

Natural Rubber–HDPE Blends with Liquid Natural Rubber as a Compatibilizer. I. Thermal and Mechanical Properties

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SYNOPSIS

The measurement of physical properties of thermoplastic natural rubber (TPNR) of NR–HDPE blends have been made at various compositions of high-density polyethylene (HDPE). The tensile properties and hardness of TPNR improve significantly with the addition of liquid natural rubber (LNR) to the blend. The degree of cross-linking also increases with increasing amount of LNR added. The LNR with molecular weight (M_w) of 50,000 and reactive terminals promotes cross-linking within the rubber phase and grafting of the polyethylene chains onto the rubber matrix system. The maximum stress and strain of the blends measured are about 7.5 MPa and 1000%, respectively. Dynamic mechanical analysis results indicate a single T_g on a $\tan \delta$ trace at about -50 and -55°C for the two types of blends, respectively. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Blends of different polymers are of considerable importance as blending provides a means of improving physical and mechanical properties. Thermoplastic natural rubber (TPNR) is a family of materials prepared by blending natural rubber with polyolefins, particularly polypropylene (PP).^{1,2} A wide range of properties is attainable by varying the compositions of natural rubber and polyolefins, and the materials are most conveniently considered as falling into two categories: When the natural rubber predominates, the blends obtained are soft, thermoplastic elastomers; at the other end of the composition range, when the natural rubber is the minor component of the blend, the materials are hard. The study on thermoplastic natural rubber with various types of rubber and polyolefins have been reported by many researchers.^{3–6} This article discusses the preparation of new TPNR using NR–HDPE blends with liquid natural rubber (LNR) as a compatibilizer. LNR with active terminals and molecular weight, M_w , of 50,000 has been prepared in the laboratory using a photo-

degradation technique.⁷ Nuclear magnetic resonance studies indicate that the active groups are composed of $-\text{OH}$, $-\text{OOH}$, and >C=O along the polyisoprene chain of the LNR. Special attention is focused on the compatibility and thermal and mechanical properties of these blends. Dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and tensile and hardness testers were used for assessing the physical properties of the blends.

EXPERIMENTAL

Materials

The materials examined were high-density polyethylene (HDPE) (Mobil), natural rubber (NR), and liquid natural rubber (LNR), which were prepared by photosensitized degradation of NR in visible light. Detailed descriptions and characteristics of the samples are given in Table I.

Blend Preparation

The blends were prepared by melt-mixing the ingredients in a laboratory cam mixer (Brabendar) at about 160°C for about 15 min. The blend compositions varied between 20 and 55% HDPE and 45

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Table I Estimation Degree of Cross-linking in the NR–HDPE Blend

Percent of LNR in Blend (%)	Blend 1		Blend 2	
	Density ρ (g/mL)	Degree of Cross-linking (mol/g)	Density ρ (g/mL)	Degree of Cross-linking (mol/g)
0	0.88	2.7×10^{-5}	0.92	1.6×10^{-5}
7	0.91	2.8×10^{-5}	0.89	2.0×10^{-5}
13	0.93	3.1×10^{-5}	0.90	2.7×10^{-5}
20	0.94	3.7×10^{-5}	0.89	4.1×10^{-5}
27	0.93	4.6×10^{-5}	0.93	4.9×10^{-5}
33	0.90	3.5×10^{-5}	0.92	3.8×10^{-5}

and 80% NR with 13% LNR. Once homogeneous mixing was assured, the blends were removed and subsequently compression-molded at about 130°C using 7 kN pressure for about 2 min into either a thin sheet of about 1 or 3 mm thickness. From this sheet, specimens were cut for all the physical analyses. Two compositions of NR/HDPE blends had been prepared, known as Blend 1 (60/40) and Blend 2 (70/30), with various percentages of LNR for detailed studies of the physical properties.

Physical Measurement

Tensile Testing

The samples of dumbbell shape were cut from thin sheet from the blend of about 1 mm thickness after 24 h of maturation time. The tensile properties were measured at room temperature (27°C) on an Universal testing machine (Model R2000, Lloyd Instruments PLC) in accordance with the test procedure of ASTM D638. The gauge was kept at 60 mm with a crosshead speed 50 mm/min. From the stress–strain curves, the following properties (average of five samples) were calculated: yield strength, ultimate tensile strength, strain at break, and Young's modulus.

Hardness

The hardness of the samples was measured on thick samples (3 mm thickness) using a hardness tester of Shore type A (Zwick Model). All the measurements were performed at room temperature.

Differential Scanning Calorimetry (DSC)

DSC experiments were done in a Mettler DSC-30 calorimeter. The Mettler TC 10A control and eval-

uation module was used to collect data and evaluate the results. Thermograms were traced from –100 to 150°C with a scanning rate of 10.0°C/min for all analyses.

Dynamic Mechanical Analysis

A Rigaku Thermal Analyzer Ver 2.22 was used. Tests were obtained from –100 to 150°C using a

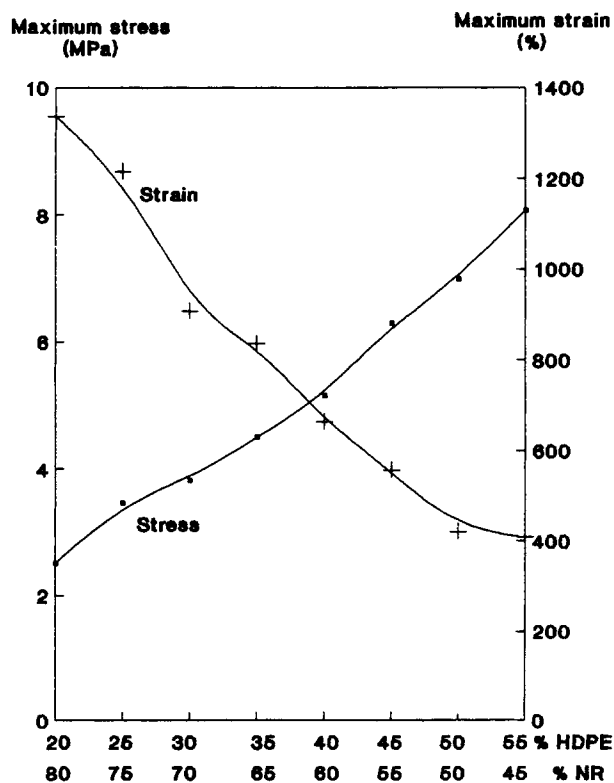


Figure 1 Maximum stress/strain for various compositions of blends with 10% LNR.

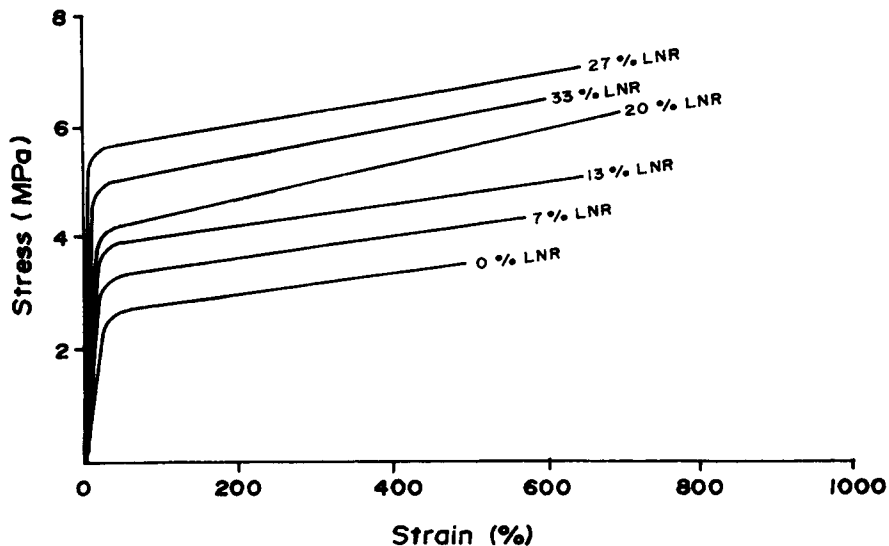


Figure 2 Stress-strain curve for Blend 1.

scanning rate of 2°C/min at oscillating frequencies of 10 Hz and the measurements were done on a tensile mode. Data collection and evaluation were done using software supplied by a Rigaku Thermal Analyzer Ver 2.22. Samples were run using a tensile mode.

RESULTS AND DISCUSSION

LNR, being similar to NR, is readily soluble in the NR phase and any chemical interactions between the NR chains and the active terminals of LNR is

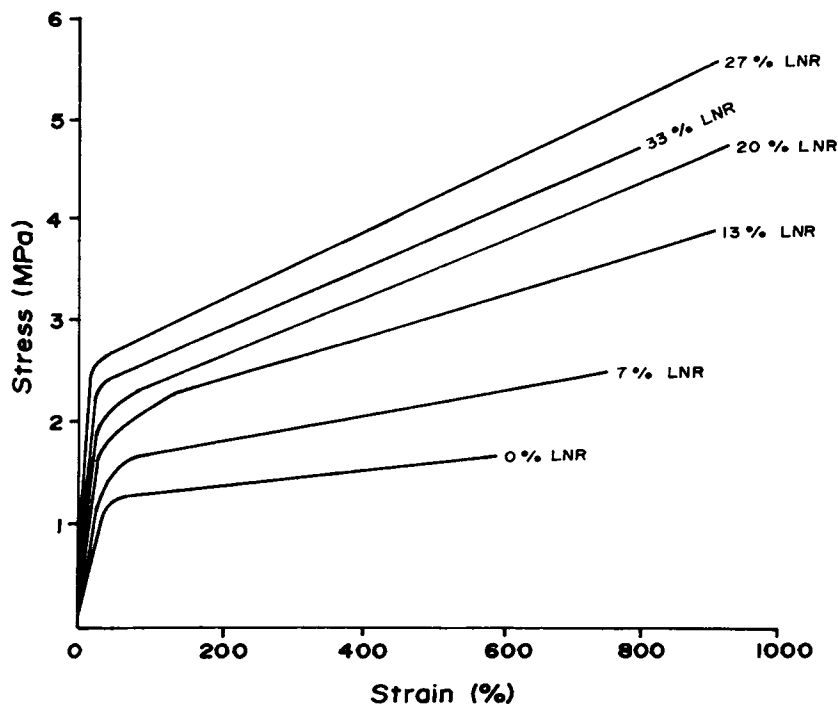


Figure 3 Stress-strain curve for Blend 2.

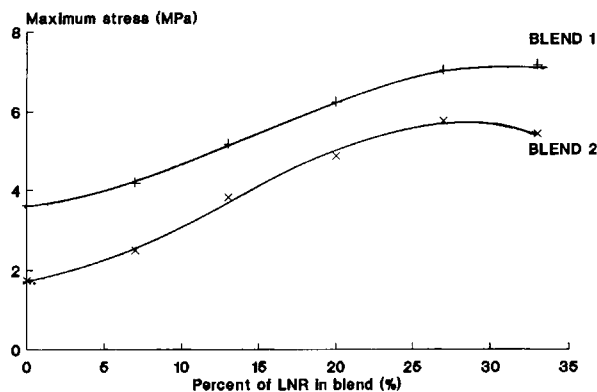


Figure 4. The effect of LNR on maximum stress.

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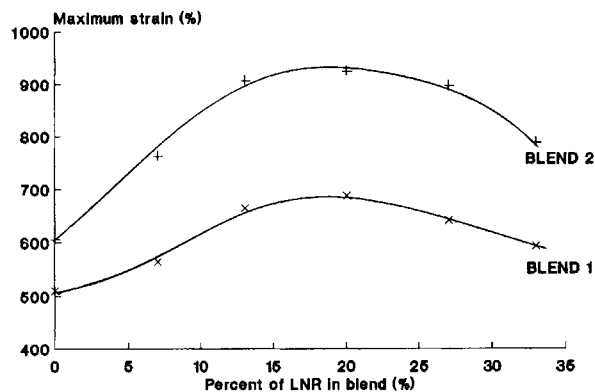


Figure 5. The effect of LNR on maximum strain.

Figure 5 The effect of LNR on maximum strain.

expected to result in the formation of chemical bonds within the NR phase. A similar situation can also be expected when the LNR chain is interphased between the NR and HDPE phases. These general chemical interactions are considered as cross-linking in this thermoplastic NR-HDPE system. The degree of cross-linking has been estimated using the Flory-Rehner equation. The results show that the degree of cross-linking increases with the addition of LNR in the blend, as shown in Table I. The degree of cross-linking reaches a maximum of about 4.4×10^{-5} mol/g for Blend 1 and 4.1×10^{-5} mol/g for Blend 2 with 27% LNR. Further addition of LNR causes the properties to decrease as denoted by 33% LNR. This effect is probably due to the excess of LNR that can act in the cross-linking and compatibilizing. The maximum stress/strain curves are depicted in Figure 1 for the various compositions of HDPE and NR. The result indicates that the blend with 60% NR and 40% HDPE gave the best properties with intermediate maximum stress/strain at about 5 MPa and 700%, respectively.

Figures 2 and 3 show the stress-strain curves for both blends with various compositions of LNR. The plot of maximum stress and strain are depicted in Figures 4 and 5. Blend 1, with a higher percentage of HDPE, has a higher maximum stress at all compositions of LNR than in Blend 2. The maximum strains of Blend 2 as compared to Blend 1 are relatively larger and almost reach 1000%.

The data of maximum stress and strain for both blends seem to linearly increase with increasing LNR concentrations and achieve the maximum with about 27% LNR. The maximum tensile stress increases by about 100% for Blend 1 and 200% for Blend 2 as compared to the sample without LNR.

A similar observation is also noted for the maximum strain.

The hardness is also found to be dependent on LNR content for both compositions, as shown in Figure 6 and Table II. In Blend 2, the increment is about 30% in hardness compared to the sample with 0% LNR.

Thermal behavior of the sample is as shown in Figure 7. The thermograms of Blend 1 indicate that

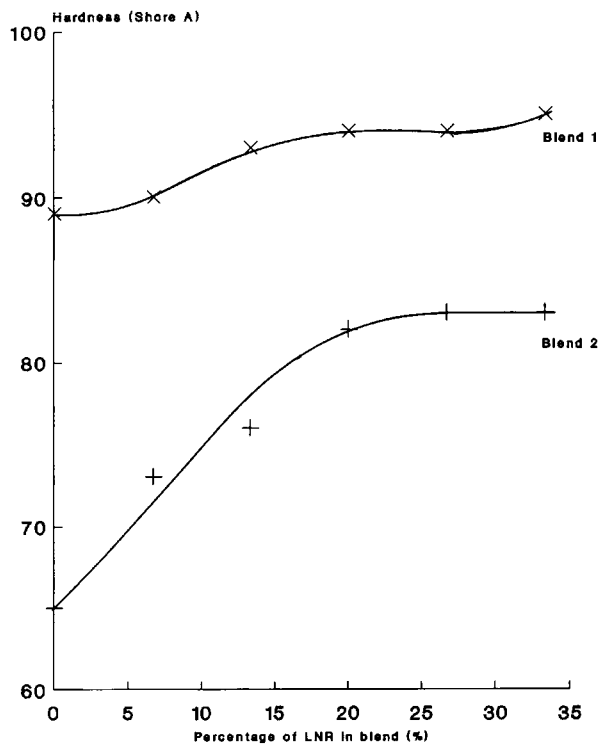


Figure 6 The effect of LNR on hardness.

Table II Physical Properties of the NR-HDPE Blend

Percent of LNR in Blend (%)	Blend 1			Blend 2		
	Maximum Stress (MPa)	Maximum Strain (%)	Hardness Shore A	Maximum Stress (MPa)	Maximum Strain (%)	Hardness Shore A
0	3.5-3.7	440-570	89	1.5-2.1	500-730	65
7	4.1-4.4	500-660	90	2.2-3.7	700-870	73
13	4.9-5.7	580-720	93	3.5-4.1	850-960	76
20	5.8-6.5	600-710	94	4.0-5.4	800-1000	82
27	6.9-7.2	740-800	94	4.9-7.0	800-980	83
33	6.8-7.4	540-600	95	4.8-5.9	680-850	83

the blend is stable up to the temperature of about 230°C. The gradual drops in the base line is probably due to the evaporation of the solvent and other trace or a severely degraded component in the sample.

The blend shows a single glass temperature (T_g) and melting point (T_m) as indicated by the DSC and DMA traces shown in Figures 8 and 9, respectively. The T_g 's for NR and HDPE are at -45 and

-110°C, respectively, and, thus, the T_g 's of the blends recorded appear to within the two T_g 's of the components.⁸ A homogeneous phase distribution appears to be strongly indicated in this system. The melting temperature (T_m) and heat of fusion (ΔH_m), determined from the DSC thermogram, are given in Figures 10 and 11. The heat of fusion is almost a linear function of blend composition. Figure 9 also

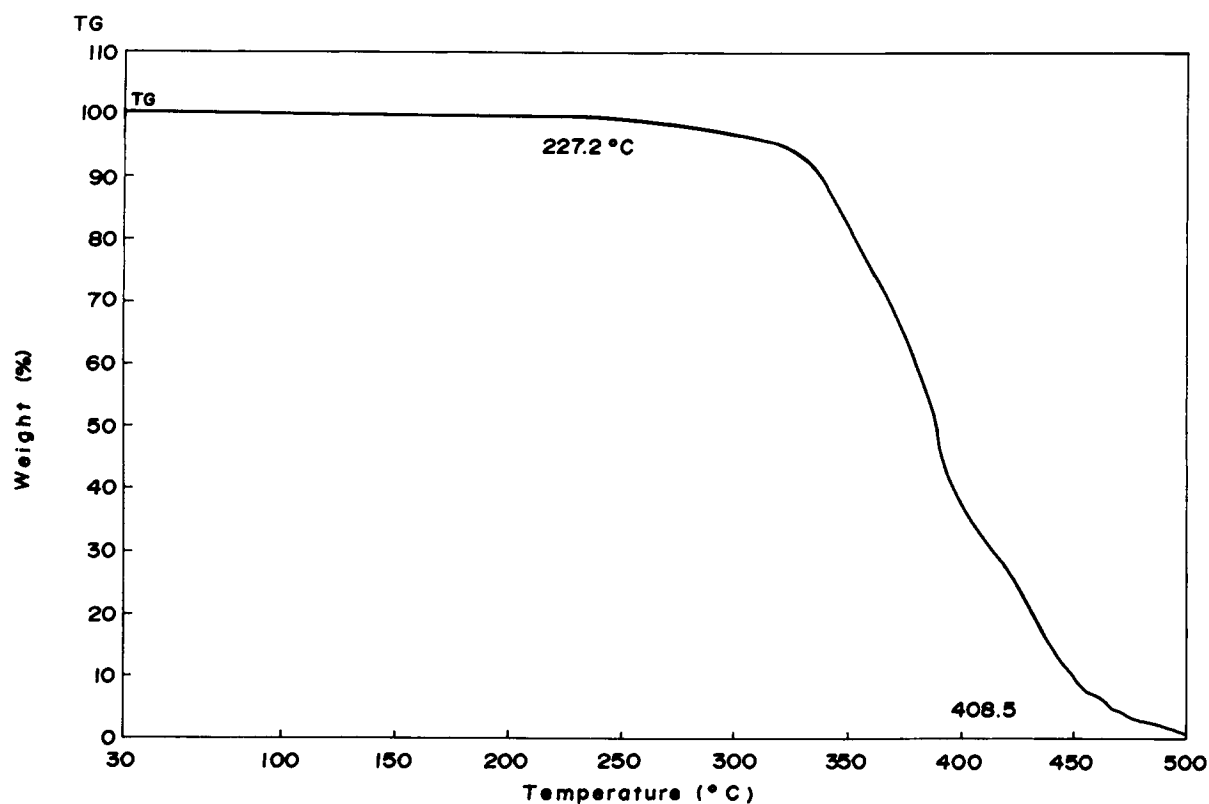


Figure 7 Typical TG thermogram for Blend 1.

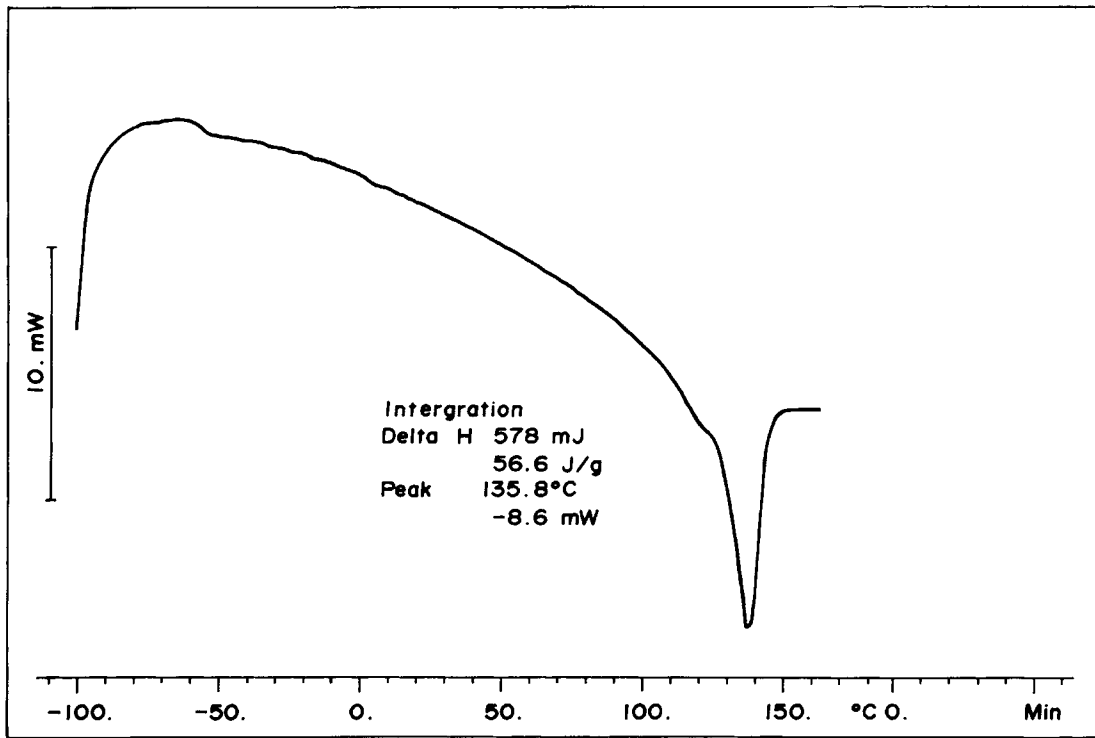


Figure 8 Typical DSC thermogram for Blend 1.

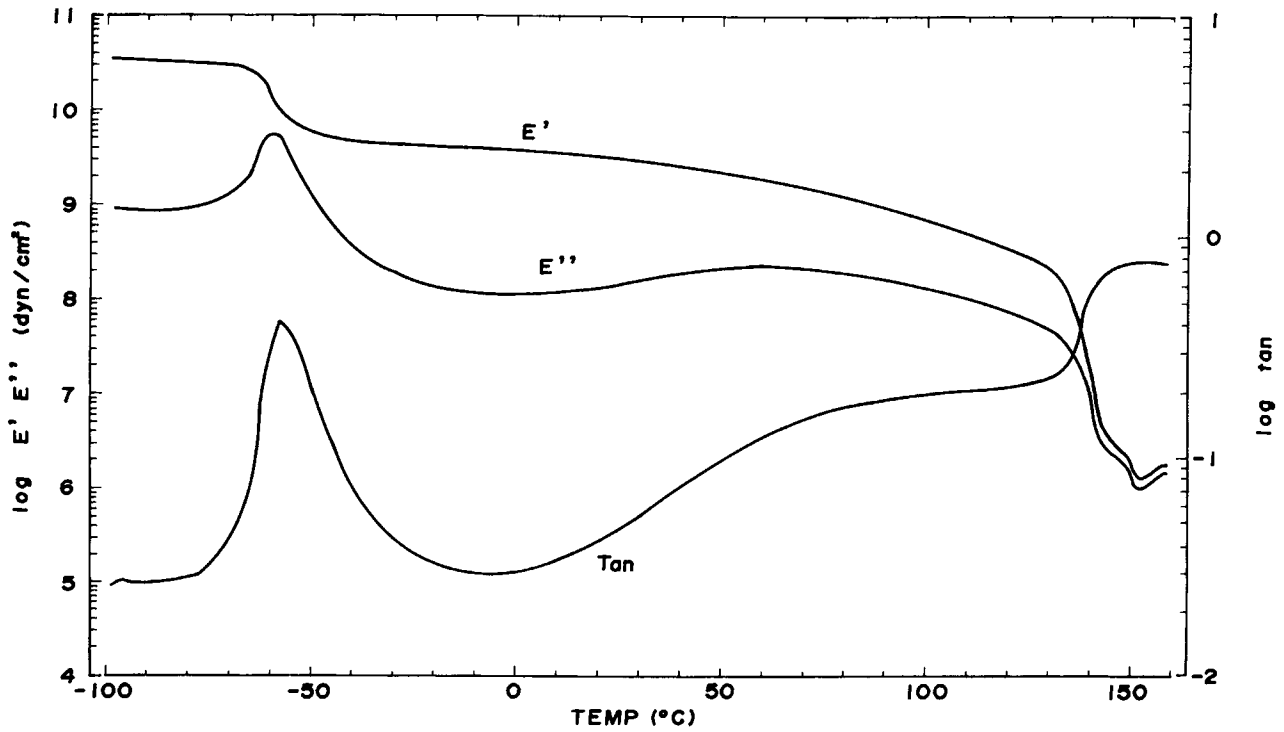


Figure 9 DMA trace for 60/40 blend with 10% LNR that shows the storage (E') and loss (E'') moduli at 10 Hz.

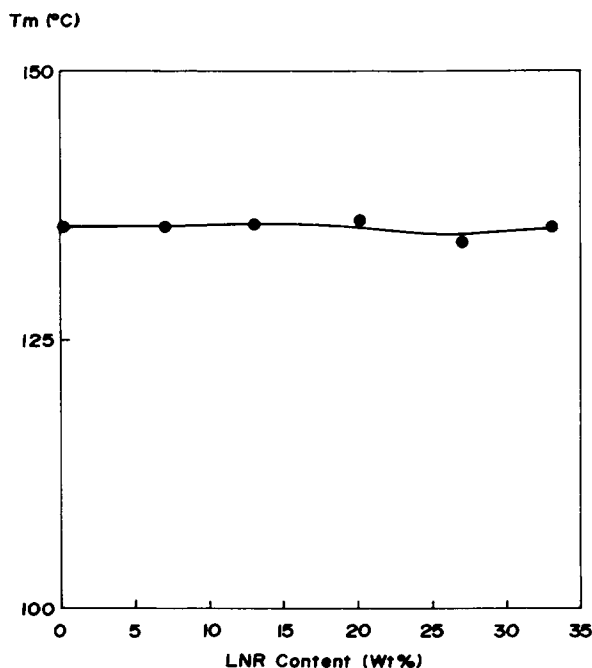


Figure 10 Melting point (T_m) of Blend 1.

shows the typical temperature dispersions of the dynamic storage modulus (E'), loss modulus (E''), and $\tan \delta$ for the NR-HDPE blend. Both types of samples exhibit a single glass transition temperature at about -46°C (70/30) and -55°C (60/40). Above 130°C , the blend exhibits a sharp drop-off in E' and E'' , which corresponds to the melting point of crystalline phase. The homogeneity of the phase distribution in the blend is further substantiated by the smoothness of the phase-contrast scanning electron micrograph.

CONCLUSION

The results presented in this article demonstrate the ability of LNR to function as a compatibilizer in the NR-HDPE blends. The phase morphology and physical properties of the NR-HDPE thermoplastic blends is improved with the addition of LNR into the blend. The insertion of cross-linkings by LNR within the NR and phase and NR-HDPE interphase is probably the main factor in influencing the physical nature of TPNR. The interphase properties of TPNR can be tailored by varying the composition of the blend and the optimum content of LNR is between 10 and 27%.

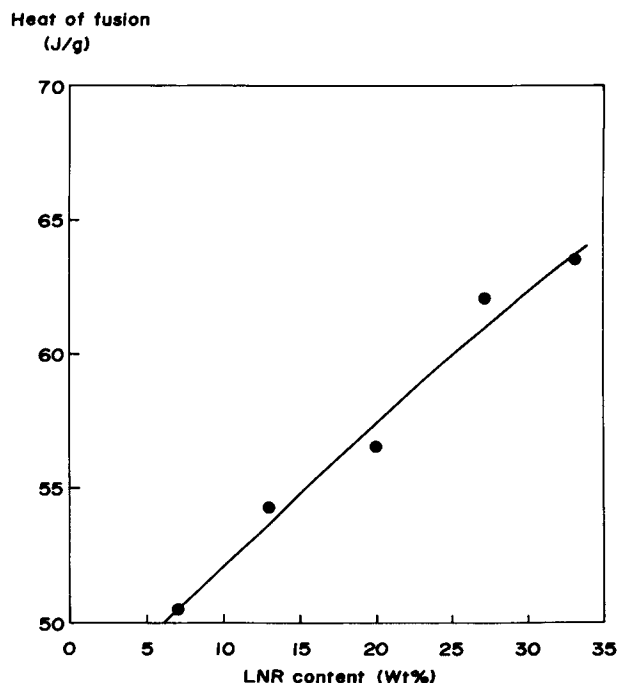


Figure 11 Heat of fusion (H_m) for the Blend 1.

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