

Miscibility Studies of PVC / ELNR Blends

M.N. Radhakrishnan Nair¹, George V. Thomas², M.R. Gopinathan Nair² (✉)

¹Department of Chemistry, D.B. College, Thalayolaparambu P.O, Kottayam, 686 605, Kerala, India

²School of Chemical Sciences, Mahatma Gandhi University, Priyadarshini Hills P.O., Kottayam, 686 560, Kerala, India
E-mail: mrg.nair@rediffmail.com

Received: 21 February 2007 / Accepted: 22 April 2007
Published online: 12 May 2007 – © Springer-Verlag 2007

Summary

Liquid natural rubber of two different molecular masses, viz., $\overline{M}_w = 4900$ and 9500, each with epoxidation of 20 and 50 mol % (L-ELNR-20, L-ELNR-50, and H-ELNR-20, H-ELNR-50) were prepared and blended with polyvinyl chloride (PVC). Miscibility of these blend systems was studied with special reference to blend ratio, mol % of epoxidation and effect of molecular mass of the liquid rubber by various techniques such as stress - strain measurement, SEM studies and DSC analysis. It was observed that PVC/L-ELNR-50 and PVC/H-ELNR-50 systems were homogenous and miscible compared to PVC/L-ELNR-20 and PVC/H-ELNR-20 blends and the maximum modification in properties was found for the former systems. Results of blends with 20 mol % epoxidised liquid rubber showed that the components are only partially miscible and hence they are heterogeneous systems. Miscibility achieved with an increase in mol per cent epoxidation of the liquid rubber is explained on the basis of the higher polar interaction between the blend components. Analysis of the blends also revealed that the lower molecular mass epoxidised rubber is aiding better property modifications than the higher molecular mass rubber. This is explained by the fact that rubber with lower chain length provides greater penetration into the PVC interstices enabling better solubilisation of the PVC segments.

Keywords

Polyvinyl chloride (PVC), Blends, Miscibility, Glass transition, Differential scanning calorimetry (DSC)

Introduction

Polymer blending offers an extraordinary rich range of new materials with enhanced characteristics regarding chemical or mechanical performance [1-2]. Correspondingly the study of binary polymer blends has been significantly increasing during the past few years due to the important implications in both science and technology [3-6]. The performance of the polymer material can be efficiently improved by combining existing polymers in a suitable way. It is realised that the properties of polymer

blends, including strength, toughness etc. have tight relationships with their internal micro phase morphology [7-9]. For a polymer blend to show superior properties, compatibility of the two components is required to an optimum extent. The compatibility is attributed to specific interactions among the component molecules. This specific interaction can be of different types, namely, dipole-dipole, ion-dipole, hydrogen bonding etc. The complimentary dissimilarity of the component structures also leads to the miscibility of the two polymers. It is well known that PVC being a proton-donating polymer interacts with oxirane ring of epoxidised oils and hydrocarbons [10]. The compatibility of PVC with epoxidized natural rubber (ENR) having different mol % of epoxidation was reported [11-13] in which the compatibility was attributed to dipole-dipole interactions.

Apart from theoretical interest related to molecular origin of miscibility, this line of research could be of practical value since PVC modification or plasticization by polymeric plasticizers is of lasting technological interest. Since epoxidation is a relatively straightforward polymer modification, it could provide a new route for preparing miscible polymer systems with polar or proton donating polymers. Thus the present work was undertaken with the main objective of studying the miscibility of polyvinyl chloride / epoxidised liquid natural rubber (ELNR) blend systems so as to explore the field of polymeric plasticizers meant for PVC.

Experimental

Materials

PVC, (K value 65, $\overline{M}_w = 1.4 \times 10^5$, density 1.37: (M/s Chemicals and Plastics, Chennai, India) was used as received. Natural crumb rubber (ISNR-5), $\overline{M}_w = 8.2 \times 10^5$, intrinsic viscosity in benzene at 30°C = 4.45dL/g, was received from Rubber Research Institute of India (RRII), Kottayam, India. 2 – Butanone (E. Merck India Ltd) was used as the solvent for blending which was dried over anhydrous calcium chloride and distilled before use. Glacial acetic acid, toluene, methanol and hydrogen peroxide (30 w/v) were of reagent grade (BDH, Mumbai). Toluene and methanol were dried and distilled before use. Thermal stabilizer, Dibutyl tin dilaurate (DBTDL) (Fluka, Switzerland) was used without purification.

Preparation of low and high molecular mass liquid natural rubber (L-LNR and H-LNR)

Liquid natural rubber with, $\overline{M}_w = 4900$ (L-LNR) and, 9500 (H-LNR) were prepared in the laboratory by the photochemical degradation of natural rubber as per reported procedure [14] regulating the irradiation time to 50 h and 35 h respectively. It was reprecipitated thrice from toluene using methanol and dried at 70-80°C in vacuum.

Preparation of epoxidised liquid natural rubber (ELNR)

Epoxidised LNR of 50 and 20 mol % epoxidation (ELNR-50 and ELNR-20) was prepared in the laboratory by the epoxidation of LNR using glacial acetic acid and hydrogen peroxide as per reported procedure [15]. L-ELNR-20 was prepared by dissolving L-LNR (25 g) in 166 mL of toluene to obtain a 15 % solution and was

stirred at 50°C for 3h with 0.55 mol of aq. hydrogen peroxide and 0.35 mol of glacial acetic acid. L-ELNR-50 was also prepared by the same procedure in which L-LNR (25 g) was dissolved in 166 mL of toluene and stirred at 50°C for 10 h with 1.1 mol of aq. hydrogen peroxide and 0.35 mol of glacial acetic acid. 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. H-ELNR-50 and H-ELNR-20 were obtained by a similar procedure using 2.2 and 1.1 mol of hydrogen peroxide respectively.

Preparation of blends

A series of blends of PVC and epoxidised liquid natural rubber were prepared from the common solvent 2-butanone as follows. A 3% (w/v) solution of PVC in 2-butanone was prepared with 4 weight % 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 5h at 50°C and cast on glass plates. The samples were then dried in vacuum at 70°C for two days to remove the traces of residual solvent.

Designation of blends

The blends were designated as follows. PVC/L-ELNR-20 (90/10) means a blend of 90 parts PVC and 10 parts epoxidised liquid natural rubber of lower molecular mass with 20 mol % epoxidation; PVC/H-ELNR-20 (90/10) means a blend of 90 parts of PVC and 10 parts of epoxidised liquid natural rubber of higher molecular mass with 20 mol % epoxidation etc. Similarly the other series of blends containing ELNR of higher mol % of epoxidation were designated as PVC/L-ELNR-50 (90/10), PVC/H-ELNR-50 (90/10) etc.

Tensile measurements

Tensile testing of the samples were done according to ASTM (D-638) test method using dumb bell shaped test specimens in a Zwick Universal Testing Machine Model 1474 at a cross head speed of 50 mm min⁻¹. At least six samples were tested in each case and the average values are reported.

SEM analysis

The fracture surface of the tensile specimen was sputter coated with gold immediately after testing and SEM observation was made using a JOEL JSM-35C scanning electron microscope and the fractographs were taken along the direction of the fracture propagation adjusting the tilt angle to 33° in all cases.

DSC analysis

DSC analysis was carried out in a Mettler-30 DSC equipped with a liquid N₂ sub ambient cooling accessory at a heating rate of 10°C /min from -100°C to +100°C. All the DSC curves are first scans.

Results and Discussion

Earlier studies revealed that blends involving epoxidised natural rubber and polyvinylchloride show a domain morphology in which ENR is dispersed in the PVC matrix. Such a blend is compatible due to the interaction of epoxy groups with PVC leading to modification in properties like impact strength etc. However, the high molecular weight of ENR is a deterrent for further modification since it would affect the diffusivity of the ENR molecules into the interstices. In this context what could be expected of the epoxidised liquid natural rubber (ELNR) is both the favourable interaction with PVC and better migration into the available spaces due to its smaller size. These factors are expected to advance the blend system to a miscible state from a level of compatibility with increase in epoxy content. Evidence to this effect has been gathered in the present work in which PVC / ELNR blend systems were prepared and analysed using DSC, SEM and tensile measurements. Four series of blends were prepared, viz., PVC/L-ELNR-20, PVC/L-ELNR-50, PVC/H-ELNR-20 and PVC/H-ELNR-50. Samples were made in different compositions, such as 90/10, 80/20, 70/30, 50/50 and 30/70 of PVC and the respective ELNR in each series.

Tensile analysis

Stress - strain curves for PVC and the blends in two series containing lower molecular mass epoxidised rubber (L-ELNR) are shown in Figures 1 and 2 respectively and the tensile data are tabulated in Table 1. Tensile curve of the unmodified PVC shows the characteristic features of a brittle material. It undergoes very small deformation under stress and failure occurs at 6 % elongation without undergoing any yield phenomenon. Tensile strength and modulus of elasticity were found to be high with values of 38.5 N/mm^2 and 2100 N/mm^2 respectively. Compared to this the blend system containing 10 % of L-ELNR showed yielding. Its yield strength is also high with a value of 35.6 N/mm^2 . However, for the same composition, PVC/ L-ELNR-50

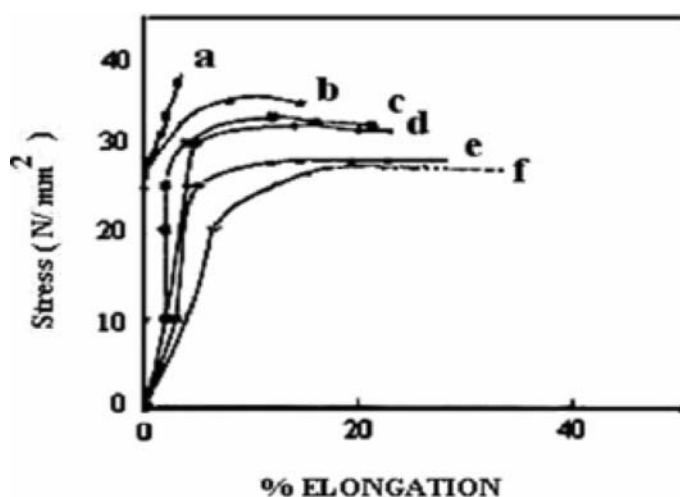


Figure 1. Stress–Strain curves of PVC and PVC/ L-ELNR-20 blends (a) PVC (b) 90/10 (c) 80/20 (d) 70/30 (e) 50/50 and (f) 30/70 compositions

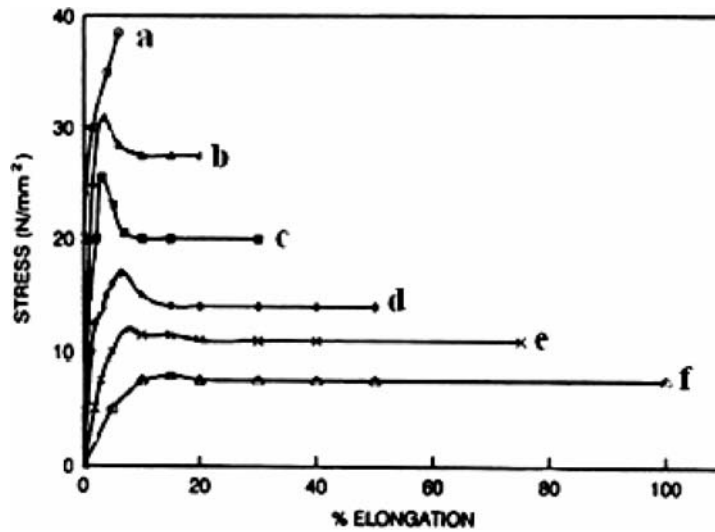


Figure 2. Stress–Strain curves of PVC and PVC/ L-ELNR-50 blends (a) PVC (b) 90/10 (c) 80/20 (d) 70/30 (e) 50/50 and (f) 30/70 compositions

shows lower yield strength of 31.3 N/mm². This trend in yield strength continues for all compositions with increasing rubber content in both the series (Table1). Similar variation is seen in terms of tensile strength, modulus of elasticity and elongation at break between the two series of blend systems. From the figures it is found that the tensile strength and modulus of elasticity of PVC/ L-ELNR-50 blends fall sharply with increasing rubber content in comparison to the PVC/ L-ELNR-20 blends. Elongation at break shows a corresponding increase.

All the above observations are consistent with the nature of the tensile curves of PVC and the blend systems. As stated before the tensile curve of PVC reveals its brittle nature. With the addition of rubber into the matrix the curve begins to show

Table 1 Tensile properties of PVC/L- ELNR-20 and PVC/L- ELNR-50 blends

Composition	Tensile strength (N / mm ²)	Yield strength (N / mm ²)	Modulus (N / mm ²)	Elongation at break (%)
PVC	38.5	--	2100	6
PVC/L-ELNR-20 (90/10)	34.1	35.6	2000	16
PVC/L-ELNR-20 (80/20)	32.00	33.4	1950	21
PVC/L-ELNR-20 (70/30)	30.5	32	1400	28
PVC/L-ELNR-20 (50/50)	28.3	27.4	790	34
PVC/L-ELNR-20 (30/70)	26.9	26.1	500	36
PVC/L-ELNR-50 (90/10)	27.5	31.3	1333	20
PVC/L-ELNR-50 (80/20)	20.0	25.4	1000	30
PVC/L-ELNR-50 (70/30)	14.0	17.2	800	50
PVC/L-ELNR-50 (50/50)	10.8	11.89	235	75
PVC/L-ELNR-50 (30/70)	7.5	8.10	148	100

yielding and ductile behaviour which becomes very prominent with increasing rubber content. Although this is the general trend for both the series of blends with L-ELNR-20 and L-ELNR-50, the variation in the nature of curves is more drastic in the case of the PVC/ L-ELNR-50 blends. The ductility is more pronounced in this case and the curve almost flattens out at high rubber content, which corresponds to a soft and flexible material. PVC/ L-ELNR-20 on the other hand is losing rigidity only at a slow pace and even at high rubber content the curves show much lower ductility and hence higher rigidity compared to the other series. The fact that the variation in properties is predominant in the case of PVC/ L-ELNR-50 blends shows greater miscibility leading to the plasticization of PVC. Almost similar results were obtained for the blends containing high molecular mass liquid rubber (H-ELNR) which is described in a later section.

Tensile fracture studies by SEM

Fracture surfaces of dumb bell shaped tensile specimens of the blends of PVC/L-ELNR-20 and PVC/L-ELNR-50 have been examined using SEM. Black regions are PVC matrix and the light regions that of LNR phase. An attempt has been made to correlate the fracture mechanism with the tensile properties of the blend systems.

Fractographs of PVC/L- ELNR-20 blends

The fractographs of PVC/L-ELNR-20 at (70/30) and (50/50) blend compositions are shown in Figure 3(a) and (b). Fracture surface of PVC/L- ELNR-20 (70/30) exhibited rough features with a few short fibrils seen along the stress axis [Figure 3(a)]. It showed a patch pattern characteristic of a brittle fracture mechanism with rapid propagation of crack front. As the L-ELNR-20 is increased to 50 %, the fracture surface became more deformed and showed the presence of coarsely dispersed phase on it. Irregular particles of varying sizes up to a few microns are seen in the micrograph[Figure 3(b)]. The deformed surface indicates that the brittleness of the matrix has been reduced to a lower level owing to the interaction with the rubber part. However, the presence of dispersed phase suggests that the system has got only limited miscibility. This may be due to the low level of epoxy groups present in L-ELNR-20 which causes insufficient interaction with the PVC matrix.

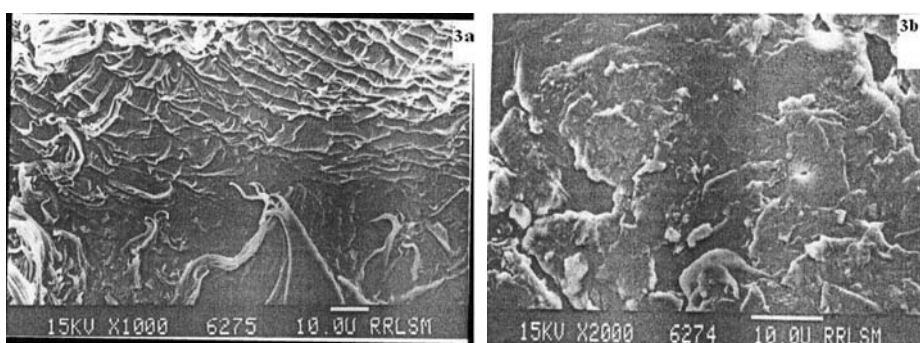


Figure 3. Tensile fractographs of (a) PVC /L-ELNR-20 (70/30) and (b) PVC /L-ELNR-20 (50/50)

Fractographs of PVC/L-ELNR-50 blends

The fractographs of virgin PVC and blends of PVC /L- ELNR-50 at 70/30 and 50/50 compositions were shown in Figures 4(a) to (c) respectively. A close look at these fractographs revealed that there is variation in the fracture mechanism of the samples with composition. The tensile fracture surface of virgin PVC [Figure 4(a)] showed that the sample undergoes a brittle mode of failure as the fracture front was characterized by an undeformed surface and closely placed line pattern. As 30 parts of L-ELNR-50 was 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 [Figure 4(b)]. On increasing the rubber content further to 50 % [Figure 4(c)] the fracture front showed higher plastic deformation. The fracture surface became highly deformed and exhibited features of fine fibrils, parabolic and wavy fracture front. Orientation of the matrix along the stress axis was also observed at the fracture surface. All these observations indicate that the ductile nature of the blend increased with rubber content. This is possible only if the rubber part and the PVC matrix interact favourably. Also it is found from the fractograph of both the blends that they are homogenous in nature. Absence of heterophase is an indication to the miscibility of the blend components which is justified by the presence of 50 mol % of epoxy groups on

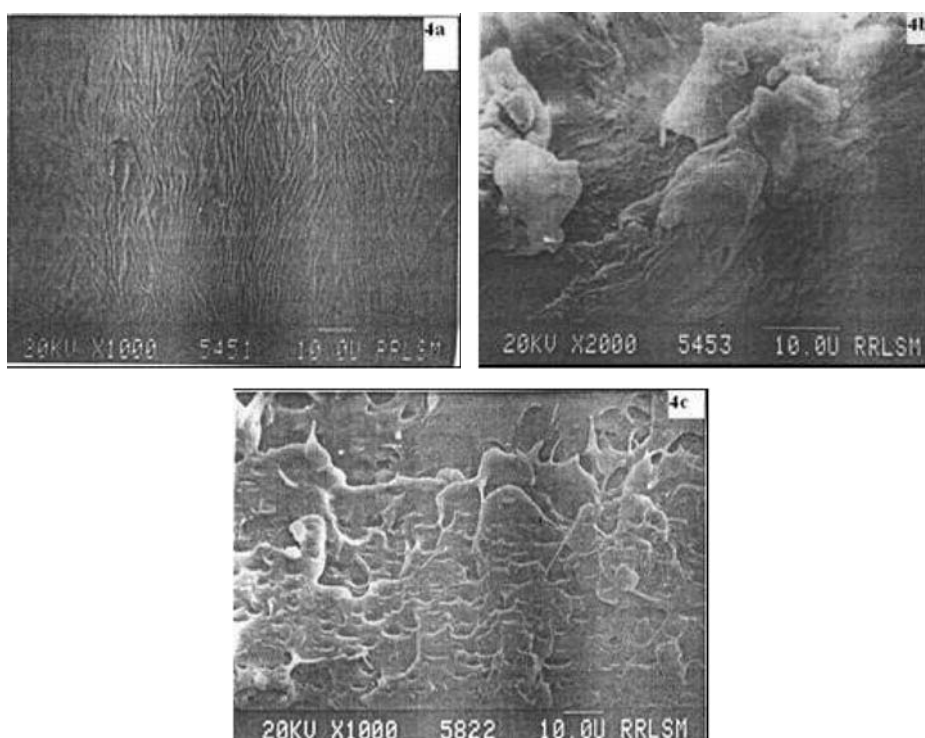


Figure 4. Tensile fractographs of (a) PVC (b) PVC /L- ELNR-50 (70/30) and (c) PVC /L-ELNR-50 (50/50)

the rubber. This was reflected in the respective tensile curve also [Figure 2], which is characteristic of a flexible and soft material.

A comparison of the blends in the above two series showed that the epoxy content influences the failure pattern of the tensile samples. PVC/L-ELNR-50 series showed ductility in all compositions whereas PVC/L-ELNR-20 series shows almost brittle behaviour at 70/30 compositions and incompatible behaviour at 50/50 composition.

DSC analysis

Differential scanning calorimetric measurements were carried out on the various ELNR modified systems and the individual components. Thermograms of PVC/L-ELNR-20 and PVC/L-ELNR-50 are shown in Figures 5(a) and 5(b) respectively. Tg values noted from these thermograms are listed in Tables 2 and 3. Introduction

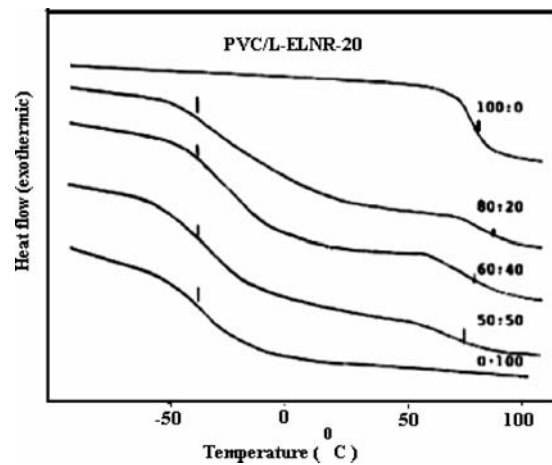


Figure 5(a). DSC thermograms of PVC/L-ELNR-20 blends

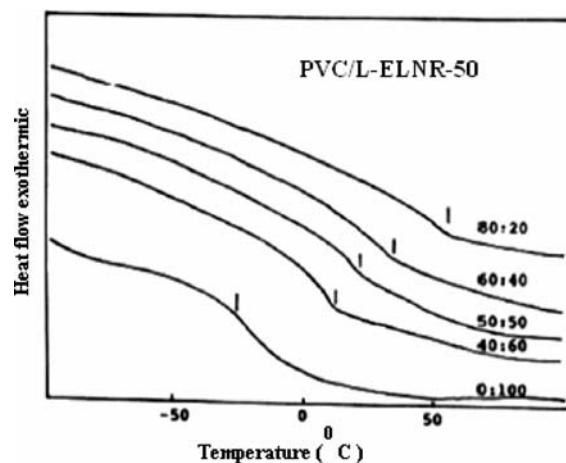


Figure 5(b). DSC thermograms of PVC/L-ELNR-50 blends

of polar groups in the form of oxirane ring obviously increased the Tg value of the low molecular mass liquid natural rubber. The values increased from -65°C to -35°C and to -20°C as the mol per cent of epoxidation was increased from zero to 20 and to 50 %. This is due to the higher intermolecular interaction existing in ELNR that was originally absent in NR.

The DSC thermograms of the PVC/L-ELNR-20 blends possess two distinct transitions as shown in Figure 5(a). For example, PVC/L-ELNR -20 (80/20) blend has transitions at 69°C and -35°C. The former value corresponds to PVC while the latter value is same as that of L-ELNR-20, which is also shown in the figure. This shows that the blend system is heterophase in nature and the two components are not miscible. The 60/40 and 50/50 blends also give similar results.

Contrary to this, the thermograms of the PVC / L-ELNR-50 blends as given in Figure 5(b) showed only a single Tg value for all compositions. The values are found to be intermediate between those of the component polymers. This corresponds to a miscible system indicating that the L-ELNR with sufficiently higher epoxy content becomes miscible with polyvinyl chloride. It provides higher interaction with the PVC matrix flexibilising the PVC segments and lowering the Tg value.

The DSC data of PVC/ L-ELNR-50 blends were tested with the commonly used Fox equation:

$$1/Tg^b = W_1/Tg_1 + W_2/Tg_2,$$

where Tg^b, Tg₁ and Tg₂ are glass transitions of the blend, component 1 and component 2 respectively and W₁ and W₂ are the weight fractions of the respective components.

Table 2 Tg values of PVC/L-ELNR-20 and PVC/H-ELNR-20 blends

Composition	Tg (°C)	
	PVC phase	ELNR phase
PVC/L-ELNR-20 (80/20)	69	-35
PVC/H-ELNR-20 (70/30)	70	-24
PVC/L-ELNR-20 (60/40)	67	-33
PVC/H-ELNR-20 (60/40)	67	-22
PVC/L-ELNR-20 (50/50)	65	-30
PVC/H-ELNR-20 (50/50)	65	-20
L-ELNR-20	-	-30
H-ELNR-20	-	-30
PVC	75	--

Table 3 Tg values of PVC/L-ELNR-50 and PVC/H-ELNR-50 blends

Composition	Observed Tg (°C)	Calculated Tg (°C)
PVC/L-ELNR-50 (80/20)	50	50.69
PVC/L-ELNR-50 (60/40)	30	29.56
PVC/H-ELNR-50 (60/40)	40	37.94
PVC/L-ELNR-50 (50/50)	20	20
PVC/H-ELNR-50 (50/50)	31	29.84
PVC/L-ELNR-50 (40/60)	23	22.15
PVC/H-ELNR-50 (40/60)	23	22.15
L-ELNR-50	-20	-
H-ELNR-50	-5	--

The experimental values are in good agreement with the theoretical values which are listed in Table 3. This type of behaviour is generally observed in miscible blends. The reason for miscibility is attributed to the increase in solubility parameter of the liquid NR to a matching level with polyvinyl chloride due to the introduction of sufficient number of epoxy groups into the diene backbone. The molecular origin of miscibility could be attributed to polar-polar interactions.

Effect of ELNR molecular mass on miscibility

Tensile curves of the PVC/H-ELNR samples [Figures 6 (A) and 6 (B)] have the same characteristics as those of the corresponding PVC/L-ELNR samples. However, tensile strength and modulus of elasticity values (Table 1 and 4) are found to be higher for the

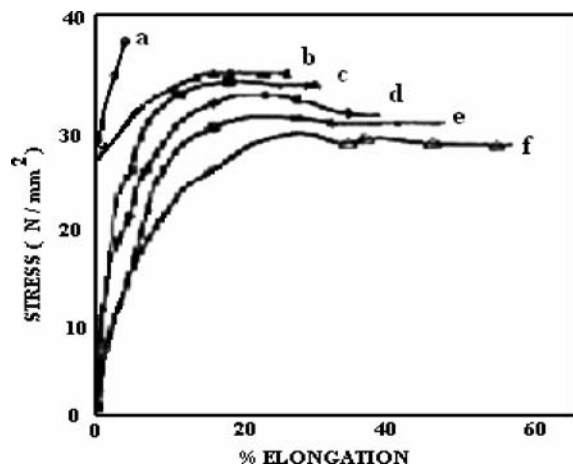


Figure 6 (A) Stress–Strain curves of PVC and PVC/ H-ELNR-20 blends (a)PVC (b) 90/10 (c) 80/20 (d) 70/30 (e) 50/50 and (f) 30/70 compositions

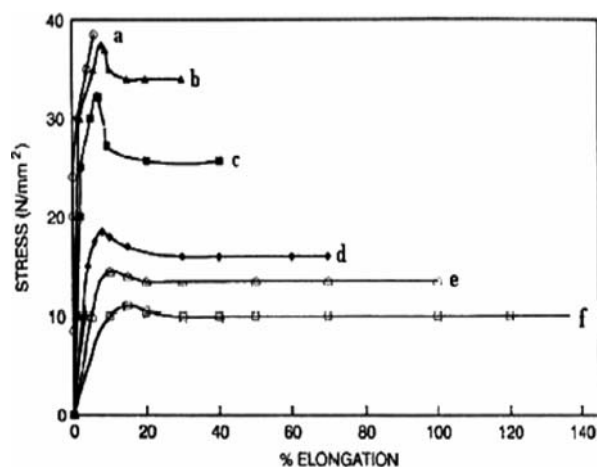


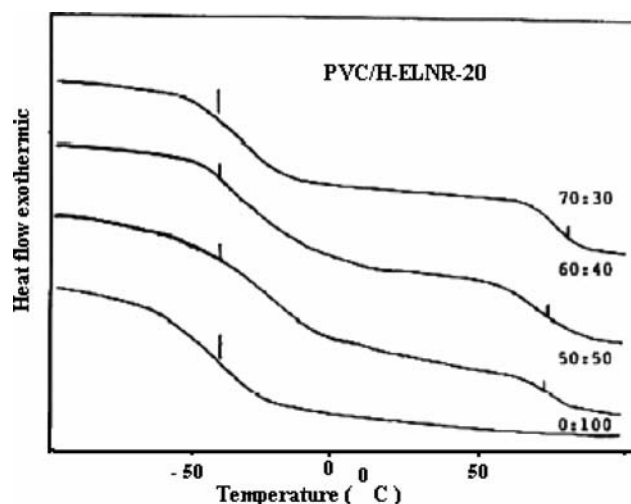
Figure 6 (B) Stress–Strain curves of PVC and PVC/ H-ELNR-50 blends (a) PVC (b) 90/10 (c) 80/20 (d) 70/30 (e) 50/50 and (f) 30/70 compositions

Table 4 Tensile properties of PVC/H-ELNR-20 and PVC/H-ELNR-50 blends

Composition	Tensile strength (N/mm ²)	Yield strength (N/mm ²)	Young's modulus (N/mm ²)	Elongation at break (%)
PVC/H-ELNR-20 (90/10)	37.1	38.2	2100	22.5
PVC/H-ELNR-20 (80/20)	35.5	36.5	2000	24
PVC/H-ELNR-20 (70/30)	34.5	35.5	1500	34
PVC/H-ELNR-20 (50/50)	31.5	32.3	900	40
PVC/H-ELNR-20 (30/70)	29	30	600	50
PVC/H-ELNR-50 (90/10)	32	34	1600	30
PVC/H-ELNR-50 (80/20)	25.2	31	1300	44
PVC/H-ELNR-50 (70/30)	16	18.3	1000	72
PVC/H-ELNR-50 (60/40)	14.9	16.6	844	84
PVC/H-ELNR-50 (50/50)	13.7	14.3	435	100
PVC/H-ELNR-50 (30/70)	10.3	10.8	348	140

PVC /H-ELNR samples compared to PVC /L-ELNR samples. For example, tensile strength and modulus values for PVC /H-ELNR-50 at (80/20) composition are 25.2 and 1300 N/mm² and for PVC /L-ELNR-50 (80/20), the values are 20 and 1000 N/mm² respectively. These higher values indicate that the plasticizing effect of H-ELNR on PVC is slightly lower than that of the L-ELNR samples. Higher values for the elongation at break at this lower level of plasticization could be due to the higher chain length of the H- ELNR part of the blend. As observed in the case of L-ELNR an increase in the mol per cent of epoxidation of H-ELNR from 20 to 50 caused an increase in the miscibility of the system which is discernible from a comparison of the tensile curves of the two series of samples, viz., PVC /H-ELNR-20 and PVC /H-ELNR-50 [Figures 6 (A) and 6 (B)]. The variation in tensile strength, modulus of elasticity and elongation at break with composition for both the series is found to be on expected lines.

Similar observations as above were obtained from the DSC analysis also. The DSC curves of PVC/H-ELNR-20 samples [Fig.7 (a)] show two different transitions

**Figure 7(a).** DSC thermograms of PVC/H-ELNR-20 blends

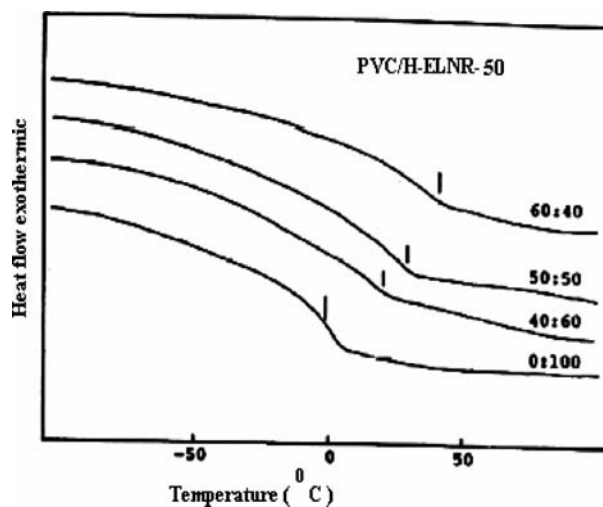


Figure 7(b). DSC thermograms of PVC/H-ELNR-50 blends

corresponding to two phases present in the samples [Table 2] indicating lower miscibility of PVC and H-ELNR-20. In the case of PVC /H-ELNR-50 [Fig. 7(b)] only a single transition is observed with all samples [Table 3] indicating a single phase and hence miscibility of the components. The data have been verified with the Fox equation [Table 3]. This behaviour is similar to the one observed in the case of L-ELNR-50 systems. However, it is to be noted that the single transition exhibited by the PVC/H-ELNR-50 systems are higher in values than the corresponding PVC/L-ELNR-50 samples. For example, T_g value for PVC /H-ELNR-50 (50/50) is 31°C and that of PVC / L-ELNR-50 (50/50) is 20°C. This obviously points towards a lower level of plasticization of PVC by H-ELNR-50. Thus it is to be concluded that the low molecular weight ELNR is more effective in the property modification of PVC. This is because of the lower chain length of the L-ELNR, which provides greater penetration into the PVC interstices, and causes better solubilisation of the PVC segments.

Conclusion

Miscibility studies conducted on PVC / ELNR blend systems with varying molecular mass of the liquid rubber possessing different mol % of epoxy content yielded useful results in the area of polymeric plasticizers. It is found that an increase in the epoxy content of the liquid rubber from 20 to 50 mol % transforms the blend system from a compatible to a miscible state. This change is evidenced by the tensile measurements, studies on fracture mechanism by SEM and DSC analysis. Tensile measurements and SEM studies clearly showed a transition from brittleness to ductility with increasing epoxy content. DSC analysis showed T_g values corresponding to the component polymers at 20 mol % of epoxidation indicating partial miscibility of a heterogeneous system, whereas it showed only a single transition at 50 mol % of epoxidation indicating phase merging which has been verified by Fox relation for all compositions. This could be due to the interplay of higher polar interaction between the blend components caused by the presence of large number of epoxy groups on the liquid rubber. Regarding the effect of variation in the molecular mass of epoxidised

liquid rubber it is found from the various analytical data that lower molecular mass aided better miscibility of the blend components. This is explained on the basis that the rubber with lower chain length provides greater penetration into the PVC interstices enabling better solubilisation of the PVC segments. Thus, epoxidised liquid natural rubber samples possessing high epoxy content and lower molecular mass are found to be useful polymeric additives which are capable of exhibiting plasticizing effect on PVC.

References

1. Paul DR, Newman S (1976) *Polymer blends*, Vols 1 and 2, Academic Press, New York.
2. Xanthos M (1992), *Reactive extrusion*, Brown SB Inc, Munich.
3. Wang Y, Zhang Q, Fu Q (2003) *Macromol. Rapid Commun.* 24: 231.
4. Kawasumi M, Hasegava N, Kato M, Usuki A, Okada A (1997) *Macromolecules*, 30:6338.
5. Galgali G, Ramesh C, Lele A (2001) *Macromolecules*, 34: 852.
6. Wang H, Zeng CC, Elkovvnh M, Lee JK, Koelling KW (2001) *Polym Eng Sci.*, 41:2036.
7. Kayano Y, Keskkula H, Paul DR (1997) *Polymer*, 38:1885.
8. Corte L, Beaume F, Leibler L (2005) *Polymer*, 46:2748.
9. Corte L, Leibler L (2005) *Polymer*, 46:6360.
10. Olabisi O, Robeson L.M, Shaw MT (1979) *Polymer-Polymer Miscibility*, Academic Press, New York.
11. Margaritis AG, Kalfoglou NK(1987) *Polymer*, 28:497.
12. Varughese KT, Nando GB, De PP, De SK(1989) *J. Mater. Sci*, 24:3491.
13. Varughese KT, De PP ,Sanyal SK, De SK(1989) *J. Appl. Polym. Sci.*,37:2537.
14. Ravindran T, Gopinathan Nair MR, Francis D (1988) *J. Appl. Polym. Sci.*, 35:1227.
15. George V Thomas, Gopinathan Nair MR (1997) *Kautsch. Gummi .Kunst.*, 50 (5):398.