resilience (% at 50°C)	42	27	27	10
Hardness (shore D)	15	24	24	63
Swelling (% increase in volume, in THF for 48 h at 25°C)	903	Soluble	877	1378

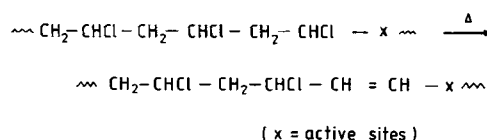
^a Molded for 5 min only (others were molded for 60 min).

the following mechanism is postulated. It is believed that the nitrile group ($-\text{C}\equiv\text{N}$) of NBR and the allylic chlorine site in PVC take part in the crosslinking reaction. It is known that at high temperatures thermal decomposition of PVC takes place via the elimination of hydrogen chloride (HCl) from an active site (a tertiary carbon or an allylic site) leading to the formation of a double bond with an adjacent chlorine atom, thus creating a new allylic chlorine site.¹⁰ Allylic chlorine sites in PVC have been shown to be the least stable and hence the most susceptible to replacement.¹¹ At high temperatures considerable HCl liberation will take place since the degradation reaction is autocatalytic.¹² The HCl that is liberated *in situ* reacts with the nitrile group in the presence of moisture, hydrolysing it to the respective amides and acids depending on the reaction conditions. The controlled hydrolysis of the nitriles to the respective amides and acids in the presence of HCl is well known.¹³ Finally, the allylic chlorines of PVC react with the amide and acid groups of NBR forming a crosslink as shown in Figure 4.

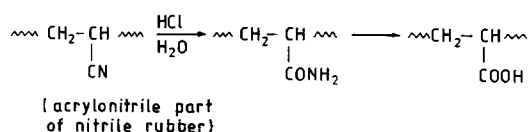
However the extent of reaction does not depend directly on the concentration of the functional groups. This is because the crosslinking reaction demands the degradation of PVC and subsequent liberation of HCl for the hydrolysis of the nitrile group. In the presence of the stabilizer TBLS, which is believed to stabilize PVC by the absorption of any liberated HCl and blockage of the allylic sites,¹⁴ the hydrolysis of the nitrile group cannot take place and accordingly, there is no chemical reaction and hence no increase in the rheometric torque in the stabilized system. On the contrary, when the percentage of the nitrile groups is increased in the NBR copolymer, more amide and/or acid groups are produced, re-

sulting in a higher degree of crosslinking. Furthermore, as shown in Figure 1, the solution-mixed blend has shown less rheometric torque than the melt-mixed blend. In the latter case the high temperature of mixing and high shearing action cause the initiation of the chemical reaction even in the mixing

Formation of allylic chlorine sites in PVC



Hydrolysis of $-\text{C}\equiv\text{N}$ group



Crosslinking reaction

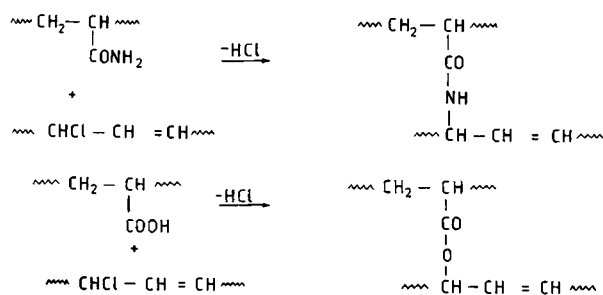


Figure 4 Proposed mechanism of the crosslinking reaction.

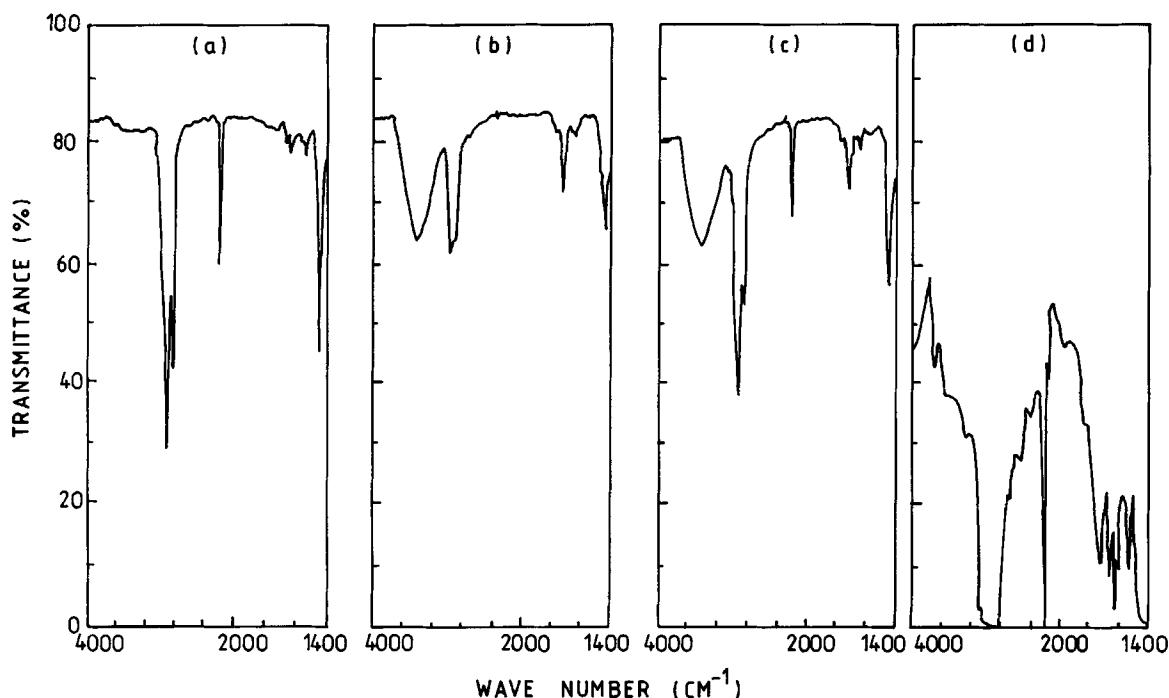


Figure 5 Infrared spectra of (a) NBR; (b) PVC; (c) solution-mixed 1 : 1 blend; and (d) melt-mixed 1 : 1 blend of PVC-NBR.

stage, though the time of mixing is not sufficient to cause a significant reaction. This is evident from Figure 1 where the minimum torque values of both the blends are identical.

Infrared Spectroscopic Analysis

Figure 5 shows the IR spectra of the neat polymers NBR, PVC, the solution-mixed, and the melt-mixed blends (molded at 120°C for 2 min). The spectra of the Brabender-mixed 50/50 PVC/NBR blend, molded for 5, 15, 30, and 60 min are shown in Figure 6. Upon comparing the spectra of the solution-mixed blend and the melt-mixed blend molded for 60 min, it is evident that certain new bonds have been formed. The presence of a broad peak (3400–2840 cm^{-1}) in the spectrum of the molded specimen can be assigned to the stretching vibrations of the newly formed N—H and O—H bonds coupled with the C—H stretching vibrations, the latter showing only a small peak at 2929 cm^{-1} as seen in the spectra of the solution-mixed blend. The $> \text{C}=\text{O}$ stretching peak that would have come from the amide, acid, or ester groups could not be distinguished clearly from the peak at 1723 cm^{-1} of PVC, which has been reported to be caused by aldehyde and ketonic groups formed during the PVC manufacturing stage.^{15,16} The peak at 1733 cm^{-1} with a small shoulder in the

lower frequency region can be visualised as one different from the peak coming from PVC.

The chemical changes that take place gradually with an increase in the molding time can be visualised from the spectra shown in Figure 6. The progressive broadening of the peaks at 3300–2800 cm^{-1} clearly indicates the formation of N—H and O—H groups in the system. The peak at 1600 cm^{-1} seen in the spectra of the melt-mixed blend and of those molded for 5 and 15 min, is the amide II band that disappears at higher molding time since most of the amides are converted to either tertiary amides or the acid groups (Fig. 4). The amide I band, which is expected at 1640–1670 cm^{-1} , is not distinguished from the C=C stretching vibrations (1665–1637 cm^{-1}). The 1530 cm^{-1} peak present at lower molding times [Fig. 6(a) and (b)] might be caused by the triazine derivative formed by the cyclization of the nitrile group.¹⁷ It disappears as the reaction proceeds since the HCl can cause the ring opening.¹⁸ The results are summarised in Table III.

Dynamic Mechanical Analysis

The temperature dependence of the dynamic storage modulus E' for the blend as well as the individual components as a function of blend ratio is shown in Figure 7. The variation of the loss tangent ($\tan \delta$)

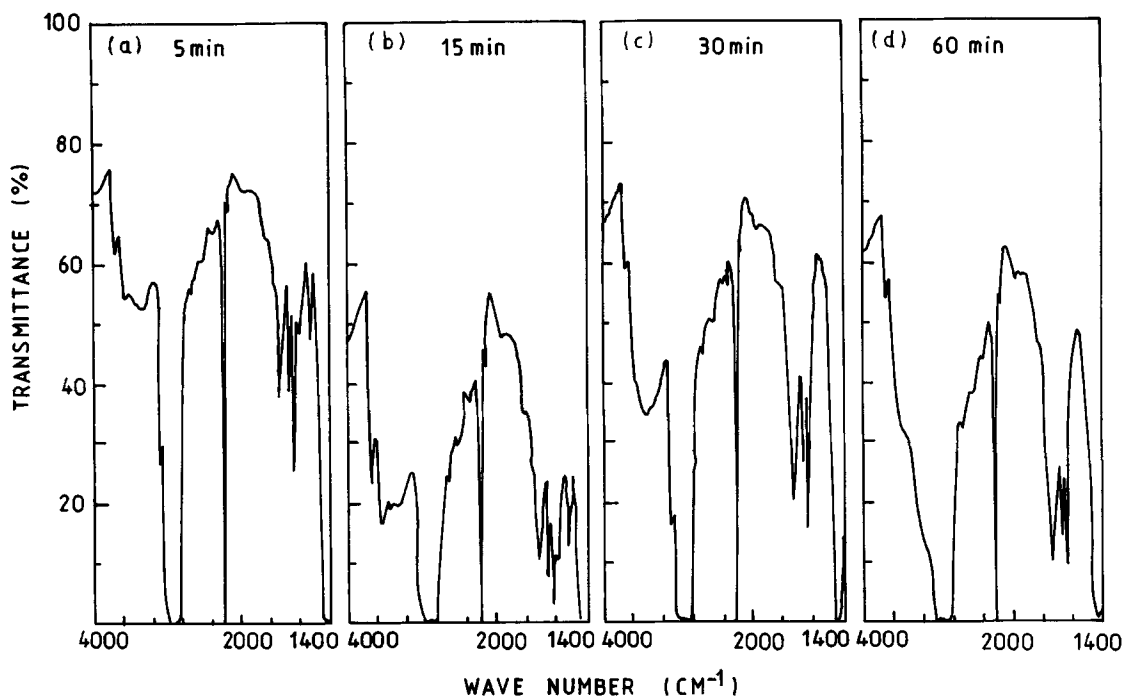


Figure 6 Infrared spectra of 50/50 PVC/NBR blend at different molding times.

with temperature is shown in Figure 8. It is apparent that all three blends show miscibility, i.e., the blends show single transitions that occur in between those of the individual components. This is true with both the storage modulus and loss tangent curves. But the transition temperature increases to the higher side as the percent of PVC is increased. It can be seen that the 25/75 PVC/NBR blend shows a sharp peak at the transition zone, whereas the other two blends exhibit broad transition regions, indicating

the presence of microheterogeneity in the latter cases. This is also observable from the increased slope of the modulus-temperature curves. Table IV summarises the glass-transition temperature of the different blends measured from the loss tangent plots.

Differential Scanning Calorimetry

The DSC thermograms of the pure polymers and the blends molded at 5 and 60 min are shown in

Table III IR Peak Assignments

Wave Number (cm ⁻¹)	Functional Group	Assignment of Band	NBR	PVC	Blend	Reference
3670-2500	Acid O—H	γ_{O-H}	—	—	3400-2840	17
3350-3200	Amide N—H	γ_{N-H}	—	—		17
3050-3000	Alkyl C—H	γ_{C-H}	2923-2847	3223-2953		17
2975-2840	Alkenyl C—H	γ_{C-H}	—	—	2221	17
2260-2200	Aliphatic C≡N	$\gamma_{C=N}$	2222	—		
1750-1725	Aliphatic ester, C=O	$\gamma_{C=O}$	—	—	1733	17
1725-1700	Aliphatic acid, C=O	$\gamma_{C=O}$	—	—		17
1722	Aliphatic CHO, C=O	$\gamma_{C=O}$	—	1722	1666	15,16
1680-1620	C=C	$\gamma_{C=C}$	1664	—		17
1680-1630	2'/3' amide I	$\gamma_{C=O}$	—	—	1600	17
1580-1520	Amide II	$\gamma_{C-N} + \delta_{N-H}$	—	—		
1560-1520	Sym. triazines	In-plane stretching	1530	—	1529-1533	17

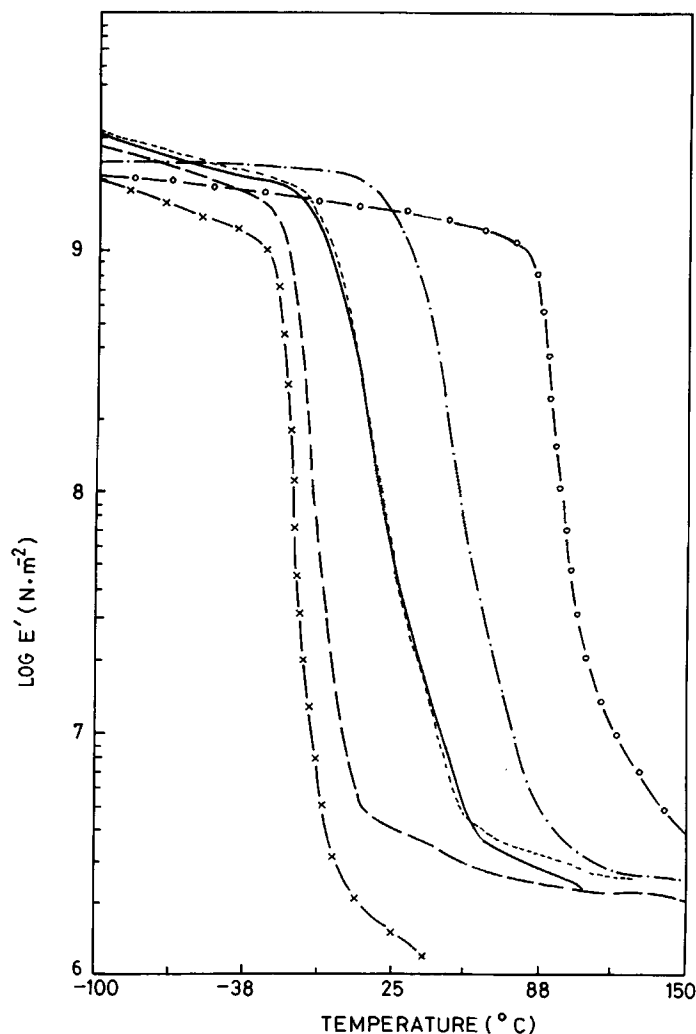


Figure 7 Plot of storage modulus (E') vs. temperature of NBR ($- \times -$); 25/75 PVC/NBR (60 min) ($- - -$); 50/50 PVC/NBR (5 min) ($—$); 50/50 PVC/NBR (60 min) ($- - -$); 75/25 PVC/NBR (60 min) ($- \cdot -$); and PVC ($- \circ -$). Blends are molded at 180°C. Molding times are indicated in brackets.

Figure 9. The results are almost similar to that of the dynamic mechanical studies except the 75/25 PVC/NBR blend. Irrespective of the molding time, 25/75 PVC/NBR and 50/50 PVC/NBR blends show single peaks in between those of the individual components that move upward in the temperature scale as the percent of PVC increases. But the 75/25 PVC/NBR blend shows three transitions that correspond to a miscible part and some microheterogeneities where the concentration of one minor component in the phase of the major component shifts the T_g of the latter. These types of heterogeneities have been observed earlier in PVC-NBR blends.⁸ This behaviour, which is different from the dynamic mechanical studies, has been explained by the hypothesis that DSC sees a smaller volume ele-

ment than mechanical spectroscopy.⁵ Another interesting observation is that the chemical reaction narrows down the width of the transition in all the blends. This has been observed in the dynamic mechanical studies of the 50/50 PVC/NBR blend also. This could be caused by the specific chemical interactions between the two moieties that enhance the miscibility. Table IV summarizes the glass-transition temperature of the blends.

Physical Properties

Figure 10 shows the stress-strain plots of the blends and Table II summarizes the physical properties. The tensile strength increases with the percent of

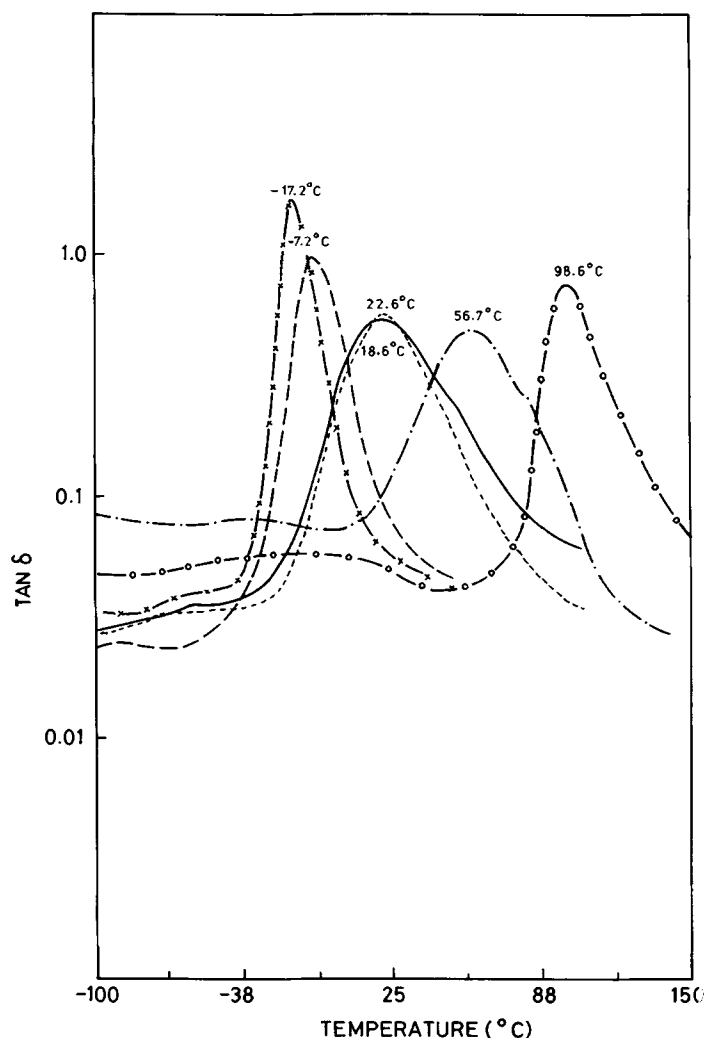


Figure 8 Plot of loss tangent vs. temperature of the blends and the single polymers (symbols as in Fig. 7).

PVC. It is apparent that the crosslinking reaction improves the ultimate properties like tensile and tear strength, as shown in the case of 50/50 PVC/NBR

Table IV Glass-Transition Temperature (in °C) Obtained from Calorimetric (DSC) and Dynamic Mechanical Analyses (tan δ)

Sample	T_g Obtained From	
	DSC	tan δ
NBR	-32	-19.2
25/75 PVC/NBR	-20.6	-7.2
50/50 PVC/NBR*	-3.8	18.6
50/50 PVC/NBR	1.2	22.6
75/25 PVC/NBR	8.6, 39, 71.5	56.7
PVC	83	98.6

* Molded for 5 min. Other blends are molded for 60 min.

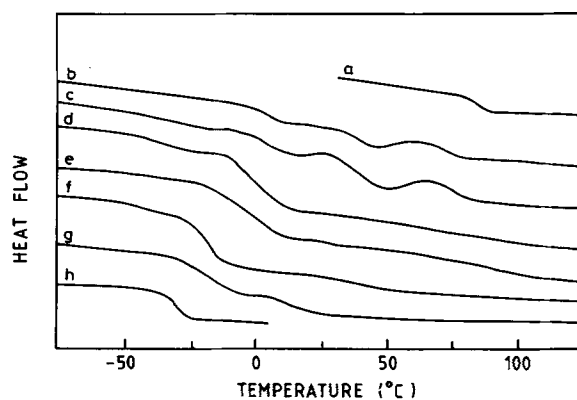


Figure 9 DSC thermograms of the blends. (a) PVC; (b) 75/25 PVC/NBR (60 min); (c) 75/25 PVC/NBR (5 min); (d) 50/50 PVC/NBR (60 min); (e) 50/50 PVC/NBR (5 min); (f) 25/75 PVC/NBR (60 min); (g) 25/75 PVC/NBR (5 min); and (h) NBR. Blends are molded at 180°C. Molding times are indicated in brackets.

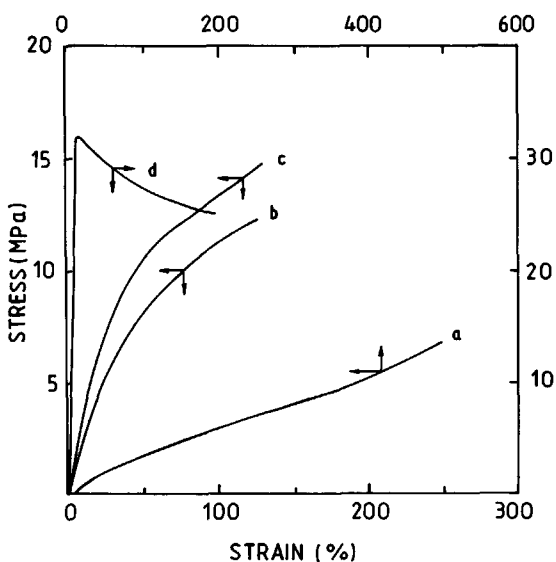


Figure 10 Stress-strain plots of the molded blends, (a) 25/75 PVC/NBR (60 min); (b) 50/50 PVC/NBR (5 min); (c) 50/50 PVC/NBR (60 min); and (d) 75/25 PVC/NBR. Blends are molded at 180°C. Molding times are indicated in brackets.

blend molded for 5 min (curve b) and 60 minutes (curve c).

CONCLUSIONS

The PVC-NBR blend is self-crosslinkable, which is evident from the rheometric, swelling, and infrared spectroscopic studies. The chemical reaction takes place between the $\text{—C}\equiv\text{N}$ group in the nitrile rubber and the allylic chlorines in PVC in the presence of HCl liberated by the degradation of PVC. Such crosslinkable blend is miscible and the chemical reaction even improves the miscibility of the blend as is evident from the dynamic mechanical and differential scanning calorimetric studies. The

blends have good processing safety and physical properties.

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