

Preparation and Properties of PVC/ELNR-30 Blends

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ABSTRACT

The mechanical and thermal properties of solution-cast blends of Polyvinyl chloride (PVC) and Epoxidized Liquid Natural Rubber having 30 mole% epoxidation (ELNR-30) have been examined using Zwick materials testing machine and heating in air circulating oven (200°C) at different time intervals respectively. The ELNR was prepared by oxidative degradation of natural rubber latex using Phenylhydrazine/Oxygen system and subsequent epoxidation with formic acid and 30% H₂O₂. Tensile strength of unblended PVC was 26.5 ± 0.5 MPa. The blends had lower tensile strength which decreased with increase in blend ratio of ELNR-30. Experimental data revealed that there was greater homogeneity in the PVC/ELNR-30 (80/20) compared with PVC/ELNR-30 (90/10). The PVC/ELNR-30 (80/20) also showed superior elongation at maximum (%) than the unblended PVC and PVC/ELNR-30 (90/10) in that order. Thermal stability decreased in the order PVC, PVC/ELNR-30 (90/10), PVC/ELNR-30 (80/20).

Keywords: Polyvinyl Chloride (PVC), Epoxidation, Liquid Natural Rubber (LNR), Blends, Mechanical and Thermal Properties

1. Introduction

Thermoplastic elastomers such as PVC/ELNR-30 blends are of wide interest in materials research and development. This class of polymers describes a wide variety of materials that have elastomeric properties at ambient temperatures and obviate the need for the vulcanization step to develop typical rubberlike elasticity. Thermoplastic elastomers are beginning to replace specialty rubbers in a wide variety of uses such as in adhesives, wire and cable insulation.

Poly (vinyl chloride), PVC, being a proton donating polymer interacts with oils and hydrocarbons resulting in plasticization of the resin. Epoxidized liquid natural rubber (ELNR) could be prepared from natural rubber (NR), in its latex form, by the oxidative degradation of NR into liquid natural rubber (LNR) using phenylhydrazine/oxygen system and subsequent epoxidation with performic acid generated *in situ* from the reaction of formic acid and hydrogen peroxide [1,2]. Natural rubber is a high molecular weight polymer while liquid natural rubber usually has molecular weight less than M_v 100,000.

Blending is an attractive technique of polymer modifications. There is scientific evidence to show that a particular polymer mixture can be made more miscible by reducing the molecular weight of one or both components [3]. This theory is based on the Flory-Huggins theory. According to the theory the enthalpy gained on mixing polymers is inversely related to their number average molecular weights. Most polymer blends are immiscible, as the formation of two or more distinct phases are usually evident. Dissolution, incorporation or absorption phenomena do take place in any blend system. It should be noted that the adhesion between the phases is particularly important in the blending process because it influences the mechanical properties of blends. The major component forms the matrix or continuous phase while the minor component forms the discrete phase. Blends of PVC and ELNR have been of great interest to researchers [3-5].

The present work involves the preparation and characterization of blends of PVC and ELNR-30. This has the potential of plasticizing the vinyl chloride polymer. A solution of PVC in 2-butanone is blended with ELNR-30.

PVC constitutes the continuous phase while ELNR-30 is the discrete phase.

2. Experimental

2.1. Materials

PVC (k-value 65 and density 1.37) was produced by LG-DAGU, China. LNR (M_v 75,000) was prepared by the depolymerization of natural rubber latex obtained from the NIG 804 clonal series; the characteristics [6] of which are given in **Table 1**. ELNR having 30 mol% epoxidation (ELNR-30) was prepared by the epoxidation of LNR. Phenylhydrazine (analytical grade) was made by Fluka. 30% hydrogen peroxide was obtained from Merck. 98% formic acid; toluene and 2-butanone were BDH Ltd products. All chemicals were used as commercially supplied.

2.2. Preparation of LNR

Three hundred milliliters of Natural Rubber Latex (20% DRC), stabilized with Vulcastab LW (3% by weight of DRC of natural rubber latex) was poured into a 1 L glass reactor, equipped with mechanical stirrer, condenser, dropping funnel and air inlet tube. After heating the latex to 60°C in a water bath, a desired amount of phenylhydrazine was slowly added and air was introduced into the latex slowly to avoid frothing. The reaction mixture was stirred for 3 h. During this period, depolymerization or degradation of natural rubber latex to liquid natural rubber (LNR) took place. About 10 mL of the reaction mixture was taken at the end of the reaction for chemical molecular weight determination. This was carried out using a Ubbelohde-type viscometer.

2.3. Preparation of ELNR

Two hundred milliliters the LNR was cooled to room temperature and diluted with 100 mL distilled water. Thereafter 15 mL of 98% formic acid was added drop wise. 61 mL of 30% H_2O_2 was slowly added after the

reaction mixture had been stirred for 15 min. The epoxidation reaction was allowed to proceed for 3 h. At the end of the reaction, the ELNR was soaked in 0.1 M Na_2CO_3 overnight in order to neutralize the epoxidizing acid. The ELNR was recovered by precipitation in methanol and the coagulum obtained was dried under vacuum at 50°C.

2.4. Preparation of Blends

5% (w/v) solution of PVC in 2-butanone was blended with 3% solution of ELNR-30 in 1:1 w/v (toluene/utane). PVC solution was added to the solutions of ELNR-0 at different blend compositions. The blends were mixed using mechanical stirrer (1 500 rpm) for 5 h at 50°C and cast on glass plates. The samples were dried under vacuum at 70°C for 2 days to remove traces of residual solvents.

2.5. Designation of Blends

The blends were designated as follows: PVC/ELNR-30 (90/10); meaning a blend of 90 parts of PVC and 10 parts of epoxidized liquid natural rubber with 30 mol% epoxidation. PVC/ELNR-30 (80/20); meaning a blend of 80 parts of PVC and 20 parts of epoxidized liquid natural rubber with 30 mol% epoxidation.

2.6. Mechanical Tests

The tensile tests were carried out using Zwick material testing machine (BTI-FBOO5TN.D14) on a dumbbell-shaped samples at room temperature (30°C). The load cell for the machine was 1kN with a Crosshead speed of 100 mm/min.

2.7. Thermal Studies

Thermal properties of the blends were studied by heating in an air circulating oven (200°C) at different time intervals. % weight-loss was recorded as a function of time (minutes).

3. Analysis and Discussion

3.1. Tensile Properties

Analytical results of the tensile properties of PVC and its blends are presented in **Table 2**. The tensile strength of the PVC sample was 26.5 MPa while those of PVC/ELNR-30 (90/10) and PVC/ELNR-30 (80/20) were 16.2 MPa and 11.8 MPa respectively. The same trend was observed for Force at 50% Elongation. The implication of these observations is that the strength of the materials decreased with increasing ratio of ELNR-30. It worth noting that the PVC/ELNR-30 (90/10) was unable to attain 100% elongation. This could be attributed to insufficient amount of ELNR-30 in the composite leading to low level of phase homogeneity. The same arguments

Table 1. Typical characteristics of latex from NIG 804.

Parameter	
Total Solid Content (TSC) (%)	45.0
Dry Rubber Content (DRC) (%)	38.5
Mechanical Stability Time (MST) (sec)	550
Coagulum Content (%)	0.05
Sludge Content (%)	0.10
Volatile Fatty Acids (VFA) (%)	0.17

Source: Okieimen and Akinlabi, 2002, [6].

also accounts for its having the lowest Elongation at break (48.7%) and Elongation at Maximum (5.2%). The PVC/ELNR-30 (80/20) material exhibits the highest Elongation at Maximum (289.1%) as against 134.4% for PVC suggesting that replacement of 20 parts per hundred (pphr) of PVC with ELNR-30 was sufficient to effect plasticization of PVC.

3.2. Thermal Studies

Results of thermal stability in terms of percentage weight loss on heating for PVC, PVC/ELNR-30 (90/10) and PVC/ELNR-30 (80/20) are given in **Table 3**. It was observed that thermal stability decreased with increase in blend ratio of ELNR-30. Whereas both the upper service temperature of natural rubber in intermittent and con-

tinuous usage are 100°C and 80°C respectively, PVC degrades completely at about 250°C; commencing with elimination of HCL gas at much lower temperature [7].

Overlay plot of % weight loss against time of heating (min) using JMP statistical software (version 3.25), presented in **Figure 1**, showed two distinct regions in the graph for PVC/ELNR-30 (80/20) and PVC/ELNR-30 (90/10). This could be associated with the 2 phase nature of the blend. The graph for PVC showed that degradation increased steadily from 5.5 %wt loss at the 30 minute mark up to 9.1 wt% loss at the 90th minute until the 150th minute. We are of the opinion that the 1st region of PVC was associated with the elimination of HCL gas from the molecule without scission of the main chain. The 2nd region which remained virtually constant represented a

Table 2. Tensile data of PVC and its blends.

	PVC	PVC/ELNR-30 (90/10)	PVC/ELNR-30 (80/20)
Tensile Strength (MPa)	26.5 ± 0.5	16.2 ± 0.5	11.8 ± 0.4
Elongation at Break (%)	341.3 ± 0.5	48.7 ± 0.6	295.7 ± 0.5
Force at 50% Elongation (MPa)	16.3 ± 0.2	10.3 ± 0.2	7.2 ± 0.2
Maximum Force (N)	53.2 ± 0.4	19.3 ± 0.3	30.4 ± 0.3
Force at 100% Elongation (MPa)	17.2 ± 0.1	-	8.4 ± 0.1
Elongation at Maximum (%)	134.4 ± 0.2	5.2 ± 0.2	289.1 ± 0.2

Table 3. Thermal data of PVC and its blends.

Material	Heating time (min)	Initial wt. (g)	Final wt. (g)	wt. loss (g)	wt% loss
PVC	30	0.1371	0.1282	0.0089	5.5
	60	0.1216	0.1130	0.0089	7.1
	90	0.1283	0.1179	0.0103	9.1
	120	0.1213	0.1113	0.0100	9.2
	150	0.0846	0.0764	0.0082	9.7
PVC/ELNR-30(90/10)	30	0.0671	0.0622	0.0049	7.3
	60	0.0571	0.0528	0.0043	9.2
	90	0.0600	0.0537	0.0063	10.5
	120	0.0571	0.0506	0.0065	11.3
	150	0.0966	0.0771	0.0195	20.2
PVC/sELNR-30(80/20)	30	0.1446	0.1300	0.0146	10.1
	60	0.1621	0.1431	0.0190	11.7
	90	0.1410	0.1220	0.0193	13.7
	120	0.1484	0.1220	0.0264	17.8
	150	0.1334	0.1046	0.0288	21.6

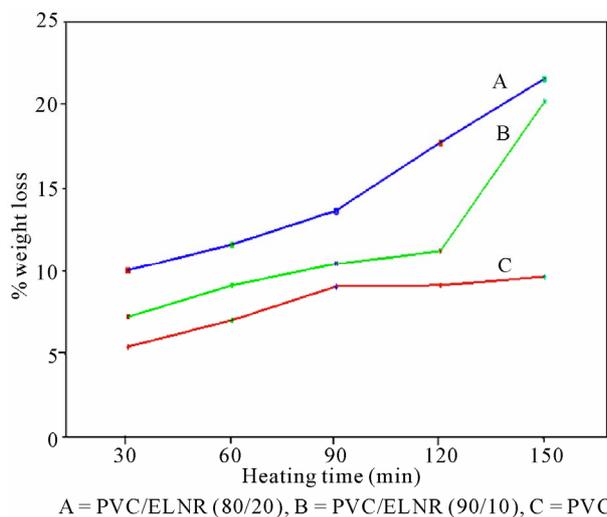


Figure 1. Overlay plots of % weight loss against heating time (min) for PVC, PVC/ELNR-30 (90/10); PVC/ELNR-30 (80/20).

situation where almost all the HCL gas in the sample was eliminated and further loss of weight could not occur since a temperature of 250°C had not been attained.

4. Conclusions

The study has shown that incorporation of ELNR-30 into PVC at a blend ratio of 20 pphr had a plasticizing effect on the polymer blend [PVC/ELNR-30 (80/20)]. Thermal stability of the blend was inferior to that of the unblended PVC. A further study on the properties of the blends is ongoing.

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REFERENCES

- [1] A. S. Hashim, S. K. Ong and R. S. Jessey, "A General Review of Recent Developments on Chemical Modification of NR," *Newsletter of the Rubber Foundation Information Center for Natural Rubber (Natur Rubber)*, Vol. 28, 2002, pp. 3-9.
- [2] P. Phinyocheep and S. Daunthong, "Ultraviolet Curable Liquid Natural Rubber," *Journal of Applied Polymer Sciences*, Vol. 78, No. 8, 2002, pp. 1478-1485. [doi:10.1002/1097-4628\(20001121\)78:8<1478::AID-APP30>3.0.CO;2-K](https://doi.org/10.1002/1097-4628(20001121)78:8<1478::AID-APP30>3.0.CO;2-K)
- [3] M. N. Radhakrishnan Nair, P. K. Biju, G. V. Thomas and M. R. Gopinathan Nair, "Blends of PVC and Epoxidized Liquid Natural Rubber: Studies on Impact Modification," *Journal of Applied Polymer Sciences*, Vol. 111, No. 111, 2008, pp. 48-56. [doi:10.1002/app.28884](https://doi.org/10.1002/app.28884)
- [4] M. N. Radhakrishnan Nair, G. V. Thomas and M. R. G. Nair, "Thermogravimetric Analysis of PVC/ELNR Blends," *Polymer Degradation and Stability*, Vol. 11, No. 2, 2006, pp. 14-18. [doi:10.1016/j.polyimdegradstab.2006.11.014](https://doi.org/10.1016/j.polyimdegradstab.2006.11.014)
- [5] F. Findik, R. Yiimaz and T. Koksall, "Investigation of Mechanical and Physical properties of Several Industrial Rubbers," *Materials & Design*, Vol. 25, No. 4, 2004, pp. 269-276. [doi:10.1016/j.matdes.2003.11.003](https://doi.org/10.1016/j.matdes.2003.11.003)
- [6] F. E. Okieimen and A. K. Akinlabi, "Processing Characteristics and Physicochemical Properties of Natural Rubber and Liquid Natural Rubber Blends," *Journal of Applied Polymer Sciences*, Vol. 85, No. 5, 2002, pp. 1070-1076. [doi:10.1002/app.10666](https://doi.org/10.1002/app.10666)
- [7] C. Hall, "Polymer Materials," Machmilian Press, Hong Kong, 1981.