# Blends of PVC and Epoxidized Liquid Natural Rubber: Studies on Impact Modification

M. N. Radhakrishnan Nair,<sup>1</sup> P. K. Biju,<sup>2</sup> George V. Thomas,<sup>2</sup> M. R. Gopinathan Nair<sup>2</sup>

<sup>1</sup>Department of Chemistry, D. B. College, Kottayam 686 605, Kerala, India

<sup>2</sup>School of Chemical Sciences, Polymer Division, Mahatma Gandhi University, Kottayam 686 560, Kerala, India

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**ABSTRACT:** Liquid natural rubber of different molecular masses L-LNR, and H-LNR were subjected to varying degree of epoxidation (L-ELNR-10, L-ELNR-20, L-ELNR-30, L-ELNR-40, L-ELNR-50, H-LNR-20, and H-LNR-50) and the products were incorporated into PVC at various compositions by the solution blending method. These blend systems were subjected to tensile testing, tensile impact measurements, and SEM studies. It was observed that blends with L-ELNR-20 showed highest impact strength modification, followed by L-ELNR-10 and L-ELNR-30. High impact properties showed by these blends are attributed to the optimum level of compatibility existing between the blend components. Tensile impact fracture studies revealed that the failure pattern for this blend system is intermediate between the brittle fracture of rigid

# **INTRODUCTION**

The use of rigid PVC is enabled by its modification through polymeric additives.<sup>1,2</sup> These additives form partially miscible blends with PVC which display phase separation but with a significant degree of polymer mixing on a molecular level producing chemically compatible phase with useful properties.<sup>3,4</sup> Polymeric additives are mainly used as processing aids and impact modifiers. Where as processing aids show compatibility with PVC without plasticisizing action, impact modifiers show only limited compatibility by virtue of which the blend forms multiphase systems. The polymeric additives are capable of exerting intermolecular forces such as donor–acceptor interaction, dipole–dipole interaction, and hydrogen bonding with PVC.

Modification of PVC by ABS is most extensively studied and reported in many research papers.<sup>5–7</sup> It was found that impact strength of PVC was greatly modified by this technique. Zhou et al. reported that SBR rubber acts as a good modifier for PVC.<sup>8</sup> Another study shows that flexural properties of PVC

PVC and ductile fracture of PVC/L-ELNR-50 samples. Blends up to 30 mol % of epoxidation showed partially compatible heterogeneous nature exhibiting domain morphology. Blends of liquid rubber with higher degree of epoxidation showed deterioration in tensile strength, modulus, yield strength, and tensile impact strength due to plasticization of PVC caused by the higher polar interaction between PVC chains and the oxirane rings. Effect of ELNR molecular weight was studied and it is found that the impact modification is higher for the L-ELNR blends compared to the H-ELNR blends. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 48–56, 2009

**Key words:** polyvinyl chloride; blends; compatibility; liquid natural rubber; epoxidation; tensile impact strength

is improved by incorporating small amounts of SAN.<sup>9</sup> Fann and et al. reported that incorporation of MBS into PVC increased the impact strength.<sup>10</sup> Zhong et al. studied blends of polyvinyl chloride (PVC) and acrylonitrile-chlorinated polyethylenestyrene (ACS) graft copolymer and found that there was a significant increase in the impact strength whereas high modulus and high tensile strength of the parent polymer were retained.<sup>11</sup> Wang and Chen studied the compatibility of PVC/NBR blends.12 Rudin et al. used copolymers of methyl styrene and methacrylonitrile as impact modifiers to PVC and found that as little as 7.5% of the copolymer has provided adequate mechanical strength and processability for commercial applications.<sup>13</sup> Polymers with oxirane groups form a specific class of polymeric additives which provide varying level of intermolecular forces with PVC depending on the oxirane content. Oxirane group can act as a proton acceptor along with the interplay of polar interactions. In this respect, polyvinyl chloride (PVC) and epoxidized natural rubber (ENR) have attracted the attention of many researchers. Varughese et al.<sup>14,15</sup> showed that ENR-50 forms miscible blends with PVC. ENR was found to act as a permanent plasticizer to PVC.<sup>16,17</sup> Also ENR induces good tear strength and enhances oil resistant properties.<sup>18,19</sup> It was reported that PVC

Correspondence to: M. R. G. Nair (mrg.nair@rediffmail.com).

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and ENR form self-crosslinkable blends.<sup>20,21</sup> Mousa et al.<sup>22,23</sup> studied various properties of dynamically vulcanized PVC/ENR blends. Margaritis and Kalfoglou studied the compatibility of epoxidized natural rubber containing 25 and 50 mol % of oxirane groups.<sup>24,25</sup> They found that 50 mol % of epoxidation lead to miscibility at the entire composition range where as 25 mol % was only partially miscible. According to them introduction of oxirane group gives a stiffer polymeric plasticizer compared with those with pendent active groups. The effectiveness of epoxidized natural rubber as a polymeric additive to chlorinated polyolefin and novolac resins was also demonstrated by other authors.<sup>26</sup> Compatibility of polyvinyl chloride with epoxidized styrenebutadiene copolymers was studied by Koklas and Kalfoglou.<sup>27</sup> SBR with 45 wt % of styrene and SBS with 30 wt % of styrene were epoxidized to different levels and blended with PVC. It was found that SBS with 35 mol % epoxidation and above act as polymeric plasticizer. Immiscibility set in below 35 mol % of epoxidation.

It has been shown that a particular polymer mixture can be made more miscible by reducing the molecular weight of one or both components. This finding is based on the Flory-Huggins theory.<sup>28,29</sup> According to this theory the enthalpy gained on mixing polymers is inversely related to their  $\overline{M}_n$ .<sup>13</sup> Thus, the blends of PVC and epoxidized liquid natural rubber have been studied and found that the latter is very effective in plasticizing PVC at appropriate epoxy contents.<sup>30</sup> The present work involves the characterization of these blend systems in terms of the impact properties and to study the effect of variation in the epoxy content and molecular weight of the liquid rubber on these characteristics so as to achieve impact modification of 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 = 4.45 dL/g, was received from Rubber Research Institute of India, Kottayam, India. 2-Butanone (E. Merck, India) was dried over anhydrous calcium chloride and distilled before use. Glacial acetic acid and hydrogen peroxide (30 w/v) were of reagent grade (BDH, Mumbai). Toluene and methanol (E. Merck, India) were dried and distilled before use. Thermal stabilizer, dibutyl tin dilaurate (DBTDL, Fluka, Switzerland) was used without purification.

TABLE I Epoxy Content of ELNR (mol %) Obtained by Different Methods

	5			
Sample	DSC	IR	NMR	Titrimetric
L-ELNR-10	7.5	9.5	7.5	9.25
L-ELNR-20	15	19	15	18.5
L-ELNR-30	22.5	28.5	22.5	21.01
L-ELNR-40	36	40.8	44	19.04
L-ELNR-50	45	51	55	23.8
H-ELNR-20	14	17.5	14	18
H-ELNR-50	44	49	43.5	17

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

Liquid natural rubber with  $\overline{M}_n = 4900$  (L-LNR) and 9600 (H-LNR) were prepared in the laboratory by the photochemical degradation of natural rubber by a prereported procedure.<sup>31</sup> L-LNR was obtained after 50 h irradiation and H-LNR after 35 h of irradiation. It was reprecipitated twice from toluene using methanol and dried at 70–80°C under vacuum. Molecular weight of the samples was determined by GPC method.

#### Preparation of epoxidized liquid natural rubber

Epoxidized liquid natural rubber (ELNR) of 10-50 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 prereported procedure.<sup>32</sup> ELNR-10 was prepared by dissolving LNR (25 g) in 166 mL of toluene to get a 15% solution and was stirred at 50°C for 3 h with 0.55 mol of 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 viz., 1.1, 1.65, and 2.2 mol of hydrogen peroxide and 5, 6, 8, and 10 h of stirring, respectively. At the end of the reaction, the product was isolated by precipitation with methanol. It was dried under vacuum and then characterized by titrimetric, IR, and NMR techniques.<sup>32</sup> Epoxy contents obtained are tabulated in Table I. Titrimetric analysis is found to be less sensitive especially at higher levels of epoxidation.

#### Preparation of blends

A series of blends of PVC and epoxidized liquid natural rubber was 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  $50^{\circ}$ C and cast on glass plates. The samples were then dried under vacuum at 70°C for 2 days to remove the traces of residual solvent.

## **Designation of blends**

The blends were designated as follows. For example, PVC/ELNR-20 (90/10) means a blend of 90 parts of PVC and 10 parts of epoxidized liquid natural rubber with 20 mol % epoxidation.

# **FTIR** analysis

IR spectra were recorded at room temperature on a Shimadzu FTIR-8400S, spectrometer (Japan) by averaging 50 scans at a resolution of  $2 \text{ cm}^{-1}$ .

#### Differential scanning calorimetry

The differential scanning calorimetry (DSC) measurements were done using a Mettler Inc. (TA 300) microcalorimeter (Germany) at a programmed heating rate of  $10^{\circ}$ C/min. The measurements were carried out in the temperature range of -100 to  $100^{\circ}$ C under dry nitrogen atmosphere (25 mL/min) using alumina crucibles. The sample weight was 4–5 mg.

#### **Tensile impact measurements**

Tensile impact testing of the samples was done according to DIN 53448 test method using a CEAST 6545/000 model tensile impact tester. The energy utilized to break the test specimen in this method was delivered by a single swing of a calibrated pendulum of the standard tension impact machine. The pendulum used could deliver a maximum of 15 J and the speed of the test was  $3.7 \text{ ms}^{-1}$ .

#### SEM analysis

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

#### **RESULTS AND DISCUSSION**

Blends of PVC and epoxidized liquid NR were prepared in two categories, viz., blends with low-molecular weight epoxidized liquid NR (L-ELNR) and blends with high-molecular weight epoxidized liquid NR (H-ELNR). In the former case, there are five series of blends with liquid rubber of varying epoxy content ranging from 10 mol % to 50 mol %. The latter category contains only two series with 20 mol % and 50 mol % epoxy content. Each series has got a number of samples with varying proportion of the blend components ranging from 10 to 70%. All the blends were subjected to tensile impact measurements and SEM studies. The effect of blend composition, epoxy content, and molecular weight of the liquid rubber on the tensile impact properties of PVC is discussed.

# Tensile impact fracture and morphological studies by SEM

Tensile impact fracture surface of PVC and some selected samples were examined using SEM. Tensile impact fracture surface of unmodified PVC is shown in Figure 1(a). Brittle mode of fracture is clearly seen in the micrograph which shows an under formed surface with planar characteristics. This changes into a ductile mode of fracture [Fig. 1(b)] on addition of 20% L-ELNR-50 which is evidenced by the irregular patch pattern on the fracture surface along with the characteristics of a single phase material. It contains voids which seem to be microcracks of 4.62 µm in length located perpendicular to the propagation of the fracture front. These could be signs of localized flow deformation occurring during the fracture process. Such a transition from brittle to ductile behavior is in agreement with a decrease in impact strength from 320 J/m to 220 J/m. Figure 1(c) shows the impact fracture surface of PVC/L-ELNR-20 (80/ 20) blend. The micrograph shows a plate like plastic fracture indicating the rigid nature of the test sample. Voids on the surface could be formed by the removal of rubber domains during the fracture process. Fracture surface is found to be less deformed compared with the previous blend system, viz., PVC/L-ELNR-50. Another feature observed in Figure 1(c) is the presence of elliptical hollows representing particles removed from the surface of observation. This is indicative of the domain morphology which is essential for impact modification and thus the sample shows impact strength of 1000 J/m. The rubber domains distributed in the matrix must have contributed greatly to the impact strength of this system.

Impact fracture surface of PVC/H-ELNR-20 (80/ 20) is shown in Figure 1(d). The fracture site shows an irregular patch pattern with a scaling effect. However, the patches have got smooth sides showing that the presence of H-ELNR-20 slows down the crack propagation rendering the material less brittle. This is reflected in the higher impact strength obtained for this composition, viz., 870 J/m. The micrograph appears heterogeneous in nature suggesting lower level of interaction between the two

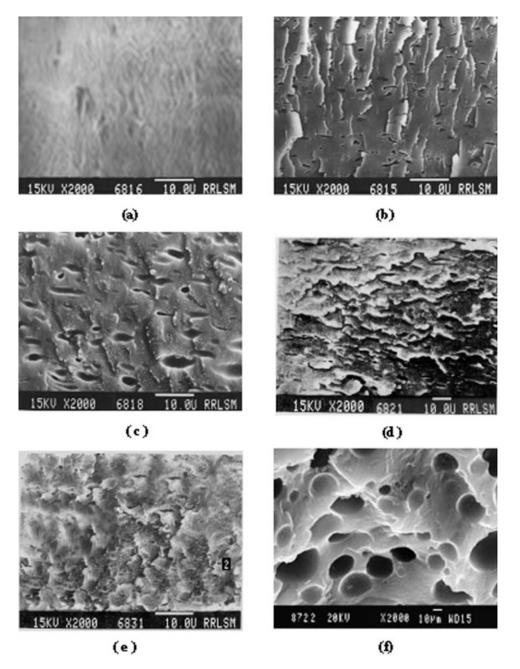


Figure 1 SEM micrographs of tensile impact fracture surface of (a) PVC, (b) PVC/L-ELNR-50 (80/20), (c) PVC/L-ELNR-20 (80/20), (d) PVC/H-ELNR-20 (80/20), (e) PVC/H-ELNR-50 (80/20), and (f) SEM micrograph of PVC/L-ELNR-20 (60/40).

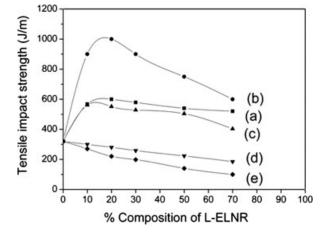
components as already observed with PVC/L-ELNR-20 blend. As the epoxy content increased to 50 mol %, H-ELNR forms homogenous blend with PVC [Fig. 1(e)]. This is obviously due to higher interaction between the two components caused by the higher epoxy content. The corresponding fracture surface shows a highly deformed pattern with ridges all around suggesting a ductile mode of fracture supporting lower impact strength similar to the corresponding PVC/L-ELNR-50 blend.

Figure 1(f) shows the fractograph of PVC/L-ELNR-20 (60/40) blend which contains higher quan-

tities of rubber. Fracture surface appears heterogeneous with large dispersion of one phase over the other. Such a morphology naturally would affect the integrity of the matrix which undergoes failure giving relatively lower impact properties compared with blends with lower rubber content.

## Tensile impact analysis

Tensile impact strength versus blend composition for all the series containing L-ELNR is shown in Figure 2. The values are found to vary with the blend

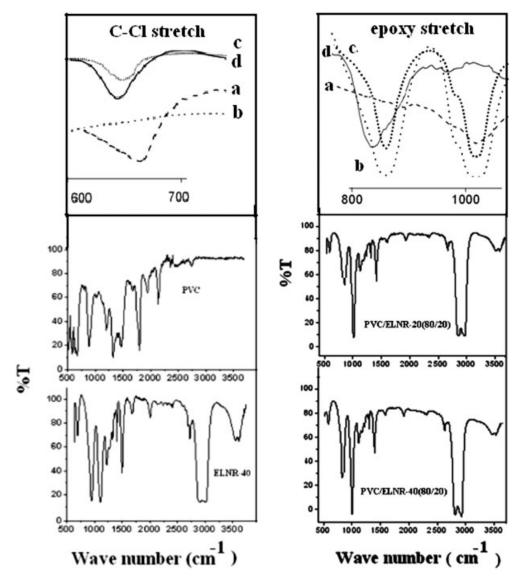


**Figure 2** Variation of tensile impact strength with % composition of L-ELNR for (a) PVC/L-ELNR-10, (b) PVC/L-ELNR-20, (c) PVC/L-ELNR-30, (d) PVC/L-ELNR-40, and (e) PVC/L-ELNR-50 blends.

composition. In the case of PVC/L-ELNR-10, PVC/ L-ELNR-20, and PVC/L-ELNR-30 blends, the values show an increase with the rubber content, which reach a maximum and decrease further. However, PVC/L-ELNR-40 and PVC/L-ELNR-50 blends show a steady decrease at all compositions. Thus it is seen that L-ELNR with lower epoxy contents, viz., L-ELNR-10, L-ELNR-20, and L-ELNR-30 are capable of imparting the impact strength of PVC where as those with higher epoxy content viz., 40 and 50 mol % tend to lower it. It is also clear from Figure 2 that the highest modification is observed for L-ELNR-20 at 80/20 composition. This is followed by L-ELNR-10 and L-ELNR-30 which show almost same level of impact modification. In other words, L-ELNR-20 shows higher level of modification compared with L-ELNR-10, which, however, decreases on further increase in epoxidation to 30 mol %, i.e., L-ELNR-30. The values are 600, 1000, and 551 J/m, respectively, for PVC/L-ELNR-10, PVC/L-ELNR-20, and PVC/L-ELNR-30 at 80/20 composition. This decrease continues with 40 mol % and 50 mol % epoxidation yielding considerably lower tensile impact strength, viz., 280 and 220 J/m, respectively, at 80/20 composition.

Thus, in the category – I blends L-ELNR-20 seems to be the best candidate for imparting the highest impact strength to PVC followed by L-ELNR-10 and L-ELNR-30. This is viewed as a natural outcome of the morphological changes occurring in the samples with the variation of epoxy content of the rubber. Optimum dispersion and adhesion of rubber particles in the PVC matrix is the basic requirement of impact modification. At the lower levels of epoxidation, the liquid rubber provides only partial miscibility with PVC chains due to insufficient interaction. As a result of this, rubber forms a separate phase as domains which are kept dispersed in the PVC matrix. The domain morphology as confirmed by SEM studies is ideal for the impact modification. Thus, it all depends on the interaction between the PVC chains and the ELNR which in turn is influenced by the epoxy content. Evidence to this effect is provided by IR spectroscopic analysis, DSC studies, and tensile measurements.

The FTIR spectra of the individual components, viz., PVC, ELNR-40, and some selected blend compositions such as PVC/L-ELNR-20 (90/10), PVC/ L-ELNR-20 (80/20), and PVC/L-ELNR-40(80/20) are shown in Figure 3. It is found that certain peaks of the components in the PVC/L-ELNR-40 blend undergo modification which can be readily explained on the basis of intermolecular interactions existing between the blend components. ELNR is supposed to interact with PVC through the oxirane oxygen which forms a weak hydrogen bond with the hydrogen of substituted carbon of PVC so that absorption characteristics of the oxirane ring and the C-Cl bond would be modified. It is quite natural that the substituted C-H (a-C-H) bond of PVC with the absorption peak of 1457 cm<sup>-1</sup> can also show peak modification, but this peaks overlaps with the  $-CH_2$  (deformation) peak of L-ELNR so that it cannot be neatly followed. Hence the nature and position of the oxirane and C-Cl peaks in the blends were examined for the purpose of assessing interaction between the two components. The C-Cl absorption peak in PVC and the oxirane peak in L-ELNR-40 appear at 679 and 872 cm<sup>-1</sup>, respectively, as shown in the above figure. These peaks were found to become slightly broad along with a shift in the center of the peak to the lower frequency region for blends containing L-ELNR-40, i.e., PVC/L-ELNR-40(80/20). The shifts were found to be 30 and 11 cm<sup>-1</sup>, respectively, for the C-Cl and epoxy absorptions. However, any such change is not observed in the case of PVC/L-ELNR-20 blends. This is because of the lack of interaction between PVC and L-ELNR at lower levels of epoxidation. These observations are further supported by DSC analysis. Figure 4 shows the DSC thermograms of PVC/L-ELNR-10 blends with (70/30), (60/40), and (50/50) compositions. It is found that each thermogram shows two distinct transitions at around 69°C and -35°C. These values correspond to the transitions of individual components, whose thermograms are also shown in the figure. Such an observation supports insufficient interaction between the blend components aiding the blend systems retaining heterogeneity. However, thermograms of PVC/L-ELNR-40 (70/30), (50/50), and (30/70) as given in Figure 5 show only a single transition. This is due to the higher level of interaction existing between the blend components which form a single phase. Thus the degree of epoxidation plays a vital role in the



**Figure 3** FTIR spectra of the blends and blend components. (top) magnified C—Cl and epoxy peaks (a) PVC, (b) L-ELNR-40, (c) PVC/L-ELNR-20 (80/20), and (d) PVC/L-ELNR-40 (80/20).

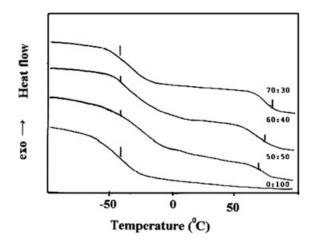


Figure 4 DSC thermograms of PVC/L-ELNR-10 blends.

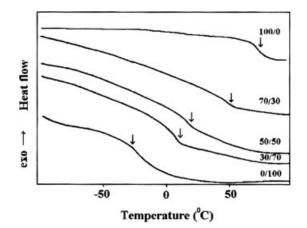


Figure 5 DSC thermograms of PVC/L-ELNR-40 blends.

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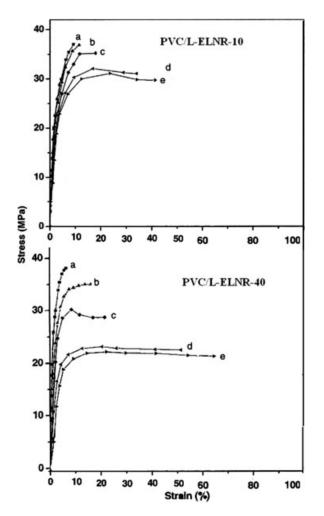


Figure 6 Stress-strain curves of PVC/L-ELNR-10 and PVC/L-ELNR-40 blends (a) PVC, (b) 90/10, (c) 80/20, (d) 50/50, and (e) 40/60 compositions.

interphase adhesion between PVC and the liquid natural rubber. This effect is also seen in the tensile behavior of the blend systems as described later.

Epoxy content of ELNR in the blend systems is found to modify the tensile properties.<sup>30</sup> However, it is observed that in the region of enhancement in impact strength there is no major sacrifice in tensile strength and modulus of elasticity (Fig. 6). For example, tensile strength values of L-ELNR-10 blends at 90/10 and 80/20 compositions are 36.5 and 35.5 N/ mm<sup>2</sup> and for the L-ELNR-20 series these values are 35.1 and 33 N/mm<sup>2</sup>, respectively, compared with 38.5 N/mm<sup>2</sup> of virgin PVC (Table II). Modulus of elasticity values PVC/L-ELNR-10 series is found to be 2200 and 1950 N/mm<sup>2</sup> for 90/10 and 80/20 compositions. In the case of PVC/L-ELNR-20 series, these values are 2100 and 1800 N/mm<sup>2</sup> for the same compositions, respectively, compared with the value of 2300 N/mm<sup>2</sup> for virgin PVC. It shows very close values for these samples. This is because, at these compositions, the tensile properties are mainly controlled by PVC phase though the rubber phase exerts controlling effect on the impact properties. Figure 6 also shows that the yield behavior of PVC becomes modified with the addition of epoxidized liquid rubber. Brittle fracture of virgin PVC is turned into ductile fracture in the presence of rubber as indicated by the yielding behavior shown by the blends. Yielding leads to viscous energy dissipation process enabling the blend systems to absorb large quantity of impact energy. However, excessive increase in L-ELNR-10 and L-ELNR-20 produces lower impact strength because it affects the integrity of the PVC matrix which undergoes rapid failure.

TABLE IITensile Data of PVC and the Blends

Tensile Data of TVC and the Diends							
Composition	Tensile strength (N/mm <sup>2</sup> )	Yield strength (N/mm²)	Modulus (N/mm²)	Elongation at break (%)			
PVC	$38.50\pm0.6$	-	2300	6			
PVC/L-ELNR-10 (90/10)	$36.50\pm0.4$	$37.50\pm0.4$	2200	9			
PVC/L-ELNR-10 (80/20)	$35.50\pm0.4$	$35.70\pm0.4$	1950	12			
PVC/L-ELNR-10 (50/50)	$31.00\pm0.3$	$32.00\pm0.3$	1200	32			
PVC/L-ELNR-20 (90/10)	$35.10\pm0.3$	$35.60\pm0.3$	2100	16			
PVC/L-ELNR-20 (80/20)	$33.00\pm0.2$	$33.40\pm0.3$	1800	21			
PVC/L-ELNR-20 (50/50)	$28.30\pm0.2$	$28.60\pm0.2$	900	35			
PVC/L-ELNR-30 (90/10)	$34.60\pm0.2$	$33.40\pm0.2$	1800	19			
PVC/L-ELNR-30 (80/20)	$30.00\pm0.1$	$31.20\pm0.1$	1450	25			
PVC/L-ELNR-30 (50/50)	$25.60\pm0.1$	$26.70\pm0.1$	700	38			
PVC/L-ELNR-40 (90/10)	$34.00\pm0.1$	$35.00\pm0.1$	1600	20			
PVC/L-ELNR-40 (80/20)	$27.5\pm0.1$	$29.00\pm0.1$	1200	30			
PVC/L-ELNR-40 (70/30)	$22.5\pm0.1$	-	550	45			
PVC/L-ELNR-50 (90/10)	$27.50\pm0.1$	$28.60\pm0.1$	1300	30			
PVC/L-ELNR-50 (80/20)	$20.00\pm0.1$	$21.40\pm0.1$	900	40			
PVC/L-ELNR-50 (70/30)	$10.80\pm0.1$	-	250	75			

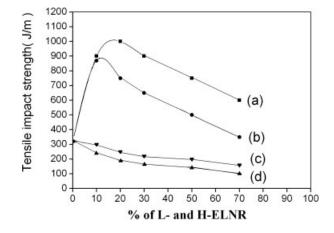
In the case of L-ELNR-40 and L-ELNR-50 based blends reduction of impact strength at all compositions is associated with drastic decrease in tensile strength and modulus of elasticity. It is an indication of excessive intermolecular interaction between PVC and the ELNR due to higher epoxy content leading to miscibility of the component polymers and eventual plasticization of PVC. This in turn affects the domain morphology of the dispersed phase and there by decreasing the impact strength. Miscibility of these blend systems is corroborated by comparable solubility parameter values, viz., [9.4 (cal/cm<sup>3</sup>)<sup>1/2</sup>] for PVC and [9.2 (cal/cm<sup>3</sup>)<sup>1/2</sup>] for L-ELNR-40 and L-ELNR-50.33 The heterogeneous nature of the blend systems may be lost at this stage and plasticization of PVC matrix would take place. As with L-ELNR-30 blends, lack of impact modification associated with lowering of tensile properties could be viewed as an intermediate behavior at which the blend morphology would show a transition from heterogeneity to homogeneity. This is prompted by an intermediate epoxy content of the rubber component.

Effect of composition on the impact strength of the blend systems as shown in Figure 2 follows a natural course. In all cases impact strength decreases with increase in rubber content. However, this decrease is minimum for blends with L-ELNR-10 and L-ELNR-20 so that the impact strength remains higher compared with virgin PVC even at higher rubber content. This shows that the heterogeneity of the system is maintained at all compositions due to the low epoxy content of the rubber. Large decrease in impact strength with composition in the case of blends with L-ELNR-40 and L-ELNR-50 is characteristic of plasticized miscible systems.

#### Effect of molecular weight of ELNR

Liquid natural rubber of molecular weight 9600 was made and epoxidized to the level of 20 and 50 mol % to yield H-ELNR-20 and H-ELNR-50. These rubber samples were blended with PVC to form two series of blends, viz., PVC/H-ELNR-20 and PVC/H-ELNR-50. Studies were conducted on these blends and the results have been compared with the corresponding L-ELNR blends.

Figure 7 shows the tensile impact strength versus composition of the above two series of blends along with those of PVC/L-ELNR-20 and PVC/L-ELNR-50 blends for the purpose of comparison. They exhibit different characteristics as revealed by the respective plot. H-ELNR-20 causes improvement in impact strength with a maximum value of 870 J/m at (90/10) composition which decreases with a further increase in the rubber content. The general trend in the variation of impact strength is similar to that of



**Figure 7** Tensile impact strength versus wt % of ELNR for (a) PVC/L-ELNR-20, (b) PVC/H-ELNR-20, (c) PVC/H-ELNR-50, and (d) PVC/L-ELNR-50 blends.

the PVC/L-ELNR-20 blends. However, peak values of impact strength are found to be lower than that of PVC/L-ELNR-20 (80/20) blend (1000 J/m) and it occurs at (90/10) composition instead of (80/20) composition for the latter.

The above results indicate lower efficiency of H-ELNR-20 in bringing about impact modification of PVC. This could be due to lower dispersability of the rubber in the matrix caused by its longer chains which affects the ease of diffusion. Again, because of the lower dispersability of H-ELNR-20 it forms bigger domains which may affect the integrity of PVC matrix. Hence, higher quantity of H-ELNR-20 is not tolerated and the maximum impact modification is shown at a lower composition, viz. (90/10) compared with (80/20) in the case of L-ELNR-20.

Plot for PVC/H-ELNR-50 blends shows continuous decrease in impact strength at all compositions similar to PVC/L-ELNR-50 blends. The impact strength of PVC, viz., 320 J/m decreases to 300 and 270 J/m, respectively, for H-ELNR-50 and L-ELNR-50 blends at (90/10) composition. These values decrease drastically with further increase in rubber content. It was already discussed that this kind of decrease is caused by plasticization of PVC which affects the domain morphology of the samples. From Figure 6 it is also seen that the impact strength of the samples based on L-ELNR-50 falls lower compared with H-ELNR-50 blends at all compositions which is contrary to the observations made in the case of H-ELNR-20 and L-ELNR-20 blends. This is the consequence of a shift from the domain morphology for ELNR-20 blends to a plasticized matrix for the ELNR-50 blends. Among the latter blends L-ELNR-50 based samples show higher plasticization effect due to its higher diffusion aided by the lower chain length compared with H-ELNR-50 blends.

# CONCLUSIONS

Blends of PVC and epoxidized liquid natural rubber of different molecular weights and different mol % of epoxidation have been prepared and characterized in terms of the impact properties. Based on these studies L-ELNR-20 seems to be the best candidate for imparting the highest impact strength to PVC followed by L-ELNR-10 and L-ELNR-30. At these lower levels of epoxidation, liquid rubber provides partial miscibility with PVC due to insufficient intermolecular interaction. This leads to domain morphology for the samples. Optimum dispersion and adhesion of rubber particles with the PVC matrix explain the observed impact modification in these blends. Lowering of impact strength with L-ELNR-40 and L-ELNR-50 is an indication of excessive intermolecular interaction between the blend components leading to miscibility of the component polymers. The heterogeneous nature of the blend systems may be lost at this stage and plasticization of PVC matrix would take place. PVC/L-ELNR-30 blends could be viewed as intermediate samples at which the blend morphology would show a transition from heterogeneity to homogeneity. Regarding ELNR molecular weight it is found that the impact modification is higher for the L-ELNR blends compared with the H-ELNR blends. Better dispersion and smaller domain size achieved with the low-molecular mass rubber samples explains the higher impact strength. Tensile impact fracture studies revealed that the failure pattern of the L-ELNR-20 based blend system is intermediate between the brittle fracture of rigid PVC and ductile fracture of PVC/L-ELNR-50 blend.

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