

An investigation of the chemical interactions in blends of poly(vinyl chloride) and nitrile rubber during processing

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Poly(vinyl chloride)–nitrile rubber blends undergo a self-crosslinking reaction (crosslinking without the aid of any external curing agents) during processing at elevated temperatures, resulting in an increase in torque, as studied by means of a Brabender Plasticorder. The extent of the reaction depends on the blend composition, processing temperature, shear rates, fill factor and the presence of a PVC stabilizer. The chemical interaction is analysed by infrared spectroscopy, which shows that the reaction involves the hydrolysis of the nitrile group by HCl liberated during the degradation of PVC. © 1997 Elsevier Science Ltd.

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INTRODUCTION

The chemical reactions occurring in the thermal processing of polymer blends have received continued attention, since they have to be processed in one way or other at elevated temperatures^{1–6}. In many a process, such as extrusion and injection moulding, the molten polymers experience relatively high rates of shear and hence non-uniform heat generation. This may result in polymer degradation and/or formation of crosslinks. It is commonly found that the melt flow rate of the material taken out from the processing stage is either higher (due to crosslinking) or lower (due to degradation) than that of the starting materials^{7,8}. Rheological properties are conveniently used to monitor the crosslinking and degradation processes in polymers^{9–11}. Numerous studies on the rheological properties of polymers with torque rheometers (e.g. the Brabender Plasticorder) have been carried out^{12–16}. Torque rheometers are multi-purpose instruments well suited for studying the flow behaviour, thermal and shear sensitivity, batch compounding, formulation of multicomponent polymer systems and so on^{17,18}. It is essentially an instrument that measures the viscosity-related torque caused by the resistance of the material to the shearing action of the plasticating process^{17,18}.

Blends of poly(vinyl chloride) (PVC) and nitrile rubber (NBR) are commercially important and have a wide range of applications^{19–22}. Watanabe²¹, in his review article, showed that in well mixed blends of most polymer pairs, the presence of two phases is evidenced by two glass transitions (measured by DMA) indicating the immiscible nature of the blend; in contrast, many authors found a single broad glass transition over a temperature range between the two T_g s of the unblended components: they reported the blend as miscible. Matsuo *et al.*²³ described the NBR/PVC blend as 'semi-compatible' at 20% acrylonitrile (AN) content and 'almost homogeneous' at 40%. In our earlier work²⁴, we

also observed from differential scanning calorimetry (d.s.c.) and dynamic mechanical analysis (DMA) that the miscibility of a PVC/NBR blend depends on blend ratio, acrylonitrile (AN) content of NBR and the testing method. So technically the PVC/NBR blend has been described as miscible, partially miscible and even immiscible, depending on the method of preparation, acrylonitrile (AN) content of NBR and the testing method. Recently, it has been shown that the blend undergoes a crosslinking reaction at high temperature without the aid of any extraneous curing agents²⁴. Such novel polymer blends that undergo thermally induced crosslinking have been termed 'self-crosslinkable polymer blends', and some examples include carboxylated nitrile rubber (XNBR)/epoxidized natural rubber (ENR)²⁵, PVC/ENR²⁶, chlorinated rubber/XNBR²⁷, chlorosulfonated polyethylene/ENR/XNBR²⁸ and sulfonated EPDM/ENR²⁹ blends.

This paper presents studies on the processability of PVC/NBR blends using a Brabender Plasticorder and the effect of thermal and shear-induced chemical reactions.

EXPERIMENTAL

Materials

Poly(vinyl chloride). NOCIL PVC S67-311 (National Organic and Chemical Industries Ltd, Bombay, India). Suspension polymerized; K value 66–69.

Nitrile rubber. Paracryl CJLT (Uniroyal Chemical Company, Connecticut, USA). Percentage acrylonitrile: 38.5–41.0; $ML_{(1+4)}$: 50.

Butadiene rubber (BR). Cisamer (Indian Petrochemical Ltd, Baroda, India). Percentage cis-1,4: 96; $ML_{(1+4)}$ at 100°C: 42. Blends of PVC and BR are included for comparison so that any effect of the nitrile group can be identified.

Tribasic lead sulfate (TBLs). PVC stabilizer (Waldies Ltd, Calcutta, India). Sp. gr.: 6.5.

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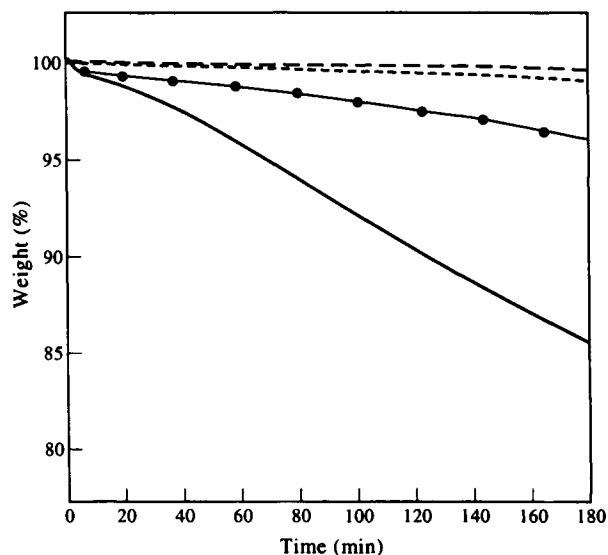


Figure 1 T.g.a. curves of 50/50 PVC/NBR blends at 160°C (---), 180°C (-●-●-), 200°C (—) and of a stabilized blend at 180°C (- - -)

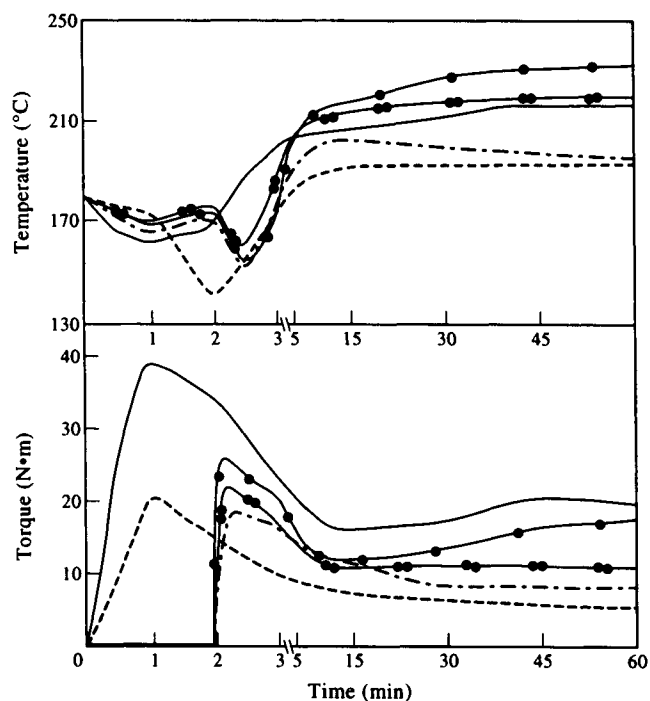


Figure 2 Changes in the torque and batch temperature during mixing of PVC (—), NBR (- - -), 50/50 PVC/BR (— - —), 50/50 PVC/NBR (-●-●-●-) and stabilized 50/50 PVC/NBR (-●●-●●-●●-)

Procedure

A Brabender Plasticorder (model PLE 330) was used in the studies. As the mixing chamber attained the set temperature, PVC was charged and allowed to soften for 2 min. Then masticated nitrile rubber was added and mixing continued. Zero time was taken as the moment PVC was charged. The charging operation normally took 15–30 s. Whenever a stabilizer was used, it had been thoroughly mixed with PVC before charging. The temperature of the batch was monitored by means of a thermocouple inserted through the bottom of the chamber. The torque and the temperature were plotted using an XY recorder.

The variables selected for the study were blend composition, processing temperature, rotor speed, fill

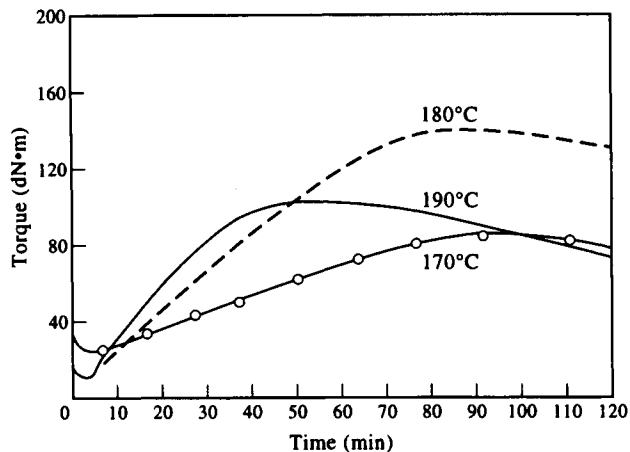


Figure 3 Rheographs of 50/50 blends of PVC/NBR at different temperatures: 170°C (-○-○-), 180°C (- - -) and 190°C (—)

factor of the chamber, and the presence of a PVC stabilizer. The mixing conditions are summarized in Table 1.

Rheographs of the PVC/NBR (50/50) blends were taken in a Monsanto Rheometer R100 at three different temperatures (Figure 3), 170, 180 and 190°C, for 120 min to find out when degradation started.

Swelling studies were carried out in tetrahydrofuran (THF), which is a common solvent for both PVC and NBR. The samples were taken out after mixing for 60 min (after 45 min in the cases where the torque decreased after attaining a maximum value), weighed (w_1) and kept immersed in the solvent at 30°C. After 48 h, the swollen samples were taken out, wiped dry and weighed (w_2). The percentage swelling is calculated as

$$\% \text{ swelling} = (w_2 - w_1)/w_1 \times 100$$

For infrared spectroscopic analysis, thin films were prepared with samples taken out after mixing for 60 min (after 45 min in the cases that showed a decrease in torque after attaining a maximum). Samples were compression moulded at 150°C for 2 min in between aluminium foils. The spectra were obtained using a Shimadzu IR 470 spectrophotometer.

Thermal analysis was carried out in a Dupont 951 thermogravimetric analyser. Isothermal thermogravimetric analysis for PVC/NBR (50/50) blend and stabilized blend was performed at three temperatures, 160, 180 and 200°C, in order to choose the time and temperature of mixing.

RESULTS AND DISCUSSION

Thermogravimetric analysis

Isothermal thermogravimetric analysis reveals the difference in the extent of degradation at different temperatures and in the presence of a stabilizer, as shown in Figure 1. At 200°C, the rate and extent of degradation is the highest, as indicated by the maximum weight loss. The weight loss is considerably less at 160°C, even after 180 min. The stabilizer completely prevents any degradation (that leads to weight loss), while the unstabilized blend degrades to some extent at 180°C. Since the degradation of PVC and the liberation of HCl is a necessary condition for crosslinking, the blend seems to form the highest degree of crosslinking at high temperature (180°C and above). The stabilizer hinders the degradation of PVC, and hence the crosslinking reaction is precluded.

Table 1 Processing variables

Variables	Blend ratio	Mixing temperature (°C)	Rotor speed (rpm)	Fill factor
Blend ratio	100/0, 75/25, 50/50, 25/75, 0/100	180	60	0.9
Mixing temperature	50/50	160, 170, 180, 200	60	0.9
Rotor speed	50/50	180	40, 60, 80	0.9
Fill factor (f.f.)	50/50	180	60	0.5, 0.7, 0.8, 0.9
Stabilizer (TBLS) (5 phr)	50/50	180	60	0.9

Table 2 Kinetics parameters for crosslinking reaction of PVC/NBR (50/50) blend

				Activation energy (kJ mol ⁻¹)
(a) From rheometer (Figure 3):				
Temperature (°C)	170	180	190	
Rate constant <i>K</i> (min ⁻¹)	0.0234	0.0620	0.0964	118.06
(b) From Brabender Plasticorder mixing (Figure 5):				
Temperature (°C)	170	180	200	
Rate constant <i>K</i> (min ⁻¹)	0.0420	0.0432	0.1970	91.81

Brabender studies

The formation of crosslinks in the system should increase the molecular weight and the viscosity, and this is to be manifested in the increase in torque during mixing. Figure 2 shows the torque–temperature–mixing time profile of the single polymers and the 50/50 blends of PVC/NBR and PVC/BR. All the systems take 3–4 min for equilibration (melting and mixing) after which the torque remains constant for some time; further increase, if any, is due to the crosslinking reaction. The 50/50 PVC/NBR blend shows a good increase in torque by the end of 30–60 min. The progressive rise in torque and temperature with time, after the initial melting and mixing, shows the gradual formation of crosslinks in the system. Of the single polymers, NBR does not show any rise in torque whereas PVC shows an increase up to 60 min. It is known that PVC undergoes thermal degradation at high temperatures to yield hydrogen chloride (HCl) and conjugated polyene structures, which are highly coloured and crosslinked^{30–32}. However, this increase in torque in the case of PVC alone is not implied in the case of the blends, as is evident from the PVC/BR blends which show only a continuous decrease in the torque values (Figure 2). This may be due to the fact that the amount of PVC is less and the extent of degradation lower in the case of the blends. BR does not contain any active group like acrylonitrile (AN), whereas NBR contains this AN group (–C≡N) which is very susceptible to reaction with acid liberated by the degradation of PVC³³. Due to this interaction, a torque rise takes place²⁴. Hence, crosslinking takes place through the AN group in NBR²⁴. Figure 2 also shows the torque–time profile of a TBLS-stabilized 50/50 PVC/NBR blend which fails to register any torque rise as there is no HCl elimination. This indicates that the active sites in PVC for the crosslinking reaction are HCl, generated during its degradation. Similar observations were made during rheometric studies.

Figure 2 further shows the changes in the processing temperature with mixing time. Initially the temperature drops below the set temperature on the addition of PVC and rubber. After this, the temperature begins to rise due to viscous dissipation. However, it is seen that major torque rises are accompanied by large increases in temperature. For

PVC/NBR (50/50) blend, the temperature rise is about 50°C (180°C to 230°C), whereas for pure PVC, it is only 30°C. This may be attributed to the heat of the crosslinking reaction, which may be further confirmed from the rheometric studies.

Monsanto rheometric experiments were carried out for longer times at three different temperatures, 170°C, 180°C and 190°C, for PVC/NBR (50/50) blend, which takes 100, 80 and 50 min to reach the maximum torque values at 170°, 180° and 190°C respectively (Figure 3). It is interesting to note that the highest torque rise is at 180°C, though the rate of reaction is higher at 190°C. This may be due to the fact that, at 190°C, degradation of the polymer sets in at an earlier stage than at 180°C. Rheometric studies also support the crosslinking reaction³⁴. The observed increase in torque at a given time is directly related to the crosslink density, particularly if the measurements are done at relatively low frequencies.

The kinetic principle of rubber crosslinking is based on the kinetic theory of elasticity. It assumes a direct relation between the calculated shearing modulus and the crosslinking density. In the rheometer, the shearing strain is constant, the shear stress or torque value is proportional to the crosslinking density. If one assumes that the crosslinking reaction follows a first-order kinetic, it can be shown that

$$\ln(M_\alpha - M) = -kt + \ln(M_\alpha - M_0) \quad (1)$$

where M = torque at time t , M_0 = minimum torque, M_α = maximum torque, and k = rate constant.

A plot of $\log(M_\alpha - M)$ versus time will give a straight line; from the graph, k , the reaction rate constant, is measured³⁵. The rate constants are given in Table 2.

The activation energy for the thermally induced crosslinking reaction for PVC/NBR is 118.06 kJ mol⁻¹, which is of the order of magnitude for the conventional curing reaction of elastomers³⁶. Recently, González *et al.*³⁵ found the activation energy for the peroxide crosslinking of diene rubber to be 139.80 kJ mol⁻¹.

Effect of blend composition

The torque–time–temperature curves of PVC/NBR blends with varying composition at 180°C are shown in Figure 4. As compared to the 50/50 and 25/75 blends, the 75/25 PVC/NBR blend shows the highest increase in torque. However, the torque reaches a maximum in about 30 min, after which it falls. This may be because degradation sets in due to shear and temperature. The batch temperature also falls after degradation. The 50/50 and 25/75 blends show continuous increase even after 60 min with continuous increase of temperature. The difference in the behaviour of the different blend compositions is attributed to the difference in the stoichiometry of the functional groups required for the reaction. The rate of the reaction is not directly dependent on the concentration of the functional groups available, since the reaction requires the degradation

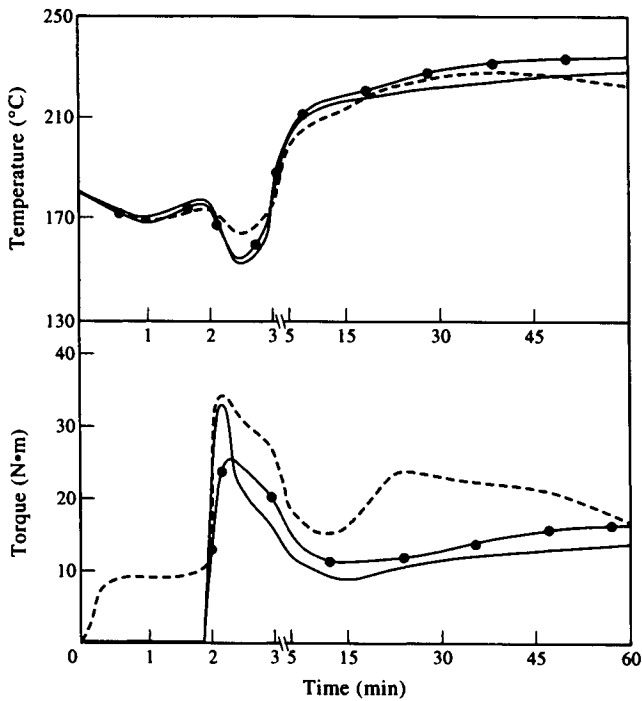


Figure 4 Changes in the torque and batch temperature during mixing of 75/25 (---), 50/50 (-●-●-) and 25/75 (—) PVC/NBR

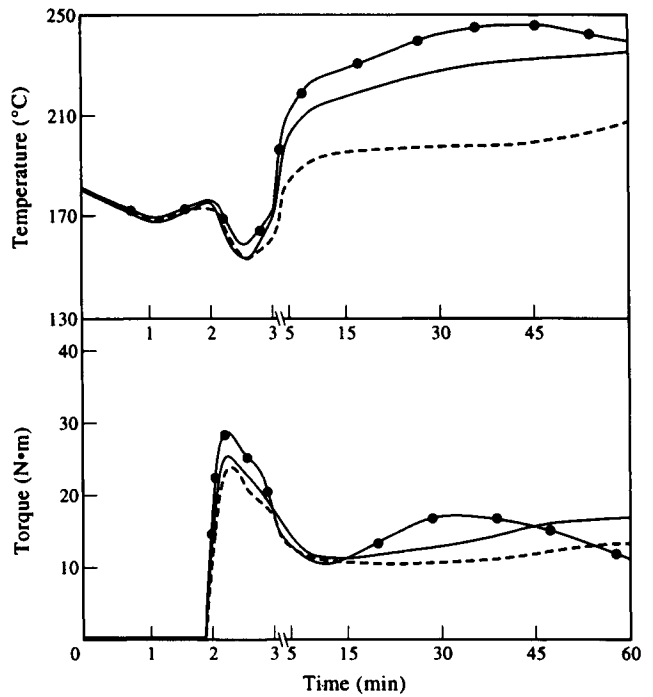


Figure 6 Changes in the torque and batch temperature during mixing of 50/50 PVC/NBR mixed at 40 rpm (---), 60 rpm (—) and 80 rpm (-●-●-)

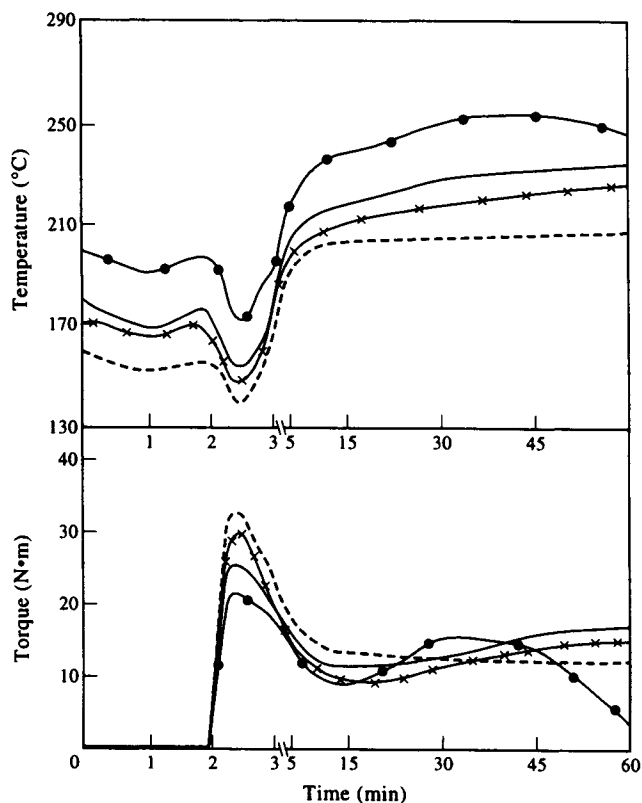


Figure 5 Changes in the torque and batch temperature during mixing of 50/50 PVC/NBR mixed at 160°C (---), 170°C (-x-x-x-), 180°C (—) and 200°C (-●-●-)

of PVC as well as the chemical changes in NBR, as explained a little further on. The figure also shows the changes in batch temperature during mixing.

Effect of processing temperature

Figure 5 displays the torque–time profiles of the 50/50

blends mixed at different temperatures. At 160°C, no rise in torque is observed even though the batch temperature increases by 40°C, indicating that no crosslinking takes place. But at 200°C, there is good chemical interaction, as manifested by a sharp increase in the torque up to 30 min, followed by a reduction in torque and temperature. This may be due to the sharp increase in the batch temperature (up to 254°C) which in turn causes degradation; it is also reflected from the t.g.a. curve (Figure 1). At 200°C, therefore, crosslinking and degradation take place simultaneously. The 50/50 blend at 170° and 180°C shows intermediate behaviour, with the torque increasing continuously, like the marching nature of rheographs. This is also reflected in rheometer curves (Figure 3). The t.g.a. curve (Figure 1) also shows a very small amount of weight loss. But the temperature rise for mixing at 170°C and 180°C is the same, about 50°C, which indicates that the rate of chemical crosslinking is also similar. The kinetic parameters (rate constants and activation energy) for crosslinking during mixing at different temperatures are calculated using equation (1), following the method of González³⁵. The results are reported in Table 2. The activation energy is 91.81 kJ mol⁻¹, which is a little lower than that of the rheometer result. It also indicates that some crosslinking takes place during mixing.

Effect of rotor speed

Figure 6 shows the mixing torque–time–temperature relation of the 50/50 blends mixed at different rotor speeds. As the rotor speed changes from 40 to 80 rpm, the rate and extent of the crosslinking reaction increase as shown by the increase in torque. At 80 rpm, the blend shows the maximum torque rise in about 30 min, followed by a decrease. As seen from the temperature–time curve, the batch temperature increases to 245°C due to the high rate of shearing at 80 rpm, resulting in a high degree of crosslinking and subsequent degradation. The blend crosslinks

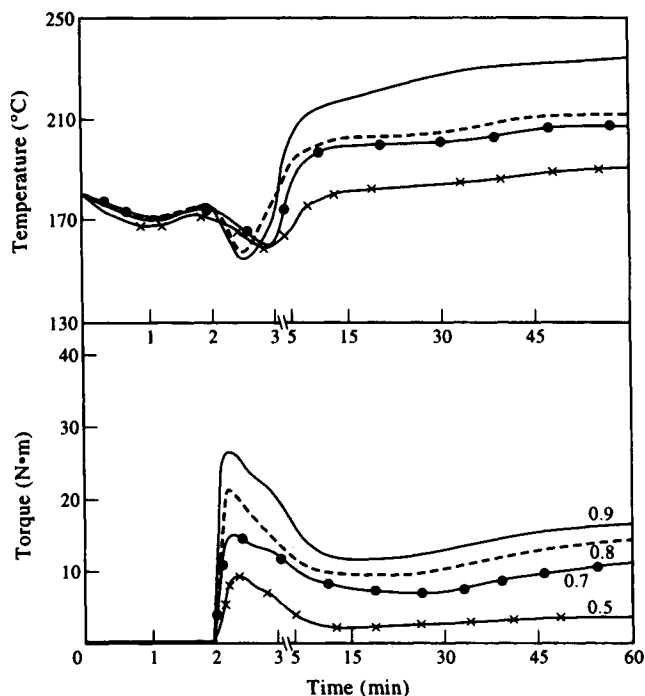


Figure 7 Changes in the torque and batch temperature during mixing of 50/50 PVC/NBR blends mixed at 0.5 (- × - × - × -), 0.7 (-●-●-), 0.8 (- - -) and 0.9 (—) fill factor

even at 40 rpm and the extent of crosslinking is in the order $40 < 60 < 80$ rpm.

Effect of fill factor

The effect of variation of percentage filling of the mixing chamber (fill factor) on the mixing torque-time-batch temperature is shown in *Figure 7*. As the fill factor increases, the torque and batch temperature rise proportionally. However, as the fill factor decreases, the resistance to the movement of the rotor also decreases. Hence, no direct relation between the fill factor and the torque or temperature rise may be drawn, as in the earlier cases.

The results are summarized in *Table 3*, which shows the torque rise ΔT_Q (difference between the minimum torque after equilibration and the maximum torque attained) and the increase in temperature ΔT (difference between the set temperature and the maximum temperature attained during mixing). For a fill factor of 0.5 no torque rise is observed (*Figure 7*), indicating that no shearing takes place. Hence the minimum fill factor will be 0.7 and, for good shearing and crosslinking reaction, the fill factor should be 0.8 or 0.9, which is reflected in the value of torque rise and temperature rise (*Table 3*, *Figure 7*).

Swelling studies

Further evidence for crosslinking is furnished by the swelling studies, the results of which are shown in *Table 3*. Both PVC and NBR and the blends are completely soluble in THF before processing. The changes in the degree of crosslinking under various mixing conditions are reflected in the different degrees of swelling of the systems after processing. The 50/50 blend mixed at a rotor speed of 80 rpm registers the lowest degree of swelling, followed by the 75/25 blend (both mixed at 180°C) and the 50/50 blend mixed at 200°C. The results are in good agreement with the mixing studies. The only exception is the stabilized blend which does not dissolve in THF, though it does not register

Table 3 Change in torque and temperature during mixing and the percentage swelling of the polymers and blends

Material	ΔT_Q (N m)	ΔT (°C)	% swelling
PVC	5	38	915
NBR	0	15	soluble
PVC/NBR:			
75/25	8.5	48	400
25/75	5	48	636
50/50	5.5	54	476
50/50 (stabilized)	0	42	1200
50/50 (160°C)	0	45	soluble
50/50 (170°C)	6.3	50	481
50/50 (200°C)	6.5	54	430
50/50 (40 rpm)	3	25	793
50/50 (80 rpm)	6.5	65	390
50/50 (f.f. 0.5)	1.0	10	soluble
50/50 (f.f. 0.7)	4	27	893
50/50 (f.f. 0.8)	4.5	30	892
50/50 (f.f. 0.9)	5.5	50	480

any torque rise. This may be due to the fact that the amount of stabilizer used (5 phr) is insufficient to prevent the total degradation of PVC. Hence, some crosslinking reaction may occur, though it is not sufficient to cause a torque rise.

Mechanism of chemical interaction

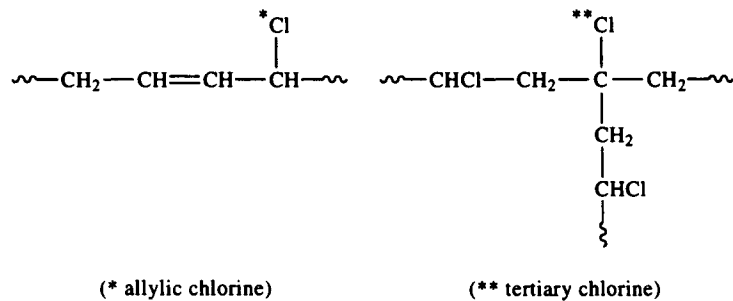
It has been reported earlier that the crosslinking reaction involves the nitrile groups in NBR and the reactive sites in PVC²⁴.

Commercially available PVC does not correspond to any single structure and is a complex mixture of many entities, which includes branching, chloroallyl groups, oxygen-containing groups and head-to-head structure^{30-32,37}. At high temperatures, PVC undergoes severe degradation via fast zip-elimination of HCl at the unstable defect sites³⁷⁻³⁹. The primary processes in the degradation are the initiation reaction of the defect or random sites, zip-elimination of HCl with simultaneous formation of conjugated polyenes, and the termination of zipping. Chain scission and other crosslinking reactions form the secondary processes³⁹. Though the coccentration of these reactive sites is low in normal PVC (for example, about 1.0 and 0.3 tertiary and allylic chlorines respectively per 1000 monomer units), as the autocatalytic degradation proceeds, more and more active sites are created with the liberation of HCl^{37,40}. Allylic chlorine sites (*Figure 8*) in PVC have been found to be most susceptible to reaction with polar groups²⁴. The nitrile groups in low molecular weight organic compounds are known to undergo hydrolysis in the presence of HCl^{33,41}. Recently, it has been shown that amide and acid functionalities are formed in NBR during aging under acidic, neutral and alkaline conditions⁴².

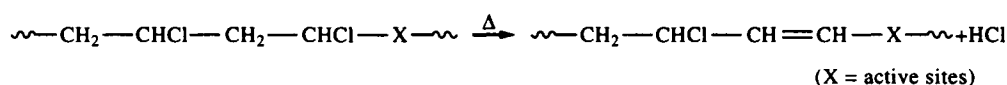
On the basis of these facts and the experimental observations, it is proposed that the crosslinking reaction takes place as follows. The HCl liberated from PVC reacts with the AN group in NBR in the presence of moisture and hydrolyses it to amide and acid functionalities, depending on the reaction conditions³³. Once the reactive sites are formed in the blend components (labile chlorine sites in PVC and amide/acid groups in NBR), they react to form crosslinks via amide and ester linkages. The probable reaction pathway is shown in *Figure 8*.

It is to be noted here that, as the crosslinking reaction proceeds, PVC undergoes degradation and this may lead to the crosslinking of PVC itself³⁷⁻³⁹. In *Figure 2*, PVC alone shows a torque rise. However, since the PVC/NBR blend does not show any rise in torque during mixing, it is presumed

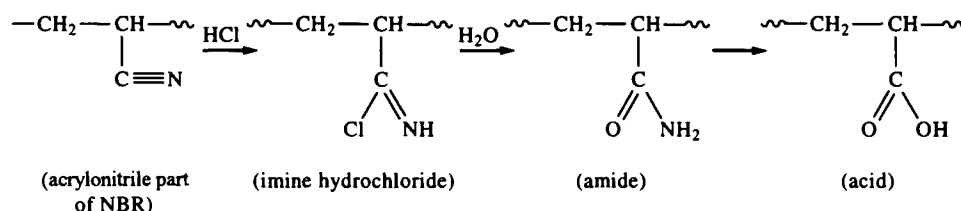
Active sites in PVC



Degradation of PVC



Hydrolysis of NBR



Crosslinking reaction

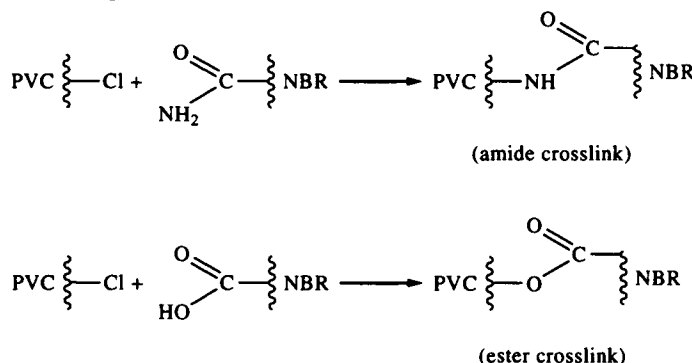


Figure 8 Proposed mechanism of the chemical interaction

that the degradation of PVC does not take place to a sufficient level to cause a torque rise in the case of the blends. Degradation of PVC depends on blend ratio; in PVC/NBR (75/25), Figure 4, both crosslinking and degradation take place simultaneously, showing more torque rise than the PVC/NBR (50/50) blend, as in this case availability of active sites of PVC is greater. But after 45 min torque and temperature decrease, indicating that only degradation is taking place. With increase of mixing temperature to 200°C, such an observation is also observed (Figure 5). The crosslinking reaction demands the degradation of PVC and subsequent liberation of HCl for hydrolysis of nitrile groups. The weight loss in isothermal degradation of the blend at 200°C (Figure 1) supports the liberation of HCl.

The significant role played by the reactive chlorine sites

and HCl in the crosslinking reaction is evident from the fact that the blend, in the presence of a PVC stabilizer such as TBLS, does not show any weight loss (Figure 1) or torque rise during mixing (Figure 2). A stabilizer such as TBLS is known to block the growing polyenes as well as to scavenge any HCl liberated by random initiation^{31,39}. Hence, in the absence of HCl, the hydrolysis of AN groups cannot take place and accordingly there is no chemical interaction between the two phases.

I.r. spectroscopic studies

I.r. spectroscopic analysis of the samples before and after processing gives an idea of the nature and type of chemical interactions occurring during the mixing of the blends. The functional group region (4000–1400 cm⁻¹) of the i.r. spectrum is used for the analysis rather than the fingerprint

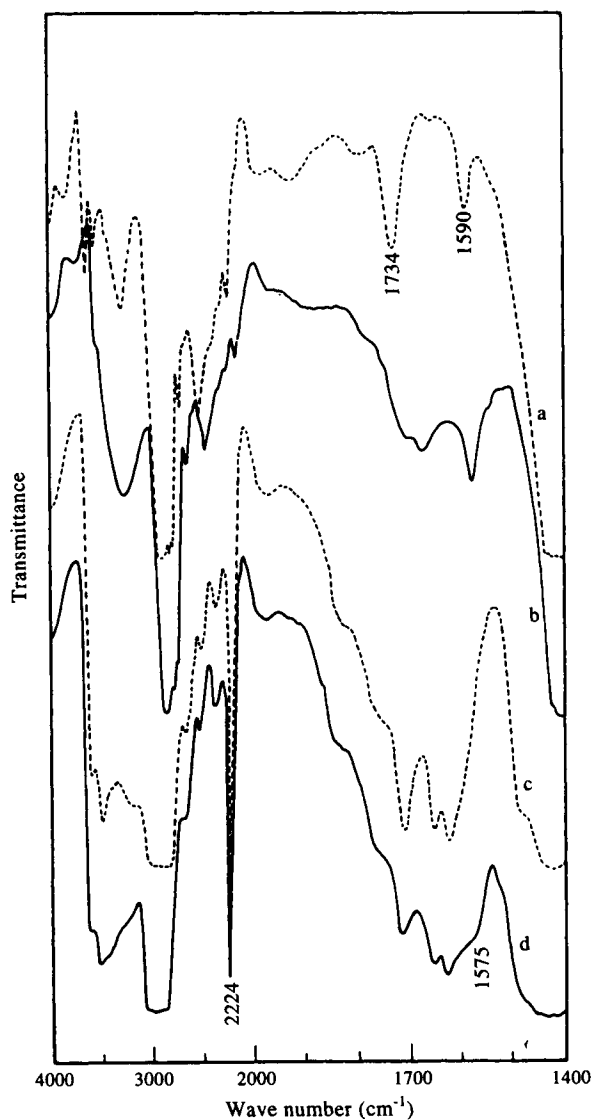


Figure 9 Infrared spectra of PVC and NBR before mixing (a, PVC; c, NBR) and after mixing (b, PVC; d, NBR) for 60 min at 180°C

region ($1400\text{--}500\text{ cm}^{-1}$) which is complicated due to the skeletal vibrations of the polymer backbone. *Figures 9* and *10* show the i.r. spectra of the individual polymers and the 50/50 blend mixed under different conditions.

Pure PVC shows two sharp absorbance peaks at 1734 cm^{-1} and 1590 cm^{-1} , which are due to the carbonyl groups formed during the manufacturing stage⁴³ and the polymer backbone defects³⁰. During processing, PVC undergoes thermooxidative degradation leading to the formation of conjugated polyenes, which absorb at $1715\text{--}1660\text{ cm}^{-1}$. The broad peak at 3280 cm^{-1} may be due to the formation of --OH groups during the degradation⁴⁴. The difference in the spectra of NBR before and after processing is the slight broadening of the band at 3510 cm^{-1} and the formation of a new band at 1575 cm^{-1} . The former is due to the formation of some --OH groups during degradation^{45,46}, while the latter corresponds to the triazine functionality generated as a result of the cyclization of adjacent nitrile groups⁴⁷. The absorption band at 2224 cm^{-1} is due to the stretching vibration of the $\text{C}\equiv\text{N}$ group.

Figure 10 shows the spectra of 50/50 blends mixed at different temperatures, and the blend in the presence of a stabilizer. A comparison of the spectra of the blends mixed for 5 and 60 min at 180°C (*Figure 10a* and *10c*) show the

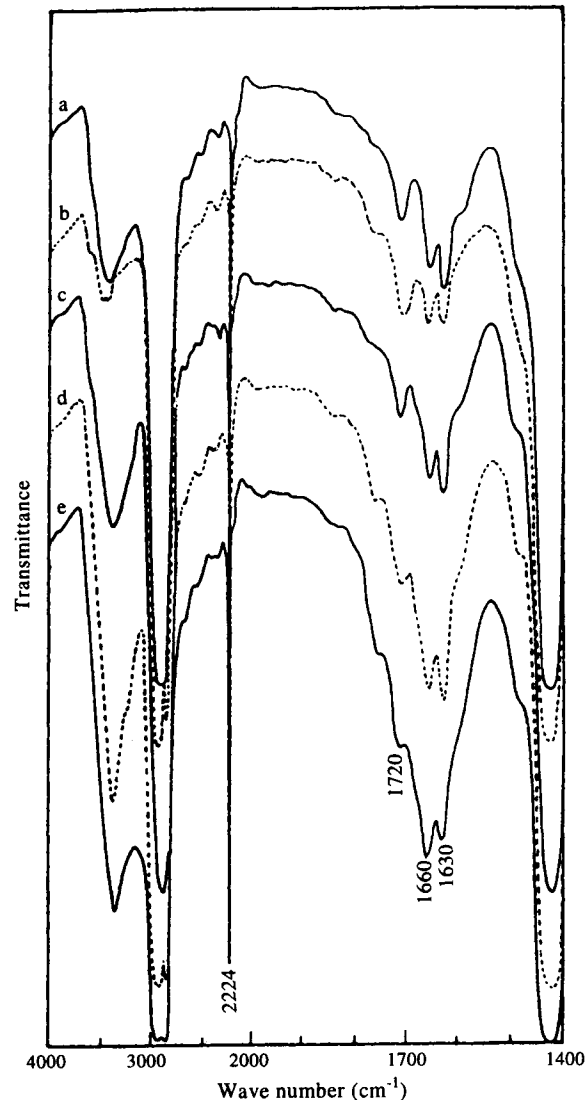


Figure 10 Infrared spectra of 50/50 PVC/NBR blends after mixing (a) for 5 min, (b) for 60 min (stabilized with TBLS), at 180°C and (c) at 160°C, (d) at 180°C, (e) at 200°C for 60 min

changes that occur during the crosslinking reaction. The broadening and the increased absorption at $3500\text{--}3200\text{ cm}^{-1}$ show the formation of O--H and N--H groups in the system, due to the hydrolysis of the nitrile group. At 160°C the peak is smaller, and at 180°C there is increased absorption, indicating the temperature dependence of the reaction. At 200°C, this peak intensity decreases, indicating that some of the --OH groups react during mixing. In spectra (*Figure 10b*), since the blend is mixed with stabilizer, it shows the same three peaks of PVC which are for polyenes absorbed at $1715\text{--}1660\text{ cm}^{-1}$. The changes in the concentration of the nitrile group are not visible since the absorption is sharp and strong⁴⁷. But in order to confirm whether any change of the intensity of the band for the AN ($\text{--C}\equiv\text{N}$) group has taken place, we have mixed separately NBR, HNBR and PVC/NBR (50/50 blend) and PVC/HNBR (50/50 blend) at 180°C for 60 min in the Brabender Plasticorder with a rotor speed of 60 rpm; i.r. spectra for each sample were taken within the range $2000\text{--}2500\text{ cm}^{-1}$. HNBR, a saturated nitrile rubber, was taken for comparison with nitrile rubber to check whether double bond has any role in the degradation of the AN group during processing. In the pure polymers (NBR, HNBR), thermal treatment does not produce any perceptible change in the intensity of the

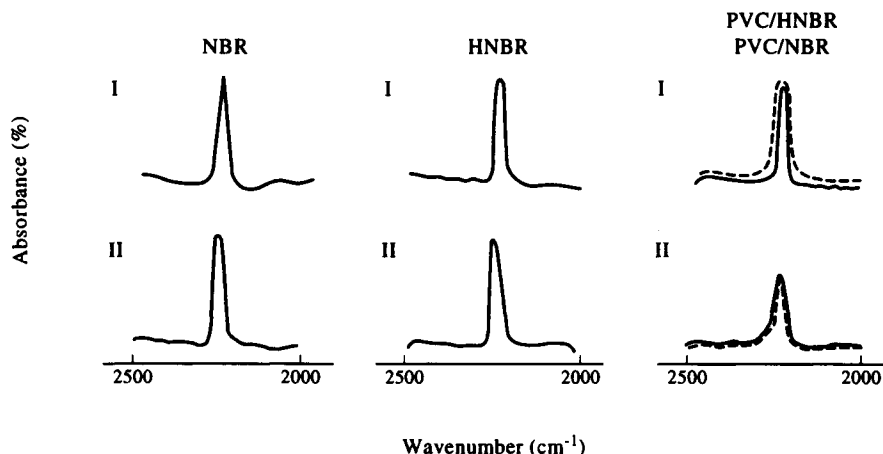


Figure 11 Effect of heat treatment on the intensity of C≡N stretching in the infrared: (I) before heat treatment and (II) after heat treatment. PVC/NBR (—); PVC/HNBR (---)

band at 2224 cm^{-1} (Figure 11). But the decrease of $-\text{CN}$ concentration in the blends is attributed to a partial hydrolysis of cyanide groups⁴⁰ by the splitting of HCl from PVC during heating in the presence of moisture inherent in the polymers. During mixing a smell of ammonia is observed, though only in the case of blends, indicating that hydrolysis³³ has taken place during prolonged mixing of the blend at 180°C , thus reducing the intensity of the $-\text{CN}$ group in the blends.

The peak centred at 1720 cm^{-1} represents the carbonyl groups of aliphatic acids, esters and ketones⁴⁷. The carbonyl groups in the amides absorb at 1630 cm^{-1} and carbon-carbon double bonds absorb at 1660 cm^{-1} . During the crosslinking reaction, the concentration of carbonyl groups increases due to the formation of amides, acids and esters, and that of carbon-carbon double bonds increases due to the simultaneous degradation. This is manifested in the broadening of the peaks and increased absorption as the processing temperature or time increases.

CONCLUSIONS

During the processing of PVC/NBR blends at high temperatures and shear rates, thermally induced crosslinks are formed in the system, as studied by means of a Brabender Plasticorder. The extent of crosslinking depends on the blend composition, processing temperature, shear rate, fill factor and the presence of a PVC stabilizer. The reaction proceeds through the hydrolysis of the nitrile groups, in the presence of HCl liberated from PVC during its degradation, to form amide and ester crosslinks, as studied by i.r. spectroscopy.

REFERENCES

- Kimura, M., Reporter, R. S. and Salee, G., *J. Polym. Sci., Polym. Phys.*, 1983, **21**, 367.
- Robeson, L. M., *J. Appl. Polym. Sci.*, 1985, **30**, 4081.
- Kimura, M., Salee, G. and Porter, R. S., *J. Appl. Polym. Sci.*, 1984, **29**, 1629.
- Godard, P., Dekominck, J. M., Devlesaner, V. and Devanx, J., *J. Polym. Sci., Polym. Chem.*, 1986, **24**, 3301.
- Henricks, P. N., Tribone, J., Massa, D. J. and Hewitt, J. M., *Macromolecules*, 1988, **21**, 1282.
- Montaudo, G., Puglisi, C. and Samperi, F., *J. Polym. Sci., Polym. Chem.*, 1993, **31**, 13.
- Prichard, J. M. and Wissbrun, K. F., *J. Appl. Polym. Sci.*, 1969, **13**, 233.
- Rudin, L. A. and Schreiber, H. P., *Polym. Eng. Sci.*, 1983, **23**, 422.
- Murakami, K. and Ono, K., *Chemorheology of Polymers*. Elsevier, New York, 1979.
- Komblowski, Z. and Torzecki, J., *Rheol. Acta*, 1983, **22**, 34.
- May, C. A. (Ed.), *Chemorheology of Thermosetting Polymers*. ACS Symposium Series, **227**, American Chemical Society, Washington, DC, 1983.
- Goodrich, J. F. and Porter, R. S., *Polym. Eng. Sci.*, 1967, **7**, 45.
- Zakrzewski, G. A., *Polymer*, 1963, **14**, 348.
- Folt, V. L. and Smith, R. W., *Rubber Chem. Technol.*, 1973, **46**, 1193.
- George, K. E., Joseph, R. and Francis, D. J., *J. Appl. Polym. Sci.*, 1986, **32**, 2867.
- Nasir, Z. A. and Ratnam, C. T., *J. Appl. Polym. Sci.*, 1989, **38**, 1219.
- Cheremisinoff, N. P., *Product Design and Testing of Polymeric Materials*. Marcel Dekker, New York, 1990.
- Leskovyansky, P. J., *J. Vinyl Technol.*, 1984, **6**, 82.
- Olabisi, O., Robeson, L. M. and Shaw, M. T., *Polymer-Polymer Miscibility*. Academic Press, New York, 1979.
- Wang, C. B. and Cooper, S. L., *J. Polym. Sci., Polym. Phys.*, 1983, **21**, 11.
- Watanabe, N., in *Thermoplastic Elastomers from Rubber-Plastic Blends*, ed. S. K. De and A. K. Bhowmick. Ellis Horwood, London, 1990, p. 198.
- Nakajima, N. and Lin, J. L., *Rubber Chem. Technol.*, 1992, **65**, 453.
- Matsuo, M., Nozaki, C. and Jyo, Y., *Polym. Eng. Sci.*, 1969, **9**, 197.
- Manoj, N. R., De, P. P. and De, S. K., *J. Appl. Polym. Sci.*, 1993, **49**, 133.
- Alex, R., De, P. P., Mathew, N. M. and De, S. K., *Plast. Rubber Process. Appl.*, 1990, **14**, 223.
- Ramesh, P. and De, S. K., *J. Mater. Sci.*, 1991, **26**, 2846.
- Ramesh, P. and De, S. K., *Rubber Chem. Technol.*, 1992, **65**, 24.
- Roychowdhury, A., De, P. P., Bhowmick, A. K. and De, S. K., *Polymer*, 1992, **33**, 4737.
- Manoj, N. R., De, P. P., De, S. K. and Peiffer, D. G., *Polymer*, 1993, **34**, 2128.
- Nass, L. I. (Ed.), *Encyclopedia of PVC*. Marcel Dekker, New York, 1977.
- Vymazl, Z., Czako, E., Volka, K. and Stepek, J., in *Developments in Polymer Degradation*, Vol. 4, ed. N. Grassie. Applied Science, London, 1982.
- Braun, D., in *Developments in Polymer Degradation*, Vol. 3, ed. N. Grassie. Applied Science, London, 1981.
- Beckwith, A. L. J., *The Chemistry of Amides*. Interscience, New York, 1970.
- Coran, A. Y., *Rubber Chem. Technol.*, 1964, **37**, 679.
- González, L., Rodríguez, A., Marcos, A. and Chamorro, C., *Rubber Chem. Technol.*, 1996, **69**, 203.
- Bateman, L., *The Chemistry and Physics of Rubber Like Substances*. John Wiley, New York, 1963.
- Hjertberg, T. and Sorvik, E. M., in *Polymer Stabilization and Degradation*, ed. R. P. Klemchuck. ACS Symposium Series, **280**, American Chemical Society, Washington, DC, 1985.
- Ivan, B., *Polym. Prepr.*, 1993, **34**, 116.
- Ivan, B., Turcsanyi, B., Kelen, T. and Tudos, F., *J. Vinyl Tech.*, 1990, **12**, 126.
- Braun, D., Michel, A. and Sonderhof, D., *Eur. Polym. J.*, 1981, **17**, 49.

41. Saul Patai (Ed.), *The Chemistry of Acid Derivatives*, Part 1. Wiley Interscience, New York, 1979.
42. Frenkel, R., Duchacek, V. and Stepek, J., *Plast. Rubber Compos. Process. Appl.*, 1974, **17**, 1159.
43. Lukas, R., Pradora, O., Michalcova, J. and Paleckova, V., *J. Polym. Sci., Polym. Lett.*, 1985, **23**, 85.
44. Baum, D. and Wartman, L. H., *J. Polym. Sci.*, 1958, **28**, 537.
45. Skowronski, T. A., Rabek, J. F. and Ranby, A. B., *Polym. Degrad. Stabil.*, 1983, **5**, 173.
46. Davis, A. and Gordon, D., *J. Appl. Polym. Sci.*, 1974, **18**, 1159.
47. Socrates, G., *Infrared Characteristic Group Frequencies*. Wiley Interscience, New York, 1980.