Crosslinking in blends of nitrile rubbers and poly(vinyl chloride)

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Crosslinking of nitrile rubber (NBR) and poly(vinyl chloride) (PVC) can be accomplished separately using ethylenethiourea (ETU) with and without the presence of sulphur (S) respectively. ETU/S combination in appropriate doses brings about ready co-crosslinking of NBR and PVC in their blends. Comparative studies of the curing characteristics of some NBR–PVC blends and some important physical properties of the blend vulcanizates have been made using the test curative (ETU/S system) and a conventional curative (tetramethylthiuram disulphide (TMTD)/sulphur (S) system). The ETU/S curative system produces crosslinking effects which in some respects are comparable with, and in some other respects are even substantially better than, those produced by the conventionalTMTD/S curative system, particularly with respect to consequential curing parameters and blend vulcanizate properties including morphological patterns and ageing behaviour.

(Keywords: co-crosslinking; nitrile rubber; poly(vinyl chloride); blends; ethylenethiourea; sulphur)

INTRODUCTION

Crosslinking of nitrile rubber (NBR) has long been carried out by employing curatives commonly suitable for the curing of diene rubber systems, such as by using appropriate doses of tetramethylthiuram disulphide (TMTD) as the accelerator and sulphur (S) as the crosslinking agent[1]. Poly(vinyl chloride) (PVC), a high tonnage thermoplastic material, does not normally require curing or crosslinking in its major and common areas of applications. However, some studies aimed at crosslinking of PVC relate to the use of peroxides[2,3], dithiols and related compounds[4–7] as the crosslinking agents. A recent study reported from our laboratory relates to the development of a crosslinking technology of PVC using diamines and polyamines as the crosslinking agents[8].

NBR–PVC blends developed long ago have been in practical use and the final step in the blend technology for the making of end-use items is the vulcanization step employing a selected curative (rubber–accelerator–sulphur) system. A conventional curative system for the NBR–PVC blend, viz. TMTD/S combination, crosslinks the NBR component only and in such vulcanized NBR–PVC blends the PVC component remains uncrosslinked for all practical purposes and therefore remains soluble and leachable. It was therefore thought to be of some interest to make a fresh investigation into the crosslinking technology of this blend system with a thrust on the development of an appropriate curative system which would lead to simultaneous crosslinking of both the components (NBR and PVC) in the blend system with the possibility of even co-crosslinking or inter-crosslinking of the component polymers, more so in view of the fact that studies of this nature have received little attention up to the current time.

EXPERIMENTAL

Materials

Poly(vinyl chloride) (PVC). Suspension-grade PVC resin (from NOCIL, India) characterized by a *K* value of 70 was used.

Nitrile rubber (NBR). Krynac 3450 (34% acrylonitrile content) obtained from Polysar, Canada, was used.

Curing agents. Rubber-grade tetramethylthiuram disulphide (TMTD), hexamethylenediamine (HMDA), ethylenethiourea (ETU), mercaptobenzthiazyl disulphide (MBTS) and sulphur (S) were used.

Fillers. Fine extrusion furnace (FEF) black, precipitated silica (Vulcasil) and activated $CaCO_3$ (Forcal-S) were separately used as fillers.

Other additives. Dioctyl phthalate (DOP), tribasic lead sulphate (TBLS) and calcium stearate were used as plasticizer, stabilizer and lubricant separately whenever necessary and as mentioned in the text. Zinc oxide (ZnO) and stearic acid combination was used as the activator system for vulcanization of NBR.

Compounding of NBR, PVC and NBR–PVC blends

Mixing schedules appropriate for PVC, NBR and NBR–PVC blends were followed. PVC was dry blended with DOP containing appropriate doses of TBLS and Ca stearate following usual procedures and it was then

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gelled on a two-roll mill at 160°C for 10 min. Curatives were later quickly mixed with the gelled PVC on the roll mill at about 140–150°C immediately before the curing process[8]. For making NBR compounds, selected additives including the accelerator–sulphur curative system were mixed with the elastomer after it was duly masticated on the cold mill. For NBR–PVC blends pieces of previously masticated NBR were mixed or blended with selected PVC compounds on an open mill. ZnO, stearic acid and the selected curative system were then uniformly mixed with the blend so formed. PVC, NBR or blends thereof were cured in a steam-heated press at a temperature of 170°C and a pressure of $\frac{1}{2}$ ton/inch^2, i.e. $7.6 \times 10^6\ \mathrm{N\,m^{-2}}$.

Characterization

Studies on curing behaviour. A Monsanto Rheometer 100 operating at 170°C (employing ±3° arc for NBR and ±5° arc for PVC and NBR–PVC blend) was used to generate curing characteristic data for the PVC (plasticized), NBR and NBR–PVC blend systems.

Evaluation of physical/mechanical properties of vulcanizates or cured compounds. Tensile properties such as tensile strength (*TS*, kg cm^{-2}), elongation at break (*EB*, %) and tensile modulus (kg cm^{-2}) of NBR and of NBR–PVC blends (70:30 and 50:50 w/w) were measured following ASTM D-412, and those for PVC and NBR–PVC blends (30:70 w/w) following ASTM D-638.

Hardness (Shore A) of the cured elastomer (NBR), plastomer (plasticized PVC) and their blends were measured following ASTM D-2240.

Tear strength of NBR and NBR–PVC blends (70:30 and 50:50 w/w) were measured following ASTM D-624, and those of PVC and NBR–PVC blends (30:70 w/w) were determined following ASTM D-1004.

The thermal stability studies of PVC compounds were done according to BS 2782-1955. The compounded PVC resin, uncured or cured, was heated at a constant temperature (200°C). The liberation of HCl due to its thermal degradation was detected by using a Congo red paper and the time period corresponding to the change in colour of the indicator paper was taken as an index of the thermal stability of the PVC-based compounds.

Hot deformation characteristics of PVC compounds were determined according to BS 6746-1946, Clause F4, based on resistance to indentation of a crosslinked PVC sheet relative to an uncrosslinked sheet at an elevated temperature (120 ± 1°C) under a specified condition of loading (3.5 ± 0.02 N) for a specified time period of 24 h. The hot deformation of the crosslinked PVC (given by the ratio of indentation of the crosslinked compound to that of the uncrosslinked compound) is expressed as per cent hot deformation.

Volume resistivity of cured NBR, PVC and of the cured NBR–PVC blends was measured according to ASTM D-257-61 using a Hewlett Packard volume resistivity measuring equipment.

Studies on swelling behaviour of crosslinked NBR compounds. Comparative evaluation of the crosslink density of vulcanized NBR, crosslinked separately using two different types of curatives, viz. ETU/S and TMTD/S, was done with the help of the Flory–Rehner equation[9]:

$$\frac{1}{M_c} = \frac{V_p + \chi V_p^2 + \ln(1 - V_p)}{d_r V_0 (V_p^{1/3} - V_p/2)}$$

where V_p = volume fraction of polymer in the swollen mass, V_0 = molar volume of the solvent (benzene), χ = polymer–solvent interaction parameter, $\chi = 0.44$ (ref. 10), and d_r = density of polymer. The results are expressed in terms of molecular weight between crosslinks (M_c). Equilibrium swelling was done at 25°C for 7 days using C_6H_6 as the solvent.

Examination of phase morphology of NBR–PVC blends using scanning electron microscopy. Selected NBR–PVC blend specimens in the form of sheets were cut to size and trimmed to the desired shape to produce a flat surface. The samples were then immersed in an acid bath containing 100 ml concentrated H_2SO_4, 32.5 ml H_3PO_4, 31.25 ml H_2O and 5 g CrO_3 for a period of 2 h at a temperature of 70°C. The specimens thus etched by the oxyacid system were washed and then dried thoroughly. The dried specimens were duly coated with gold in a sputter coater and examined in a scanning electron microscope.

RESULTS AND DISCUSSION

Additives

One of the most conventional curative systems used for the crosslinking of NBR–PVC blends (70:30 w/w) is a combination of an accelerator (tetramethylthiuram disulphide (TMTD)) and sulphur (S), which cures only the elastomer component, viz. the NBR, and is incapable of crosslinking or curing the plastomer component, viz. the PVC.

In this study we tried to develop a curing or vulcanization system for NBR–PVC blends, which will be able to cure both (elastomer and plastomer) components of the blend so that, in the final step, simultaneous crosslinking or even co-crosslinking or inter-crosslinking of the blend constituents would take place. Preliminary investigations were made using a few common rubber accelerators (such as MBTS, TMTD, etc.) in the presence or absence of sulphur (S). Some other additives (such as HMDA and ETU) were also tried separately as curative systems under specified time–temperature–pressure conditions to fulfil the set objective.

Additives effecting crosslinking of PVC only. Among the selected curatives only HMDA and ETU transformed PVC into a crosslinked product (170°C, $\frac{1}{2}$ ton/inch^2, i.e. $7.6 \times 10^6\ \mathrm{N\,m^{-2}}$, <30 min) as revealed by high values of gel content[11] (>75% in tetrahydrofuran (THF) solvent at 27°C) for the products (*Table 1*). Optimum doses for the curatives are 1.0 phr for HMDA and 0.5 phr for ETU. HMDA and ETU, however, failed to bring about curing of NBR under similar conditions. Heating of only PVC without HMDA or ETU under prescribed conditions (170°C, $\frac{1}{2}$ ton/inch^2, i.e. $7.6 \times 10^6\ \mathrm{N\,m^{-2}}$, 30 min) did not bring about any measurable degree of crosslinking and the PVC products so obtained remained infinitely soluble in THF, producing no gel at all. Additives other than HMDA and ETU are, however, unsuitable for crosslinking PVC as indicated by the solubility tests.

Table 1 Preliminary assessment of curatives for NBR and PVC

	Curatives (phr)					
Polymer	ETU	HMDA	MBTS	TMTD	S	Gel content (%)
PVC	0.5					75.3
	0.5				1.0	75.1
		1.0				85.1
		1.0			1.0	84.9
					1.0	0
			2.0			0
				2.5		0
NBR	2.0					0
	2.0				1.0	96.2
				2.5		90.1
				2.5	0.5	98.2
			2.0			86.2
			2.0		1.0	92.3

Additives effecting crosslinking of NBR only. The rubber accelerators such as MBTS and TMTD separately, and each in the presence of S as well, acted as good curatives for NBR. TMTD/S combination is conventionally used as the curative system for the vulcanization of NBR or NBR–PVC blends. Each of the above rubber accelerators failed to crosslink PVC even in the presence of S, yielding soluble products (*Table 1*).

Examination of ETU as a common crosslinking agent. Even though ETU (1–4 phr) alone failed to effect crosslinking of NBR, it proved to be quite effective in this respect giving products of high gel content (96% in THF at 27°C) when used in the presence of small doses of sulphur (0.6–1.75 phr). Sulphur in the above dose range used in presence of appropriate doses of ETU did not measurably hinder the crosslinking of PVC, and the gel content of ETU-crosslinked PVC done in the absence or in the presence of S under otherwise comparable conditions were reasonably close and as high as 75–90%.

The above preliminary experiments point to the conclusion that a blend of NBR and PVC would be amenable to simultaneous crosslinking of each component possibly involving some degree of co-crosslinking or inter-crosslinking if appropriately treated thermally in the presence of a combination of ETU and S in optimum doses.

Curing characteristics of PVC and NBR using ETU or ETU/S system as the curative as studied by Monsanto Rheometer

PVC–ETU system. PVC, plasticized and appropriately stabilized with the incorporation of DOP (40 phr) and TBLS (7.0 phr) respectively, was mixed with different doses of ETU and the curing of the different compounds was separately studied rheometrically at 170°C. The curing characteristic data are shown in *Table 2*.

Over the ETU range of 0.25 to 4.0 phr, the attainable minimum torque, taken as an index of plasticity of the test compound at the processing temperature, ranged mostly between 1.41 and 1.58 N m. The maximum torque shows an increasing trend, as expected, with increasing dose of the curative (i.e. ETU, 0.25–4.0 phr). The difference between the maximum and minimum torque consequently shows an increasing trend, beginning from as low a value as 0.23 N m corresponding to the use of 0.25 phr ETU to as high a value as 3.73 N m corresponding to the use of 4.0 phr ETU. The increasing trend in the crosslink density with increasing ETU dose thus indicated is also reflected in the increasing trend in the gel content (a value of nearly 60% gel content corresponding to the use of 0.25 phr ETU increases to a value of 95% gel content for the use of 4.0 phr ETU).

The ETU-induced crosslinking of PVC is by and large scorch safe over the full dose range of ETU studied here; there is, however, an initial sharp lowering of scorch time with the use of up to about 1.0 phr ETU, and thereafter, the scorch time remains practically unchanged even with four-fold increase in the ETU dose (*Table 2*). The optimum cure time ranges between 25 ± 3 min over the range of ETU dose studied. The cure rate computed from the steady part of the torque rise zone of the rheometric curves follows an increasing trend with increase in the ETU dose (*Table 2*).

NBR–ETU/S system. The curing characteristics of ETU/S-induced crosslinking of NBR are likewise presented in *Table 3*. Different combinations of the curative components ranging from high ETU (4.5 phr) and low S (0.6 phr) to low ETU (0.5 phr) and high S (1.75 phr) doses in six sets of experiments were studied and the cure data for them may be compared with those for the conventionally cured (using TMTD/S combination in 2.5 phr/0.5 phr dose ratio) NBR compounds, each having been cured at 170°C. The base NBR compound in each case was made up of 5.0 parts of ZnO and 1.0 part of stearic acid for 100 parts of NBR. It was found that systems containing low ETU and high S doses produced crosslinking effects which are much better than those produced by high ETU and low S doses as revealed by torque difference, maximum torque and cure rate data. However, when viewed against the cure data produced by the TMTD/S (conventional curative) system, the ETU/S curative system appears to produce some effects which are inferior to those produced by the TMTD/S curative system, particularly with respect to cure rate and optimum cure time. However, the low ETU and high S

Table 2 Curing characteristics of PVC compounds and physical properties of the cured compounds. Curing conditions: temperature 170°C, pressure 7.6×10^6 N m^{-2}. Base mix formulation: PVC 100.0, TBLS 7.0, DOP 40.0, Ca stearate 1.0 (parts by weight)

	Uncrosslinked PVC	ETU (phr)						
		0.25	0.5	0.7	1.0	2.0	3.0	4.0
Rheometric properties								
Max. torque (N m)	–	1.73	2.03	2.87	2.68	2.71	4.69	4.71
Min. torque (N m)	–	1.50	1.58	1.99	1.44	1.41	1.49	1.58
Torque difference (N m)	–	0.23	0.45	0.88	1.24	1.30	3.20	3.73
Search time (min)	–	21.0	20.0	11.5	5.2	5.0	5.3	5.1
Optimum cure time (min)	–	21.0	28.0	27.5	25.2	27.0	25.0	25.0
Cure rate (N m min^{-1})	–	0.024	0.028	0.038	0.045	0.052	0.143	0.196
Physical properties								
Thermal stability at 200°C (min)	34.5	24.0	17.0	11.0	10.5	7.5	5.5	5.0
Volume resistivity (ohm cm)	4.0×10^{14}	8.3×10^{12}	4.7×10^{12}	3.7×10^{12}	3.1×10^{12}	2.7×10^{12}	2.2×10^{12}	1.9×10^{12}
Gel content (%)	–	62.2	75.3	79.1	84.3	87.7	89.2	94.6
Tensile strength (kg cm^{-2})	199.0	231.3	253.4	241.6	228.2	218.7	212.5	204.3
100% modulus (kg cm^{-2})	150.0	152.1	158.7	153.6	149.2	147.4	148.3	143.1
Elongation at break (%)	285	300	300	300	300	267	258	250
Tear strength (kg cm^{-1})	20.4	19.3	18.7	17.6	16.2	17.0	13.8	12.1
Hot deformation (%)	100	61.1	57.2	56.1	54.4	49.6	46.1	40.2
Hardness at 27°C (Shore A)	86	86	86	87	87	87	88	88

Table 3 Curing characteristics of NBR compounds and physical properties of the vulcanizates. Curing condition: temperature 170°C; pressure 7.6×10^6 N m^{-2}. Base mix formulation: NBR 100.0, ZnO 5.0, stearic acid 1.0 (parts by weight)

	Curative system (phr)						
ETU	4.5	3.0	2.0	2.0	1.0	0.5	0
S	0.6	1.0	1.0	1.5	1.75	1.75	0.5
TMTD	0	0	0	0	0	0	2.5
Rheometric properties							
Max. torque (N m)	3.30	4.52	4.21	6.12	6.55	6.24	7.12
Min. torque (N m)	0.84	0.68	0.84	0.84	0.82	0.84	0.72
Torque difference (N m)	2.46	3.84	3.38	5.29	5.73	5.40	6.41
Scorch time (min)	1.25	1.25	1.37	1.13	1.15	1.35	1.83
Optimum cure time (min)	12.0	12.0	10.7	10.8	10.5	11.2	4.0
Cure rate (N m min^{-1})	0.19	0.31	0.28	0.58	0.63	0.69	2.08
Physical properties							
Tensile strength (kg cm^{-2})	15.3	22.7	25.6	24.6	23.6	20.8	21.6
Elongation at break (%)	710	635	631	543	512	565	340
200% modulus (kg cm^{-2})	8.3	12.0	13.2	13.1	9.1	9.8	13.2
Tear strength (kg cm^{-1})	1.2	1.0	1.9	1.1	1.0	1.0	0.8
Volume resistivity (ohm cm)	3.7×10^{10}	4.4×10^{10}	3.2×10^{10}	4.8×10^{10}	5.1×10^{10}	3.5×10^{10}	8.6×10^{10}
Gel content (%)	94.9	95.8	96.2	97.2	97.2	97.9	98.2
Hardness at 27°C (Shore A)	41	42	45	44	44	43	46
Mol. wt. between crosslinks (g mol^{-1})	–	–	13084	–	–	–	6954
Solvent intake (%)	–	–	88	–	–	–	80

curative system yields NBR vulcanizates showing high gel contents which are comparable with those produced by the TMTD/S system.

Physical and mechanical properties of crosslinked PVC and vulcanized NBR systems

Some physical and mechanical properties such as tensile strength (*TS*), tensile modulus, elongation at break (*EB*), tear strength, hardness and volume resistivity of the cured compounds are shown in *Table 2* for the PVC system and in *Table 3* for the NBR system.

On comparing different property data for PVC compounds in *Table 2*, particularly *TS*, modulus and tear strength, it is reasonable to conclude that a low ETU dose in the range of 0.5–0.7 phr produces the optimum effect giving a *TS* value in the range of 240–250 kg cm^{-2}, modulus at 100% elongation in the range of 150–160 kg cm^{-2} and a tear strength of the order of 18–19 kg cm^{-1}.

Duplicate experiments for curing of PVC with different doses of S (0.5–2.0 phr) show that sulphur produces little additional effect and it remains practically as an inert additive in the ETU-induced cure of PVC, and the curing characteristics as well as the physical properties of the non-sulphur PVC systems remain practically unchanged in the presence of sulphur.

Comparison of physical properties for NBR vulcanized by different dose combinations of ETU and S under the

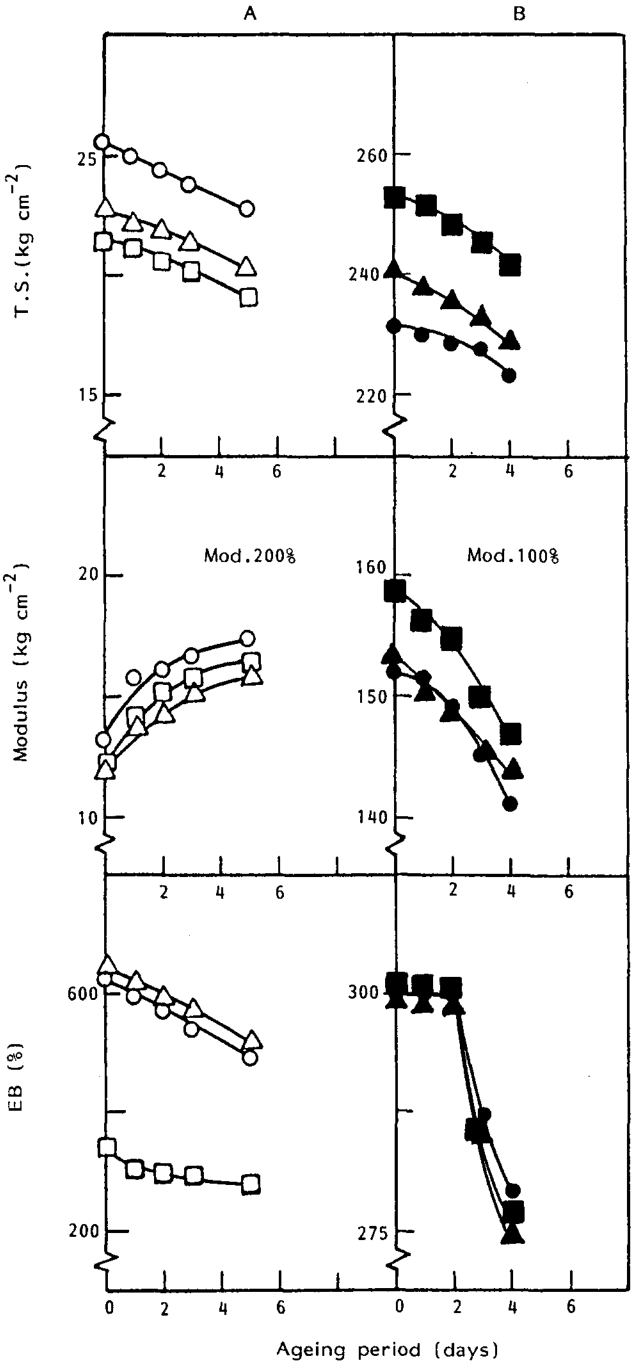


Figure 1 Physical properties of NBR and PVC vulcanizates. Effect of air ageing at 100°C. (A) NBR systems; data given for each curve are ETU, S and TMTD (phr): (○) 2.0, 1.0, 0.0; (△) 3.0, 1.0, 0.0; (□) 0.0, 0.5, 2.5. (B) PVC systems; data given for each curve is ETU (phr): (●) 0.25; (■) 0.5; (▲) 0.7

specified condition is shown in *Table 3*. The corresponding data for the TMTD/S system are also indicated in the table for comparison. Using ETU dose of 2.0 phr and S dose in the range of 1.0–1.5 phr, NBR vulcanizates are obtained which are characterized by higher *TS*, *EB* and tear strength and almost comparable modulus at 200% elongation when compared with the corresponding data for the conventional TMTD/S-cured NBR system. Both ETU/S and TMTD/S systems produce nearly the same order of volume resistivity for the vulcanizates.

One distinctive difference between the ETU accelerated and TMTD accelerated S cure of NBR is that in the case of the former relatively high *EB* values (500–700%) are commonly obtained under different doses of ETU and sulphur, while in the latter case the value of the parameter is much lower (300–400%). This may be understood and interpreted on the basis of two considerations: (i) that the ETU/S system induces relatively low crosslink density and/or (ii) that it leads to the establishment of relatively flexible crosslinkages. This is also borne out in large measure by a higher molecular-weight value between crosslinks for the ETU/S-induced crosslinked NBR and also by higher swelling of the said vulcanizates (expressed in terms of per cent solvent intake by the gel) when compared with those for the TMTD/S-induced NBR vulcanizates (*Table 3*).

Ageing behaviour of the crosslinked PVC and NBR systems

Heat ageing behaviour. The difference between the physical properties of ETU/S- and TMTD/S-induced NBR vulcanizates and their heat ageing behaviour at 100°C, showing changes in the tensile parameters and elongation at break, are shown in part A of *Figure 1*. Similar data for ETU-induced crosslinked PVC (plasticized) are shown in part B of *Figure 1*.

For the NBR vulcanizates the *TS* and *EB* follow a decreasing trend on ageing, showing a drop of nearly 11–12% in *TS*, and nearly 18–23% in *EB* in 120 h. The modulus at 200% elongation for the NBR vulcanizates, however, follows an increasing trend on ageing and in this respect the ETU/S and the TMTD/S crosslinking systems produce almost comparable ageing trends.

For ETU-induced crosslinked PVC, both *TS* and modulus follow a decreasing trend on ageing. *EB*, however, remains practically unchanged for nearly 48 h at 100°C and the values of the parameter follow a decreasing trend on further ageing. About 3–5% drop in *TS* and nearly 5–7% drop in modulus are observed for ageing over a period of 4 days at 100°C. The drop in *EB* beginning from about 48 h of ageing and continuing up to an ageing period of 4 days (96 h) is within 8–10% in general. While the trends of change in *TS* on ageing for vulcanized NBR and crosslinked PVC systems are similar (falling trend), though not of identical or comparable magnitude, the trends of change in modulus and *EB* for the two systems are distinctly different. With respect to modulus, the changes follow opposite trends as shown in *Figure 1* for the two systems, and with respect to *EB*, PVC exhibits a greater resistance to ageing, more so (showing practically no change) over the initial phase. It would be interesting to see how these differences and similarities in the trends of change in the physical properties (mechanical) of the two cured polymer systems (NBR and PVC) would balance or reinforce each other in their blends under different sets of conditions of crosslinking for different blend ratios using different curative systems.

Oil ageing behaviour. The oil ageing characteristics showing retention of *TS*, modulus at 200% elongation and *EB* for an ageing period of 24 h in a standard hydrocarbon oil for both crosslinked NBR and crosslinked PVC were examined at a temperature of 100°C (*Table 4*). Change-over in the curative system for NBR from the conventional TMTD/S combination to the ETU/S used in the present studies does not produce any significant difference in the oil resistance of the

Table 4 Oil ageing behaviour of the cured PVC and NBR vulcanizates. Ageing condition: temperature 100°C, period 24 h

		Curative system (phr)					
		PVC compounds[a]			NBR compounds[a]		
	ETU	0.25	0.5	0.7	2.0	3.0	0
	S	0	0	0	1.0	1.0	0.5
Properties	TMTD	0	0	0	0	0	2.5
TS before ageing (kg cm^{-2})		231.3	253.4	241.6	25.6	22.7	21.6
TS after ageing (kg cm^{-2})		228.0 (98.6)	249.1 (98.3)	235.0 (97.3)	24.9 (97.2)	22.0 (96.9)	20.9 (96.7)
Modulus[b] before ageing (kg cm^{-2})		152.1	158.7	153.6	13.2	12.0	13.2
Modulus after ageing (kg cm^{-2})		150.8 (99.2)	153.8 (96.9)	149.1 (97.1)	14.6 (110.6)	13.4 (111.6)	13.8 (104.5)
EB (%) before ageing		300	300	300	631	635	340
EB (%) after ageing		288 (96.0)	284 (94.5)	281 (93.7)	600 (95.1)	600 (94.5)	325 (95.6)

[a] Data in the parentheses indicate percentage retention of the corresponding property after oil ageing

[b] Data shown correspond to modulus at 100% elongation for PVC and 200% elongation for NBR

Table 5 Curing characteristics of NBR–PVC blends (70:30, 50:50 and 30:70 w/w) and physical properties of the blend vulcanizates. Curing condition: temperature 170°C, pressure 7.6 × 10^6 N m^{-2}

		Curative system (phr)					
	Blend	70:30		50:50		30:70	
	ETU	2.0	0	2.0	0	2.0	0
	S	1.0	0.5	1.0	0.5	1.0	0.5
	TMTD	0	2.5	0	2.5	0	2.5
Rheometric properties							
Max. torque (N m)		4.37	3.10	3.62	1.71	2.32	0.96
Min. torque (N m)		1.81	1.27	0.85	0.79	1.13	0.59
Torque difference (N m)		2.57	1.83	2.77	0.92	1.19	0.37
Scorch time (min)		2.0	2.4	4.0	9.0	7.0	12.0
Optimum cure time (min)		12.5	14.5	17.0	17.0	17.5	18.0
Cure rate (N m min^{-1})		0.452	0.373	0.203	0.057	0.085	0.028
Physical properties							
Gel content (%)		81.0	72.0	82.5	66.0	83.0	47.0
Volume resistivity (ohm cm)		7.0 × 10^{10}	1.1 × 10^{10}	2.2 × 10^{11}	4.3 × 10^{11}	1.6 × 10^{12}	2.9 × 10^{12}
Tensile strength (kg cm^{-2})		104.0	65.5	140.0	120.0	220.0	186.0
200% modulus (kg cm^{-2})		20.0	18.0	35.0	14.0	98.0	87.0
Elongation at break (%)		582	478	590	625	410	450
Tear strength (kg cm^{-1})		2.4	2.0	6.0	6.6	10.5	11.0
Hardness at 27°C (Shore A)		50	53	62	60	72	71

vulcanizates, and the retention of properties average about 97%, 105–110% and 95% for *TS*, modulus and *EB* respectively, irrespective of the curative system and irrespective of small variations in their dose around the optimum dose. PVC also shows very good oil resistance properties before and after crosslinking, showing a retention of properties of the order of 97–99%, 96–100% and 94–99% for *TS*, modulus and *EB* respectively, with a very slow decreasing trend in each parameter, with increase in the dose of the crosslinker (ETU) up to about 0.7 phr.

Evaluation of ETU/S combination as a co-crosslinker in NBR–PVC blends

We are now in a position to evaluate the role and effectiveness of the ETU/S system in establishing two different types of networks simultaneously in NBR–PVC blends, keeping in view at the same time the possibilities of its role as a co-crosslinker resulting in the formation of what may be termed 'unified networks'. To appreciate these roles and possibilities we also made an independent and parallel study on the vulcanization of the NBR–PVC blend system using TMTD/S combination as the curative, as practised conventionally in the relevant industry up to the current date. Results relating to the curing characteristics studied rheometrically using a Monsanto Rheometer and physical properties of the cured and vulcanized products are given in *Table 5*.

Curing characteristics. Using the ETU/S and TMTD/S combinations as the curatives separately for each of the three different NBR/PVC blend ratios, viz. 70:30, 50:50 and 30:70 (w/w), the results obtained on taking the curative components in optimum doses are shown in *Table 5*. It may be seen from comparison of data given in this table that the maximum torque (torque developed at a cure time of 20 min) and the torque difference (difference between the maximum torque and the minimum torque) are usually higher for the ETU/S curative system. The ETU/S system is, however, more scorchy (showing relatively low scorch time at the high temperature of cure (170°C)), even though the compounds show indefinite stability against any degree of premature curing under ambient or slightly elevated temperatures (data not shown). The optimum cure time (*OCT*) for 50:50 and 30:70 NBR-PVC blends using the two curative systems are more or less close or comparable, but for the 70:30 blend the ETU/S curative system produces an *OCT* which is slightly lower than that produced by the TMTD/S curative system. Also it is seen that between the two curative systems, ETU/S produces in general a significantly higher cure rate (determined from the slope of the initial steady part of the torque rise zone for each system) in each case.

Physical properties of the vulcanizates. Table 5 also provides an interesting summary of the physical properties of the blend vulcanizates. The ETU/S system generally results in a cure that shows a much higher gel content, indicating its more efficient and superior role as a crosslinking system over the TMTD/S system—presumably through the former's effective functioning as a co-crosslinker resulting in not only simultaneous and parallel formation of NBR-based networks and PVC-based networks, but also possibly a good degree of interlinked NBR-PVC networks at the same time, more so for blends containing a lower proportion of NBR. The results of gel content difference given by the blend vulcanizates using the two curative systems run nearly parallel to rheometric results particularly with respect to the torque difference data which may roughly be taken as a relative index of the crosslink density developed under the influence of the two curatives in a given blend system. The ETU/S curative system generally produces vulcanizates which show significantly higher *TS* and tensile modulus and for the 70:30 NBR-PVC blend system, it apparently produces a tougher blend vulcanizate that exhibits a substantially high *EB* compared to that produced by the TMTD/S curative system. However, this difference in *EB* is substantially narrowed down and, in fact, the trend is reversed for higher PVC content, as in the 50:50 and 30:70 NBR-PVC blends. The tear strength and hardness data follow a different trend of variation for the two curative systems. For the 70:30 blend the ETU/S-cured vulcanizate shows a higher tear strength but a lower hardness value compared to those produced by the TMTD/S curative system, and for the 50:50 and 30:70 blend systems the variation in the respective properties follows just the opposite trend, but with a much narrowed percentage difference. With respect to volume resistivity of the blend vulcanizates, the 50:50 and 30:70 blends show nearly similar trends of variation of the property, the ETU/S crosslinked system showing a slightly lower volume resistivity value. But the nature of the difference is just the opposite for the 70:30 blend where the ETU/S curative system produces a somewhat higher volume resistivity value. The volume resistivity values, however, follow an increasing trend as the PVC content in the blend keeps on increasing.

Effect of filler incorporation

Some data on the curing characteristics and physical properties of the vulcanizates for 70:30 NBR-PVC blend using ETU/S and TMTD/S curative systems separately are presented in *Table 6*. Data corresponding to the use of carbon black (FEF), precipitated silica (Vulcasil) and activated $CaCO_3$ (Forcal-S) are shown alongside the data for the corresponding gum compound, to enable a comparative evaluation of the role of the three different fillers in the blend. The relative role and efficiency of the ETU/S and TMTD/S systems can also be compared from the tabulated data.

From a comparison of the torque data in *Table 6*, particularly the maximum torque developed and the torque difference, it is indicated that with respect to ETU/S curative system FEF produces significant reinforcing effect while, for use of Vulcasil and Forcal-S as fillers, the reinforcing effects are much subdued or marginal. With respect to TMTD/S curative system, however, the reinforcing effect for incorporation of FEF and Forcal-S as fillers is moderate in nature and the reinforcing effect is slightly improved in the Vulcasil-filled system, where both the maximum torque and the torque difference show relatively high values. In each case of

Table 6 Curing characteristics of filled NBR-PVC (70:30) blends and physical properties of the filled vulcanizates. Comparative evaluation of ETU/S and TMTD/S combinations as curatives. Curing condition: temperature 170°C, pressure 7.6×10^6 N m^{-2}. Curatives: for ETU/S, ETU 2.0 phr, S 1.0 phr; for TMTD/S, TMTD 2.5 phr, S 0.5 phr

	Types of filler							
	Without filler		FEF		Vulcasil		Forcal-S	
Curative system	ETU/S	TMTD/S	ETU/S	TMTD/S	ETU/S	TMTD/S	ETU/S	TMTD/S
Rheometric properties								
Max. torque (N m)	4.37	3.10	5.65	4.16	4.63	4.41	4.58	3.71
Min. torque (N m)	1.81	1.27	1.88	1.76	2.03	1.58	1.47	1.13
Torque difference (N m)	2.57	1.83	3.77	2.46	2.60	2.82	3.11	2.58
Scorch time (min)	2.0	2.4	1.5	1.7	2.2	1.5	1.7	3.2
Optimum cure time (min)	12.5	14.5	15.5	12.7	10.5	10.7	11.5	9.3
Cure rate (N m min^{-1})	0.452	0.373	0.554	0.452	0.486	1.220	0.610	0.429
Physical properties								
Gel content (%)	81.0	72.0	92.7	89.1	90.3	89.6	93.7	88.1
Volume resistivity (ohm cm)	7.0×10^{10}	1.1×10^{10}	8.1×10^9	5.5×10^9	8.3×10^{10}	5.9×10^{10}	4.6×10^{10}	3.7×10^{10}
Tensile strength (kg cm^{-2})	104.0	65.5	180.0	142.0	164.0	124.0	125.0	83.0
200% modulus (kg cm^{-2})	20.0	18.0	50.0	55.0	52.0	44.0	24.0	23.0
Elongation at break (%)	582	478	550	575	600	575	615	610
Tear strength (kg cm^{-1})	2.4	2.0	15.0	13.0	20.0	18.0	7.0	8.0
Hardness 27°C (Shore A)	50	53	66	68	70	70	60	60

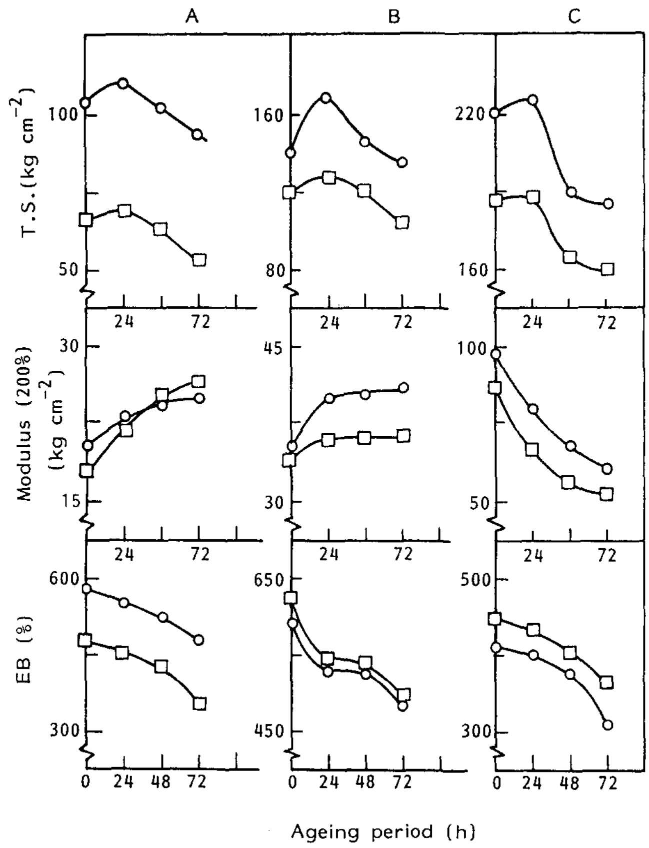


Figure 2 Physical properties of NBR–PVC blend vulcanizates. Effect of air ageing at 100°C. (A), (B) and (C) refer to 70:30, 50:50 and 30:70 NBR–PVC blend ratio. Data given for different curves are ETU, S and TMTD (phr): (○) 2.0, 1.0, 0.0; (□) 0.0, 0.5, 2.5

unfilled and FEF- or Vulcasil-filled blends, the ETU/S curative system produces scorch safety which is close to or comparable with that produced by the TMTD/S curative system. In the Forcal-S filled blend system, however, TMTD/S curative system induces the highest scorch safety.

Consideration of *TS*, tear strength and modulus at 200% elongation for the different filled vulcanizates for the 70:30 blend system also indicates that, with respect to imparting reinforcement, the fillers used are in the order FEF > Vulcasil ≫ Forcal-S. Filled vulcanizates show development of different degrees of hardness depending mainly on the nature of the filler used and, with respect to the hardness exhibited, the fillers follow the order Vulcasil > FEF ≫ Forcal-S. For development of high tear strength and high modulus along with high hardness, Vulcasil filler appears to be a better choice, while for a combination of high *TS*, high modulus and moderately high tear strength, FEF filler would be the right choice for making filled (70:30) NBR–PVC blend vulcanizates and in either case ETU/S curative system appears to produce better balanced effects over TMTD/S curative systems.

Ageing behaviour

Heat ageing behaviour. The heat ageing characteristics of the NBR–PVC blend vulcanizates at the three selected blend ratios using the two different curatives (ETU/S, TMTD/S) in each case are shown in *Figure 2*, the ageing having been done for different lengths of time at 100°C and the data considered and compared being *TS*, modulus at 200% elongation and *EB*. The ageing behaviour of 70:30 and 50:50 blends are by and large similar to that of NBR, but with some change in the pattern of *TS* variation with hours of ageing. For a blend having PVC as the major component such as the 30:70 blend, the ageing pattern is more or less similar to that for PVC. A close examination of the ageing curves clearly reveals that an ageing period of 24–36 h is somewhat critical and the trend of change in a given specific property passes through a sharp change (showing a sharp or distinct change in the slope of the curve, an inflection or a maximum). For the 70:30 filled blends the ageing pattern observed is more or less similar to that observed for the unfilled system. The two curative systems (ETU/S and TMTD/S) produce almost similar ageing patterns in each blend system and the pattern also remains more or less comparable, showing no significant differences with respect to use of different types of fillers (*Figure 3*), indicating that fillers play almost inert roles during ageing of the blend vulcanizates according to normal expectations.

Oil ageing behaviour of unfilled blends. The oil ageing characteristics of the different blend vulcanizates (unfilled) and those of filled vulcanizates based on 70:30 NBR–PVC blends using the two curative systems (ETU/S and TMTD/S) in each case are given in *Table 7*. Oil ageing properties (24 h of ageing at 100°C in a standard hydrocarbon oil) of the different unfilled blends appear to be close for vulcanizates given by both the curative system. Higher PVC content in the blend apparently tends to make the vulcanizates more oil-resistant. With respect to change in modulus on ageing, the ETU/S cured 70:30 blend is much different from all other vulcanizates shown in *Table 7* in view of

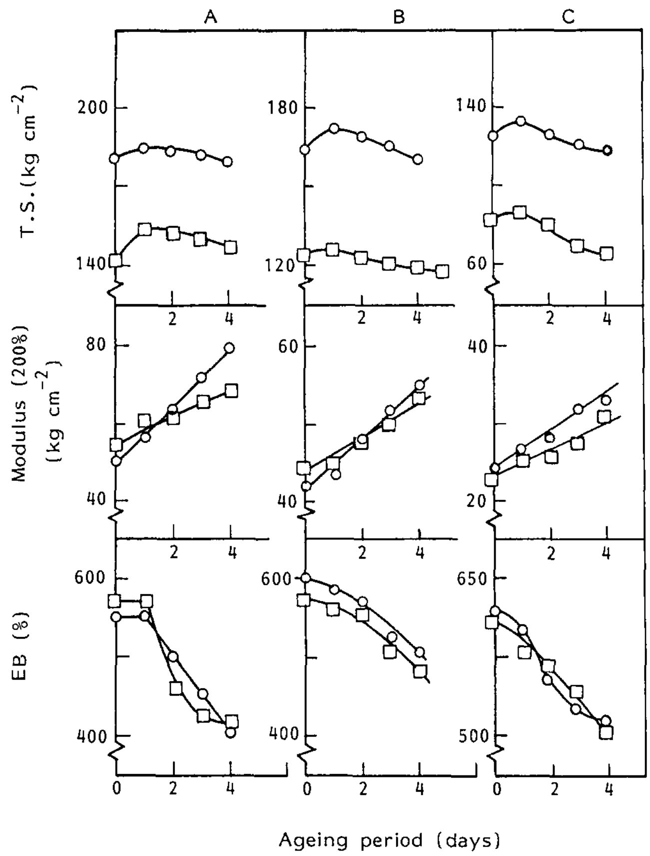


Figure 3 Physical properties of filled NBR–PVC (70:30) blend vulcanizates. Effect of air ageing at 100°C. Curves under (A), (B) and (C) refer to use of FEF, Vulcasil and Forcal-S as filler respectively. Curative system used: (○) ETU/S combination; (□) TMTD/S combination

Table 7 Oil ageing behaviour of NBR–PVC gum and filled blend vulcanizates^a. Ageing condition: temperature 100°C, period 24 h

		NBR–PVC blend ratio											
		70:30								50:50		30:70	
	Curative system	Gum		FEF filled		Vulcasil filled		Forcal-S filled		Gum		Gum	
Properties		ETU/S	TMTD/S	ETU/S	TMTD/S	ETU/S	TMTD/S	ETU/S	TMTD/S	ETU/S	TMTD/S	ETU/S	TMTD/S
TS before ageing (kg cm^{-2})		104.0	65.5	180.0	142.0	164.0	124.0	125.0	83.0	140.0	120.0	220.0	186.0
TS after ageing (kg cm^{-2})		147.0	92.5	183.4	149.0	168.0	125.7	128.0	83.8	190.0	138.0	207.0	173.0
		(141.0)	(141.2)	(101.8)	(104.9)	(102.4)	(101.4)	(102.4)	(100.9)	(136)	(115)	(94.1)	(93.0)
200% modulus before ageing (kg cm^{-2})		20.0	18.0	50.0	55.0	42.0	44.0	24.0	23.0	35.0	34.0	98.0	87.0
200% modulus after ageing (kg cm^{-2})		48.0	27.0	53.0	58.0	42.7	44.3	25.3	25.0	58.0	53.0	154.0	147.0
		(240)	(150)	(106.0)	(105.4)	(101.7)	(100.7)	(105.4)	(108.7)	(166)	(155)	(157)	(169)
EB (%) before ageing		582	478	550	575	600	575	615	610	590	625	410	450
EB (%) after ageing		475	447	537	562	591	569	600	594	425	455	332	408
		(81.6)	(93.5)	(97.6)	(97.7)	(98.5)	(98.9)	(97.6)	(97.4)	(72.1)	(72.8)	(80.9)	(90.6)

^{a}Data in the parentheses indicate percentage retention of the corresponding property after oil ageing

the fact that it shows about 140% increment in modulus while the rest of the vulcanizates, irrespective of blend ratio and irrespective to the curative system used, show an increment of only 50–70% in modulus.

Oil ageing behaviour of filled blends. The filled vulcanizates (for 70:30 blend), however, show much superior oil ageing characteristics and the ageing trend for ETU/S and TMTD/S cured systems are more or less parallel and comparable in terms of retention of *TS*, modulus and *EB*, and by and large, the retention is about 102–105% for *TS*, 100–109% for modulus at 200% elongation and 97–99% for *EB*.

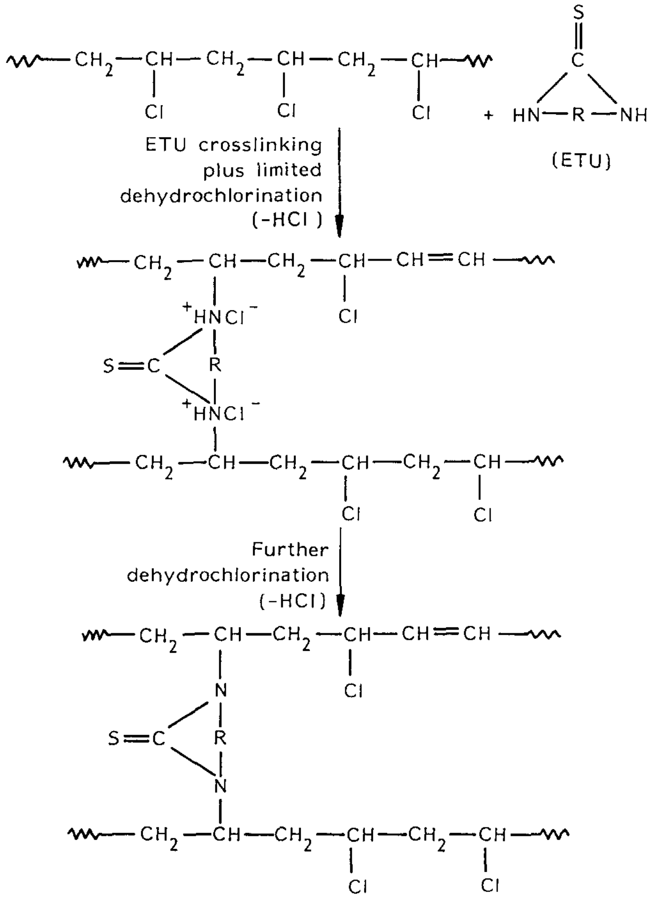
Phase morphology

Phase morphology of three blend samples, viz. an uncured blend, a blend cured with the TMTD/S system, curing only the NBR component and leaving the PVC component uncured, and a blend cured with the ETU/S system, allowing simultaneous crosslinking and possibly inter-crosslinking of NBR and PVC chains based on 70:30 NBR–PVC composition, was studied using scanning electron microscopy. The SEM micrographs obtained under comparable conditions for the three blends are shown in *Figure 4*.

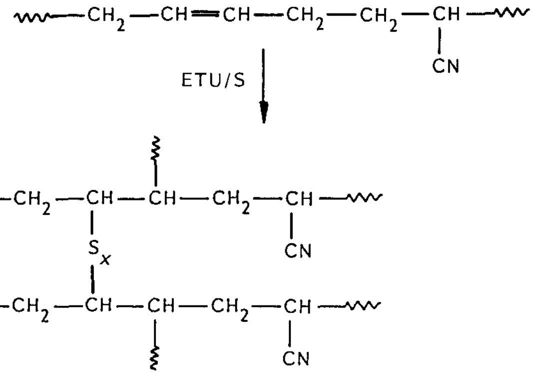
Comparative examination of the micrographs (a) and (b) reveals that phase morphology of the (unfilled) vulcanized blend undergoes a minor (though distinct) variation when only the rubber component is allowed to crosslink (using TMTD/S system as the curative). In either case, however, the large domains of PVC (the white zones or specks) are distributed somewhat unevenly in the NBR matrix (black background). The size of the PVC domains is, however, usually smaller on average in the TMTD/S-cured blend system. The phase morphology is, however, altogether different in the ETU/S-cured blend system (micrograph (c)). The PVC domains appear more uniformly dispersed and distributed into much finer domains all through. Simultaneous crosslinking allowing formation of two different types of networks at the same time and possible inter-crosslinking allowing unification of two different types of networks at least in part apparently makes this uniformity in phase morphology possible in the ETU/S-cured blend system. This also goes to explain well the differences in the physical properties profile (*TS*, modulus, tear strength and gel content) of the blends cured by the ETU/S system and by the TMTD/S system—the former expectedly producing higher gel content and higher mechanical properties for comparable vulcanizates much as a consequence of some degree of interpenetration of networks and some inter-crosslinking leading to substantial fragmentation of the PVC phase domains and ultimately to their uniform distribution through the NBR phase.

MECHANISM OF CROSSLINKING

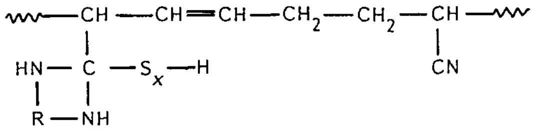
Considering the reactions involved in the amine-induced dehydrochlorination of PVC and diamine- or polyamine-induced crosslinking of this polymer, the ethylenethiourea (ETU) induced crosslinking of PVC is likely to involve the following sequence of reactions:



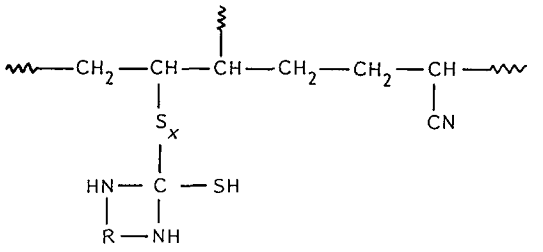
ETU-accelerated S vulcanization of NBR (separately) would lead to the simultaneous formation of NBR-based network via establishment of sulphur (disulphide/polysulphide) crosslinks between the NBR chains:



It is also likely that some pendant groups including ETU and S would be formed along the NBR chains:



or



(R = –CH$_2$ — CH$_2$ —)

The ETU moieties thus linked with NBR chains may subsequently react with neighbouring PVC chains leading ultimately to some degree of unification of the NBR and PVC networks.

In the blend vulcanizates, the sequence of reactions as above apparently leads to loss of unsaturation of the NBR chains and at the same time limited generation of unsaturation in the PVC chains as a consequence of ETU-catalysed thermal dehydrochlorination, which results in a measurable lowering of the glass transition temperature (T_g) of the PVC[12]. Thus, while incorporation of PVC would expectedly stiffen NBR, limited generation of chain unsaturation via dehydrochlorination of PVC would expectedly lead to some enhancement of flexibility of the system in view of lowering of T_g of the residual PVC[8,12]. The observations in properties of the blend vulcanizates made should be viewed in the light of these possibilities and what is observed must be taken as the overall balanced effect of blend ratio and its variation in crosslinking and structural changes in the chain segments.

CONCLUSIONS

ETU/S combination in optimum dose proportions brings about simultaneous crosslinking of NBR and PVC in their blends at 170°C under 7.6×10^6 N m^{-2} pressure

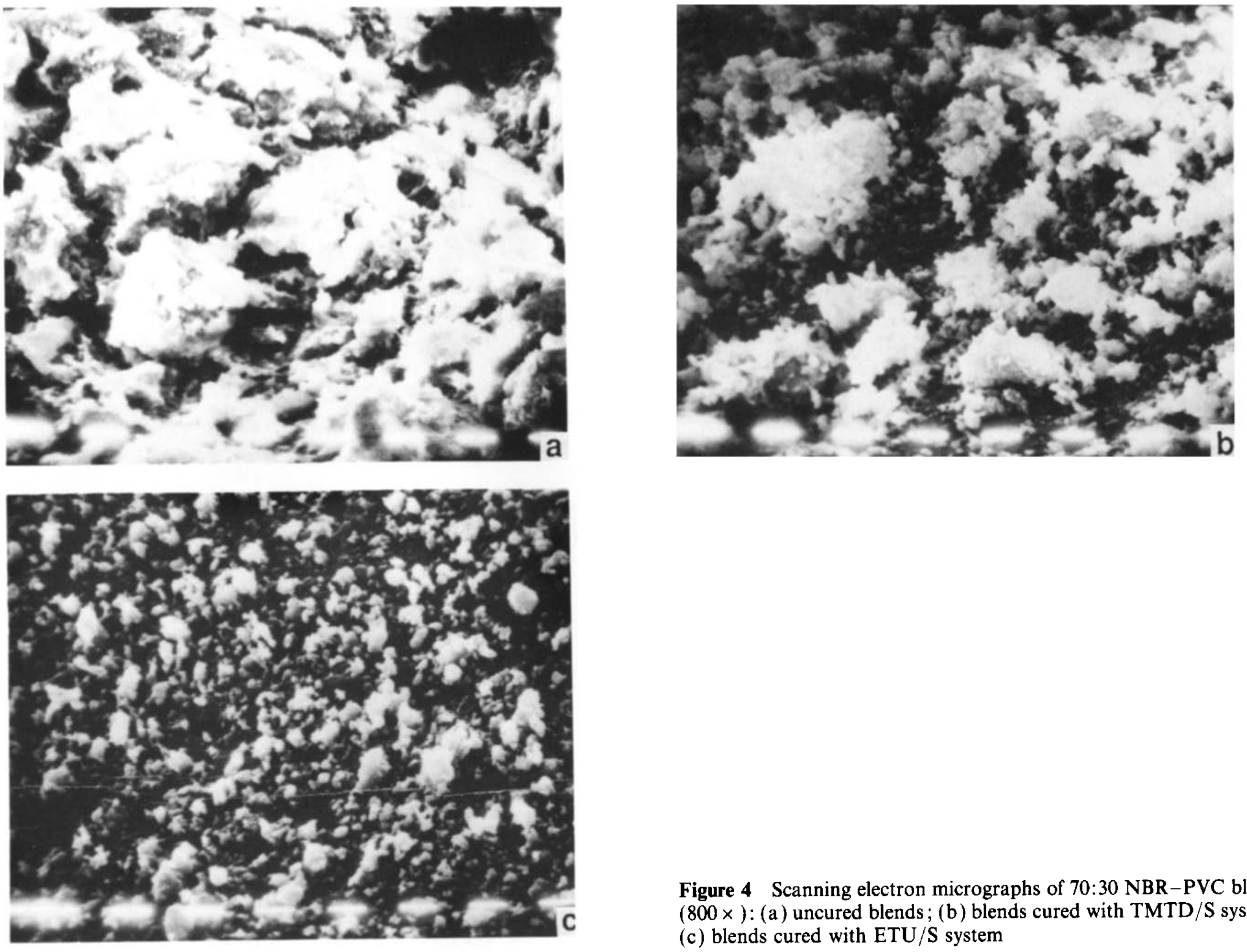


Figure 4 Scanning electron micrographs of 70:30 NBR–PVC blends (800 ×): (a) uncured blends; (b) blends cured with TMTD/S system; (c) blends cured with ETU/S system

leading to high crosslink density and gel content for the cured blends. Some degree of inter-crosslinking leading to unification of two types of networks is considered to be a distinct possibility in this process. ETU/S combination with its role as a co-crosslinker and inter-crosslinker for NBR–PVC systems in their blends produces a much better balance of curing characteristics, vulcanizate physical properties and better uniformity in phase morphology than those produced by TMTD/S combination, which apparently plays a limited role in view of its curing ability being restricted to only NBR.

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