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Plasticizing effect of epoxidized natural rubber on PVC/ELNR blends prepared by solution blending

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A series of polymer blends of poly(vinyl chloride) (PVC) and epoxidized liquid natural rubber (ELNR) were prepared and characterized. The aim of the work was to study the plasticizing effect of ELNR on the PVC/ELNR blend systems. Thermal properties of the samples were studied by differential scanning calorimetry (DSC). The glass transition temperature of the samples decreased with both degree of epoxidation and the percentage of composition of the samples. The scanning electron microscope (SEM) studies point to the two phase morphology. Tensile test results for the blend samples have been compared. From tensile tests, it was found that elongation of the materials increased with degree of epoxidation. On the other hand, tensile strength and modulus of the material decreased with the epoxide content. A good plasticization effect was observed for samples of ELNR with wt. 50% of epoxidation.

Key words: *polyvinyl chloride; epoxidized natural rubber; plasticizing effect; blend*

1. Introduction

Polymer blends and alloys have received widespread attention for the last several decades. Polymer blends are defined as physical mixture of two or more polymers. They may be divided into different categories: so-called miscible blends in which the components exist in a simple homogeneous phase and immiscible ones in which the components exist in two distinct separated phases. Generally, the former ones offer various advantages over the latter. The origin of miscibility between the polymer pairs has been understood based on theoretical background and experimental results [1, 2]. Most polymers are thermodynamically immiscible. In immiscible polymer blends,

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morphology is affected by the composition, viscosity ratio, interfacial tension, processing conditions etc. [3–5]. Several studies have been reported in which epoxidised polydienes were used as polymeric plasticizers to PVC. Margaritas et al. [6] reported the plasticization of PVC with epoxidised polybutadiene (EPB) as a function of the degree of PB epoxidation, its microstructure and molecular weight.

As a part of the miscibility studies of chlorinated polymers with epoxidized polyhydrocarbons [7], the compatibility behaviour of PVC with epoxidized natural rubber has been reported. Epoxidized liquid natural rubber (ELNR) forms a new class of modified elastomers with special properties such as increased oil resistance and wet traction, decreased air permeability and the ability to be highly reinforced with a silica filler without coupling agents. Also it is well known that epoxidized oils are used as PVC plasticizers. A common industrial practice is to modify PVC compositions by incorporating a diverse array of additives in order to obtain a polymer with satisfactory processing and end-use performance. The required modifications are more extensive and diversified than those practiced with other polymers of major industrial importance. However, the industrial application of PVC in the form of the resulting materials is more versatile. In flexible and semi-rigid PVC formulations, plasticizers are key ingredients, although other compounding ingredients (e.g. stabilizers) are also extremely important. Plasticizers impart flexibility and play an important role in heat processing by reducing the viscosity of the molten material to ensure good flow properties. The theory of plasticization has been reviewed by many investigators [8–11]. The effects of various concentrations of plasticizers on the mechanical properties of polymers and copolymers in a high concentration range have been reported [9, 11–15]. In addition to the melt flow properties, the flexibility, extensibility, and rigidity of final products at room temperature are influenced by the addition of plasticizers [16–18].

The main objective of the present work was to study the extent of property modification of PVC attainable by blending it with modified liquid natural rubber. For this purpose, a series of blends with various degrees of epoxidation has been prepared. The effect of the degree of epoxidation as well as of the amount of ELNR on the property modification was investigated and the role of epoxidized natural rubber as a plasticizer has been discussed.

2. Experimental

Materials. PVC (*K* value 65, density 1.37 g/cm^3) was supplied by M/s Chemicals and Plastics Ltd., Chennai. NR (ISNR-5, $\bar{M}_v$ = 820 000, intrinsic viscosity in benzene at 30 °C = 4.45 dl/g) was supplied by the Rubber Research Institute of India, Kottayam. Thermal stabilizer, dibutyl tin dilaurate (DBTDL) (Fluka, Switzerland) was used without purification. 2-Butanone used as the solvent for blending was supplied by E. Merck India Ltd. This was dried over anhydrous calcium chloride and distilled before use. Glacial acetic acid, toluene, methanol and hydrogen peroxide (30 v/v) were of reagent grade. Toluene and methanol were dried and distilled before use. Hydroxyl terminated liquid natural rubber (HTNR) of number average molecular weight 4600 was prepared in the laboratory by the photochemical degradation of natural rubber as per reported procedure [19]. It was reprecipitated thrice from toluene using methanol and dried at 70–80 ºC in vacuum before use.

Preparation of ELNR. Epoxidised LNR of 10 to 50 mol % epoxidation (ELNR-10, ELNR-20, ELNR-30 ELNR-40 and ELNR-50) was prepared in the laboratory by the epoxidation of LNR using glacial acetic acid and hydrogen peroxide as per reported procedure [20]. ELNR-10 was prepared by dissolving LNR (25 g) in 166 dm^3 of toluene to obtain a 15% solution and was stirred at 50 ºC for 3h with 0.55 mol of aqueous hydrogen peroxide and 0.35 mol of glacial acetic acid. Other ELNR samples, with 20, 30, 40 and 50 mol % of epoxidation were also prepared by the same procedure using appropriate amounts of hydrogen peroxide and 5, 6, 8 and 10 hours of stirring, respectively. At the end of the reaction, the product was isolated by precipitation from methanol. It was dried in vacuum and then characterized by titrimetric, IR and NMR techniques [21, 22].

Preparation PVC/ELNR blends. A series of blends of PVC and epoxidised liquid natural rubber with 10, 20, 30, 40 and 50 mol % of epoxidation were prepared from the common solvent 2-butanone as follows. A 3% (w/v) solution of PVC in 2-butanone was prepared with 4 wt. % of DBTDL (based on PVC) as a thermal stabilizer. This solution was then added to the rubber solution in 2-butanone at various compositions. It was thoroughly mixed using a magnetic stirrer for 5 h at 50 ºC and cast on glass plates. The samples were then dried in vacuum at 70 ºC for two days to remove the traces of residual solvent. The cast samples were characterized by various analytical methods such as thermal analysis, tensile measurements and scanning electron microscopy. The blends were designated as, for example PVC/ELNR-50(80/20), the abbreviation meaning a blend of 80 parts PVC and 20 parts ELNR of 50 mol % epoxidation.

Measurements. DSC measurements were done using a Shimadzu DSC60 thermal analyzer (Japan) at a programmed heating rate of 10 °C/min. The experiments were carried out in the temperature range 30–300 °C under dry nitrogen atmosphere (25 mV/min) using aluminium crucibles. The sample weight was 4–5 mg. For measuring subambient transition, the DSC was performed with a Mettler Inc (TA 300) microcalorimeter, (Germany).

Stress-strain behaviour was studied on a Zwick 1474 Universal Testing Machine (Germany) as per ASTM D 412-80 test method at a constant cross head speed of 500 mm/min using dumb bell shaped test specimens. At least five samples were tested in each case and the average value was taken as the result for determining Young's modulus, tensile strength and elongation at break.

Tensile fracture surfaces of thin films were examined using a JEOL 5400 SEM (Tokyo, Japan) at 20 kV using magnifications 500 to 1000 to study the morphology of the samples. The surface was sputter coated with Au/Pd alloy in a sputter coating machine (Balzers SCD 050, Germany). A minimum of five photographs were taken for each sample for analysis.

3. Results and discussion

Property modification of PVC has been accomplished with the help of modified liquid natural rubber. A few series of blends were prepared and subject to tensile testing, SEM studies, and DSC analysis. The compositions of the blends prepared are given in Table 1.

Table 1. Compositions of PVC/ELNR blends

Blend	PVC [%]	ELNR-50 [%]	Blend	PVC [%]	ELNR-20 [%]
PVC/ELNR-50 (90/10)	90	10	PVC/ELNR-10 (90/10)	90	10
PVC/ELNR-50 (80/20)	80	20	PVC/ELNR-10 (80/20)	80	20
PVC/ELNR-50 (70/30)	70	30	PVC/ELNR-10 (70/30)	70	30
PVC/ELNR-50 (50/50)	50	50	PVC/ELNR-10 (50/50)	50	50
PVC/ELNR-50 (30/70)	30	70	PVC/ELNR-10 (30/70)	30	70
Blend	PVC [%]	ELNR-40 [%]	Blend	PVC [%]	ELNR-20 [%]
PVC/ELNR-40 (70/30)	70	30	PVC/ELNR-30 (70/30)	70	30
PVC/ELNR-40 (50/50)	50	50	PVC/ELNR-30 (50/50)	50	50
PVC/ELNR-40 (30/70)	30	70	PVC/ELNR-30 (30/70)	30	70
Blend	PVC [%]	ELR-20 [%]			
PVC/ELNR-20 (70/30)	70	30			
PVC/ELNR-20 (50/50)	50	50			
PVC/ELNR-20 (30/70)	30	70			

3.1. Differential scanning calorimetry (DSC)

The thermograms of selected samples are given in Figs. 1 and 2. The T_g values obtained from the thermograms are listed in Table 2. T_g of PVC was found to be 80 ºC which is a slightly lower value than that expected of solution cast blends. The corresponding values of ELNR-10, ELNR-20, ELNR-30, ELNR-40 and ELNR-50 were found to be –39, –31, –27, –24 and –20 ºC, respectively. The introduction of polar groups in the form of oxirane rings obviously increased the T_g value of LNR. The values increased from –65 ºC to –39 ºC and to –20 ºC as the degree of epoxidation was increased from zero to 10 and to 50 mol %. This is due to a stronger intermolecular interaction existing in ELNR that was originally absent in NR. The DSC thermograms of the ELNR-10 blends possess two distinct transitions, viz., PVC/ELNR-10 (70/30) exhibited transitions at 71°C and –36 °C (Fig. 1). The same trend is observed for PVC/ELNR-20 and PVC/ELNR-30 blends. On the other hand, ELNR-40 and ELNR -50 samples show a single transition for all compositions studied (Table 2). For example PVC/ELNR-40 (70/30) and PVC/ELNR-50(70/30) exhibited transitions at 56 and 32 ºC,

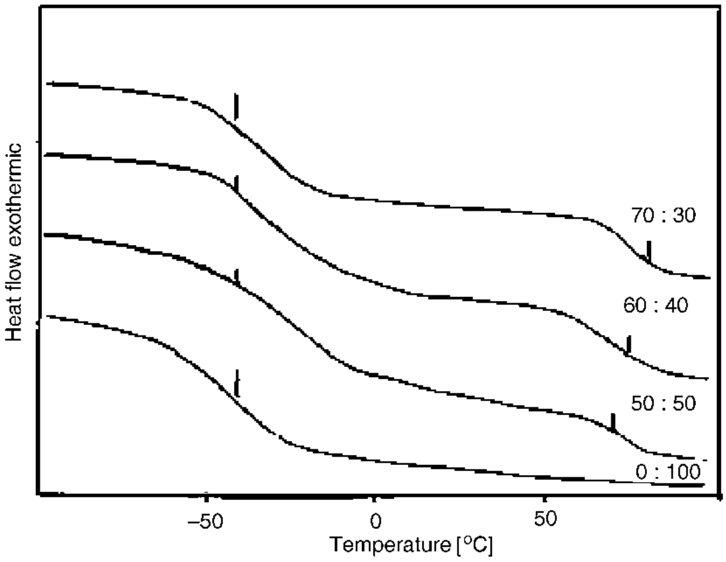

Fig. 1. DSC thermograms of PVC/ELNR-10 blend in various compositions

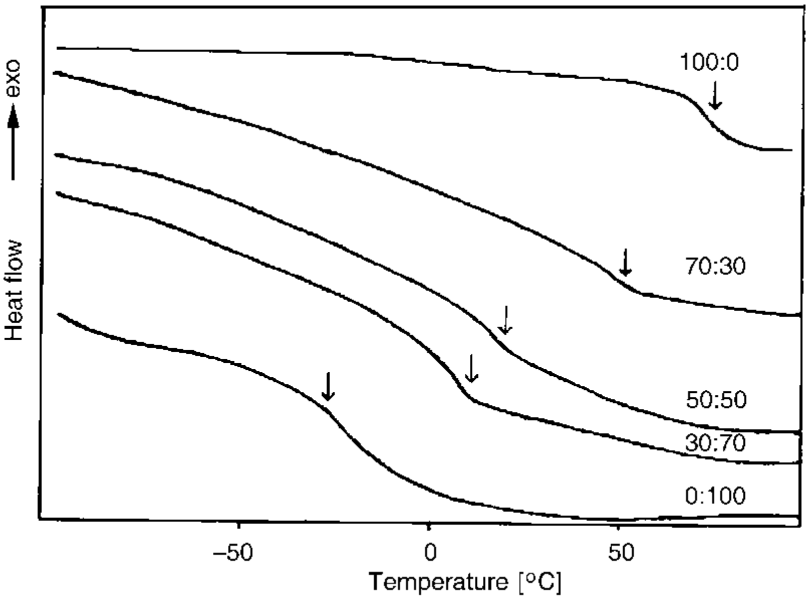

Fig. 2. DSC thermograms of PVC/ELNR-40 blends in various compositions

respectively (Fig. 2). The values are found to be intermediate between those of the component polymers. This corresponds to a miscible system indicating that the ELNR with a sufficiently high epoxy content becomes miscible with polyvinyl chloride.

Table 2. Transition temperatures (T_g) of PVC/ELNR blends and components

Sample	T_g of PVC phase [°C]	T_g of ELNR phase [°C]
PVC/ELNR-10 (70/30)	71	–36
PVC/ELNR-10 (50/50)	69	–35
PVC/ELNR-10 (30/70)	67	–33
PVC/ELNR-20 (70/30)	63	–30
PVC/ELNR-30 (70/30)	60	–20
PVC/ELNR-40 (70/30)	56	–
PVC/ELNR-40 (50/50)	42	–
PVC/ELNR-40 (30/70)	48	–
PVC/ELNR-50 (70/30)	32	–
PVC/ELNR-50 (50/50)	20	
PVC/ELNR-50 (30/70)	12	
ELNR-10	–	–39
ELNR-20	–	–31
ELNR-30	–	–27
ELNR-40	–	–24
ELNR-50	–	–20
PVC	80	–

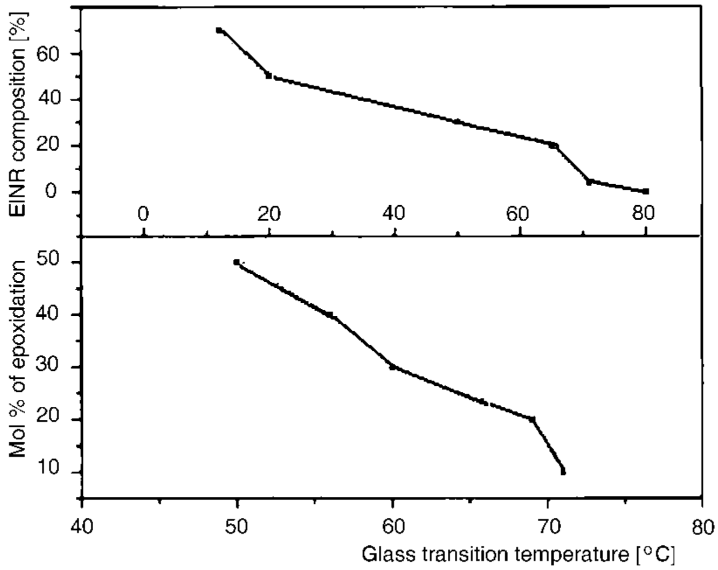

Fig. 3. Variation of glass transition temperatures with composition and degree of epoxidation of ELNR

It provides a stronger interaction with the PVC matrix flexibilising the PVC segments and lowering the T_g value. The variation of glass transition temperature with the degree of epoxidation is shown in Fig. 3. It also indicates the variation of T_g of the representative blends PVC/ELNR-50 with percentage composition of ELNR.

The observed trend in variation of T_g is explained based on a higher degree of miscibility and subsequent plasticization achieved with ELNR of higher epoxidation. The reason for miscibility is attributed to the increase in the solubility parameter of liquid NR to a matching level with polyvinyl chloride due to introduction of sufficient number of epoxy groups into the diene backbone. The molecular origin of miscibility could be attributed to polar–polar interactions. Plasticization of PVC by polymeric or liquid plasticizers enhances the segmental mobility which in turn modifies the material properties and the glass transition temperature of the polymer.

3.2. Tensile properties

The stress-strain measurements were carried out on selected samples from all the series of blends, viz., PVC/ELNR-50, PVC/ELNR-40, PVC/ELNR-30, PVC/ELNR-20 and PVC/ELNR-10 and the tensile curves so obtained are presented in Figs. 4, 5. For the sake of comparison, the tensile curve of unmodified PVC was also presented in Fig. 5. The data obtained from these curves have been given in Table 3.

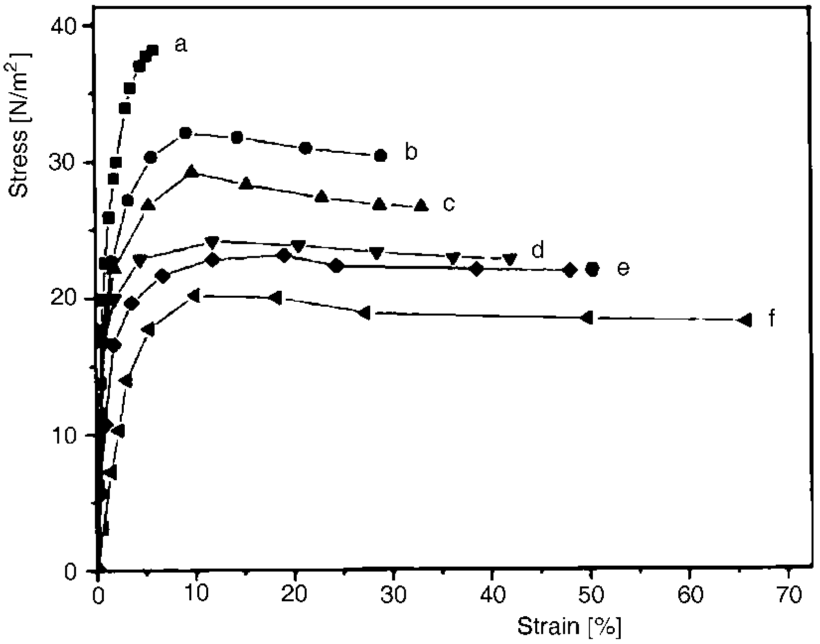

Fig. 4. Tensile curves of PVC/ELNR (50/50) blends: a) PVC/ELNR-10, b) PVC/ELNR-20, c) PVC/ELNR-30, d) PVC/ELNR-40 e) PVC/ELNR-50

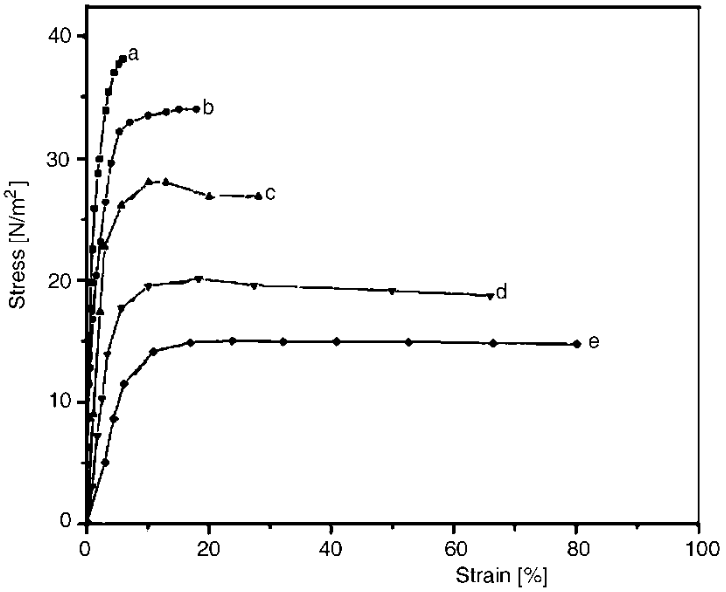

Fig. 5. Tensile curve of PVC/ELNR-50 blends of various compositions: a) PVC, b) PVC/ELNR-50(90/l0), c) PVC/ELNR-50(80/20), d) PVC/ELNR-50(50/50), e) PVC/ELNR-50(30/70)

Table 3. Tensile properties of PVC and PVC/ELNR blends

Blend	Tensile strength [N/mm^2]	Young's modulus [N/mm^2]	Elongation [%]
PVC	38	3200	6
PVC/ELNR-10(90/10)	37	3200	9
PVC/ELNR-10(80/20)	35	2900	12
PVC/ELNR-10(70/30)	34	2800	17
PVC/ELNR-10(50/50)	32	2500	29
PVC/ELNR-10(30/70)	30	2300	35
PVC/ELNR-20(70/30)	33	2570	20
PVC/ELNR-20(50/50)	29	2100	33
PVC/ELNR-20(30/70)	24	1800	42
PVC/ELNR-30(70/30)	30	2530	23
PVC/ELNR-30(50/50)	24	2000	42
PVC/ELNR-30(30/70)	20	1500	60
PVC/ELNR-40(90/10)	35	2980	15
PVC/ELNR-40(80/20)	30	2670	20
PVC/ELNR-40(70/30)	28	2500	29
PVC/ELNR-40(60/40)	26	2360	38
PVC/ELNR-40(50/50)	23	1950	48
PVC/ELNR-40(40/60)	22	1500	60
PVC/ELNR-40(30/70)	16	1000	72
PVC/ELNR-50(70/30)	26	2430	40
PVC/ELNR-50(50/50)	20	1700	66
PVC/ELNR-50(30/70)	9	800	96

The tensile curve of unmodified PVC shows characteristic features of a brittle material (Fig. 5, curve a). It undergoes a very small deformation under stress and failure occurs at 6% elongation without undergoing any yield phenomenon. The tensile strength and modulus of elasticity were found to be very high with values 38 N/mm^2 and 3200 N/mm^2, respectively. It is observed that addition of 10 parts of ELNR-40 and ELNR-50 to PVC formed a blend that shows a yield point which is not observed for unmodified PVC. The yield strength was found to be 34 N/mm^2 for PVC/ELNR-50(90/10). Consistent with this tensile strength, modulus and elongation at break also showed a variation. The first two values are lower than that of PVC whereas elongation at break is higher (Table 3). The tensile curves of samples with composition ranging from 20 to 70 parts of ELNR-40 showed variation with respect to the rubber content. The change in nature of the curves becomes more pronounced with higher ELNR-40 content. The yield point becomes broader and finally it disappears and the tensile curve tends to flatten out. The samples behaved like soft flexible mass when ELNR-40 and ELNR-50 content became too high, viz. 70%. (Table 3).

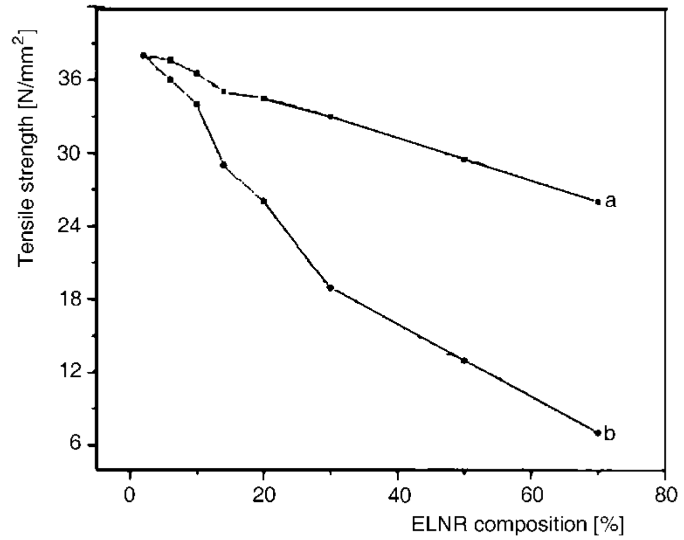

Fig. 6. Variation of tensile strength with composition of: a) PVC/ELNR-20, b) PVC/ELNR-50

Variations in tensile strength, modulus and elongation at break with composition of the blends are given in Figs. 6, 7. It is clearly seen that the strength and modulus values decrease while elongation at break increases with ELNR-50 content. At higher level of rubber content, the tensile strength decreases to a very low value. For example, the tensile strength of PVC/ELNR-40 (90/10) was 35 N/mm^2 whereas that of 30/70 blend was 16 N/mm^2 and for PVC/ELNR-50 blends for the same composition the values are 34 and 9 N/mm^2, respectively. A similar variation was also observed in the modulii. The modulus drops from 2980 N/mm^2 for PVC/ELNR-40 (90/10) to 1000 N/mm^2 for (30/70) composition. The elongation at break shows a large increase with increasing rubber content. For example, it rose from a low value of 15% for PVC/ELNR-40 (90/10) to a very high value of 72% for PVC/ELNR-40 (30/70).

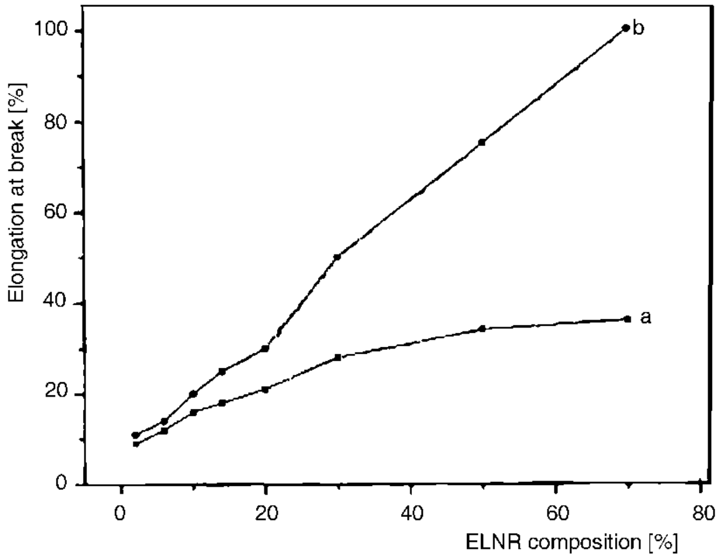

Fig. 7. Variation of elongation at break with composition of: a) PVC/ELNR-20, b) PVC/ELNR-50

The above variation in properties showed that brittle and rigid nature of PVC stands modified with addition of ELNR-50. Hence it can be concluded that ELNR-40 and ELNR-50 exhibit a plasticizing effect on rigid PVC. The above results are in conjunction with the manifestation of single T_g values, which is lower than that of unplasticised PVC, obtained in the DSC analysis of these blend systems.

The tensile strength and modulus decrease and the elongation at break increases. The glass transition temperature tends to decrease with the extent of plasticization of PVC. Plasticization of PVC by ELNR enhances the segmental mobility which in turn modifies the material properties. Although variation in the nature of the tensile curves is observed with rubber content in these blend systems, the trend in the variation suggests that the blends are more heterogeneous in nature. Figure 8 shows the variation of tensile strength and elongation at break versus degree of epoxidation. It can be seen from the figure that the rubber with higher extent of epoxidation provides drastic variation in the yield strength. For example, the yield strength for PVC/ELNR-20 (80/20) is 34 N/mm^2 and the yield strength of PVC/ELNR-50 (80/20) is 28 N/mm^2.

The solubility parameters of PVC ((9.4 (cal/cm^3)$^{1/2}$), ELNR-40 and ELNR-50 ((9.2 (cal/cm^3)$^{1/2}$) in these blend systems are comparable and hence the two components tend to be compatible. As a result of the compatibility, the heterogeneous nature of these blend systems has been lost and plasticization of PVC matrix took place. This is the reason for a drastic decrease in tensile strength and modulus values in PVC/ELNR-40 and PVC/ELNR-50 blends which being miscible, lead to plasticization.

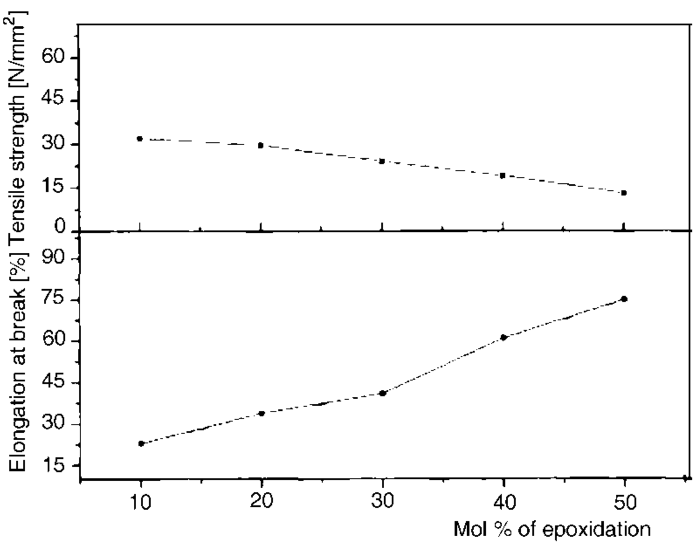

Fig. 8. Variation of elongation at break and tensile strength with the degree of epoxidation in ELNR

These results can be explained based on interaction between the blend components. In the case of rubber with low degree of epoxidation, the interaction between the components is limited but the rubber with higher degree of epoxidation interacts more strongly with PVC affecting all the tensile properties viz., tensile strength, tensile modulus, elongation at break and tensile fracture mechanism.

3.3. Morphological studies using SEM

Fracture surfaces of dumb-bell shaped tensile specimen from selected samples of the blends have been examined using SEM. An attempt has been made to correlate the morphology of fracture surface with the tensile properties of the blend systems.

The fractographs of PVC, PVC/ELNR-10(50/50), and PVC/ELNR-50(50/50) are given in Fig. 9a–c. The tensile fracture surface of rigid PVC (Fig. 9a) showed that the sample undergoes a brittle mode of failure as the fracture surface is characterized by waviness and closely placed line patterns. The stress-strain curve of the material also showed a brittle mode of fracture. The sample undergoes failure without showing a yield point and it has got the highest tensile strength (38 N/mm^2) among all the samples. As the epoxy content of ELNR increases, the brittle fracture changes gradually into a ductile one. On increasing the rubber content to 50%, the fracture front shows increase of plastic deformation. The fracture surface becomes highly deformed and exhibits features of fine fibrils, parabolic and wavy fracture front. Orientation of the matrix along the stress axis is also observed at the fracture surface. All these observations indicate that the ductile nature of the blend increases with rubber content. This finding is supported by the respective tensile curve, being also in conformity with the fact that the higher amounts of epoxidised rubber in major quantity provide loose and flexible character to the material. This is also reflected in the tensile curve being characteristic of a very flexible and soft material. The results indicate that the epoxidized rubber is miscible with PVC rendering it more flexible. In other words, the ELNR-50 tends to plasticize PVC as a manner generally observed with the commercial PVC plasticizers. This is evident from the tensile curves which show higher extent of elongation and ductile behaviour.

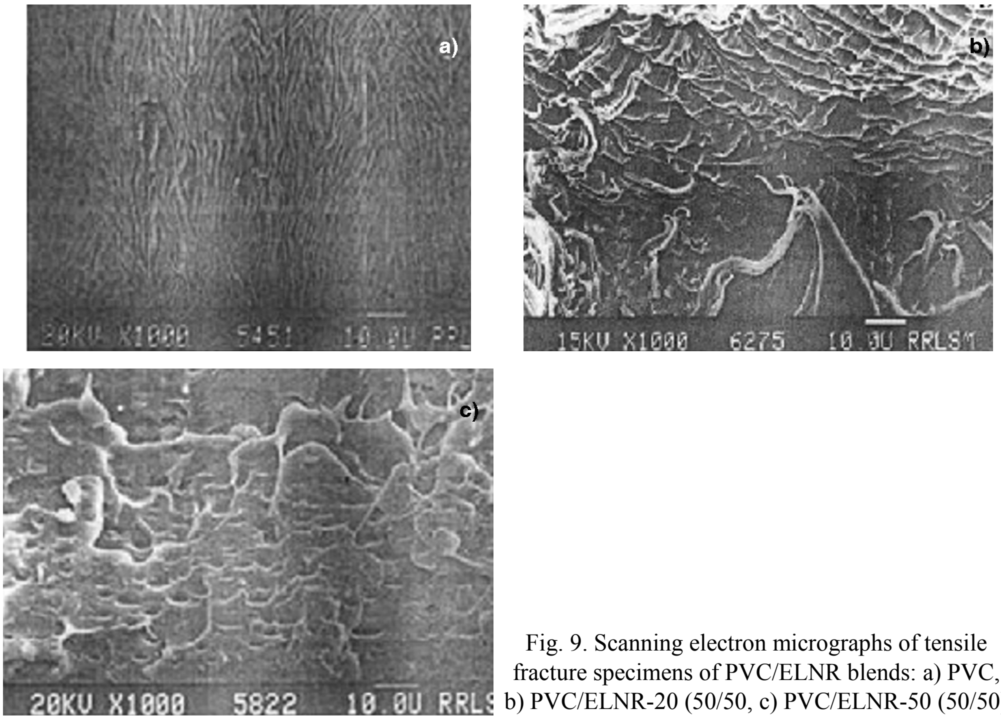

Fig. 9. Scanning electron micrographs of tensile fracture specimens of PVC/ELNR blends: a) PVC, b) PVC/ELNR-20 (50/50, c) PVC/ELNR-50 (50/50)

A comparison of the blend systems shows that the epoxy content influences the failure pattern of the tensile samples. With 30 parts of ELNR-50 added into PVC there seems to be a change in the appearance of the fracture surface to a deformed state. This corresponds to a shift from the brittle fracture to a ductile fracture mechanism which means that the matrix has become more flexible. This is reflected in the tensile test results discussed above. In the case of 70/30 composition, ELNR-50 based blends show ductile fracture mechanism (Fig. 9c). But PVC/ELNR-20 blend deformed in a manner similar to an incompatible blend showing a coarse fracture surface (Fig. 9b). The ductile fracture behaviour of the former is attributed to a higher extent of interaction between the PVC and ELNR with 50 mol % of epoxidation. The lower extent of interaction of the two components is discernible from the brittle mode of fracture in the other systems, viz., PVC/ELNR-20 and PVC/ELNR-10 where the degree of epoxidation is much lower at 10 and 20 mol %. These observations along the tensile behaviour indicate that the brittle nature of PVC stands modified by the ELNR-50 in these blends. A comparison of the fracture surfaces of PVC/ELNR-50 and PVC/ELNR-20 shows that the PVC/ELNR-50 is found to be a miscible system but PVC/ELNR-20 blend shows heterogeneous nature. It is concluded, therefore, that the epoxidized liquid NR with high extent of epoxidation gives blend showing ductile nature with PVC.

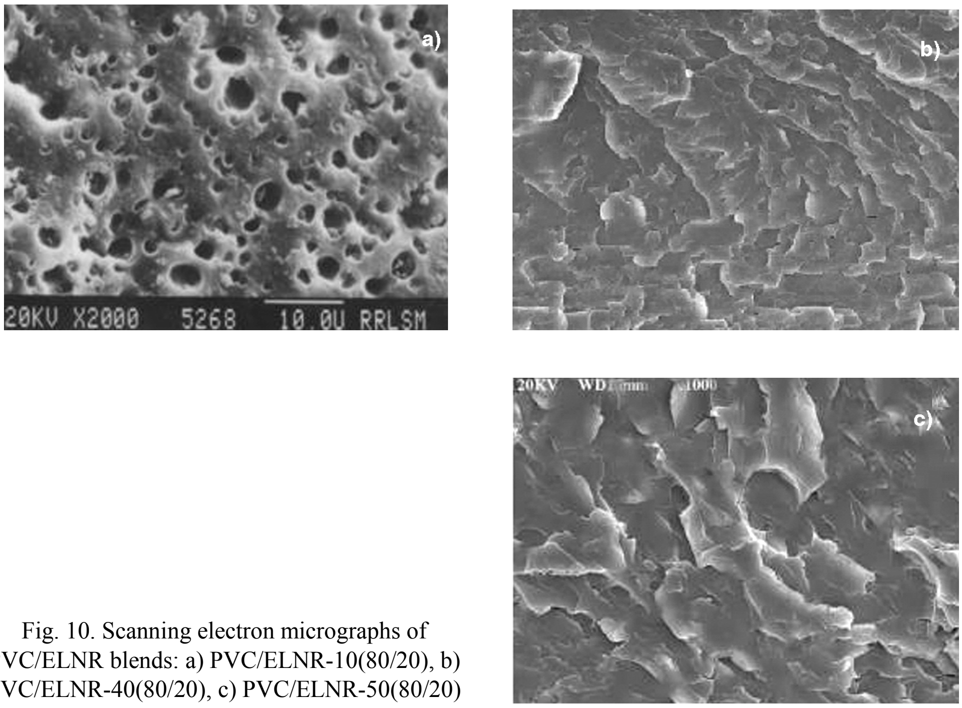

Fig. 10. Scanning electron micrographs of PVC/ELNR blends: a) PVC/ELNR-10(80/20), b) PVC/ELNR-40(80/20), c) PVC/ELNR-50(80/20)

The scanning electron micrographs of PVC/ELNR-10, PVC/ELNR-20, PVC/ELNR-30, PVC/ELNR-40 and PVC/ELNR-50, blends at 80/20 compositions were studied. Micrographs of selected compositions, viz., PVC/ELNR-20(80/20), PVC/ELNR-40(80/20) and PVC/ELNR-50(80/20) are shown in Fig. 10. The micrographs of PVC/ELNR-10 (Fig. 10a) show coarse dispersion of the ELNR phase in the continuous PVC matrix. The same pattern is observed in the case of blends with 20 and 30 mol % of epoxidation with more uniformity in distribution of the dispersed phase and reduction in size. Upon increase of the degree of epoxidation, the dispersed phase gets more uniformly distributed with reduction in the domain size. This trend continues and at 40 and 50 mol % the two phases cannot be distinguished, exhibiting the features of homogeneous blend systems (Figs. 10b, c). The effectiveness in the dispersion is attributed to higher interaction between the two phases promoted by the epoxy groups. Thus it can be inferred that with increase in mol % of epoxidation the interaction increases changing the blend systems from a compatible to miscible level.

4. Conclusions

The role of degree of epoxidation and composition of epoxidized natural rubber on the property improvements of PVC/ELNR blends was investigated in this study. Tensile strengths and modulus values decreased by the addition of ELNR. This seemed to be due to plasticization of PVC. At higher ELNR concentrations, the tensile strength at yield also decreased because of plasticization of the matrix. The elongation at break increased with the ELNR content. SEM micrographs revealed that the addition of ELNR with 50 mol % of epoxidation into PVC matrix changed it into a flexible mass. The study suggests that ELNR-40 and ELNR-50 act as PVC plasticizers.

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