Liquid Natural Rubber (LNR) as a Compatibilizer in NR/LLDPE Blends

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ABSTRACT: The effects of molecular weight of LNR, as a compatibilizer in NR/LLDPE blends, were studied. Rheological studies and mechanical properties of the blends showed that the molecular weight of LNR played a very important role in determining their performance. The blends that contained 15–25% LNR with an M_w of 4.8×10^5 and an M_n of 1.66×10^5 showed the highest mechanical properties. Outside this range of molecular weight, the compatibilizing property of LNR is no longer effective due to inhomogeneous blends. Improvements in the mechanical properties were in consonance with the increase in gel contents of the blends. The additions of LNR in the blends were able to reduce the interfacial tension; therefore, they improved the interaction between the phases of the blends. The studies also confirmed that, within the concentration range investigated, the LNR solvent did not influence the blend properties. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1776–1782, 2000

Key words: natural rubber; liquid natural rubber; polyethylene; compatibility and molecular weight

INTRODUCTION

Polymer blending is one of the fastest growing areas of polymer technology. Economically, it is an attractive technique of polymer modifications. It does not involve sophisticated machinery and new polymer synthesis. It also offers the prospect of recycling the blend. It has been estimated that the thermoplastic elastomer sector alone registers 10–15% annual growth.[1]

There are three basic procedures for preparing thermoplastic elastomer, i.e., simple melt blending, simple mixing of slightly vulcanized rubber with plastics, and blends by dynamic vulcanization.[2] Most of the polymer blends are immiscible with the formation of two distinct phases. Normally the physical properties of the blends are improved either by adding compatibilizers such as liquid natural rubber (LNR),[3–5] block copolymer,[6] or certain functional polymers to act as a compatibilizer via the technique called functionalization.[7]

LNR has a potential to be a good compatibilizer in thermoplastic natural rubber (TPNR) blends.[4,8] Ibrahim and Sahrim[9] claim that the active groups such as —OH, —OOH, and C=O available along the isoprene chain of LNR are able to improve the compatibility of the NR (natural rubber)/polyolefin blends. Gelling and Mente[10] report the role played by the size of molecular chain of LNR in influencing the physical properties of its vulcanisate. At low molecular weights of ca. 6000, LNR acts as a bulk viscosity modifier, while at higher molecular weights of ca. 30,000, LNR covulcanisates into the rubber network reducing or negating vulcanisate property loss. Their efficiency in

this respect depends on the molecular weight of LNR.

Ibrahim et al.[3,9,11] observed that, with the addition of LNR into the NR/polyolefin blends, the torque values increase, depending on the amount of LNR added. They indicate that LNR contents of 15–25% impart maximum torque values. They also report that the NR/LLDPE (linear low density polyethylene) blends with LNR as a compatibilizer,[3] show the highest torque values in the NR/polyolefin systems studied.[4] The highest torque indicates the strongest interaction between the phases of the blend. The increases in torque values are not observed immediately upon the addition, but sometime later. They argue that it indicates LNR played its role as dynamic vulcanization agent in the blends. Other properties, such as crosslink density and Shore hardness, also show the same trend. In both cases it is believed that LNR acts as a curing agent. The curing effect is more effective when the content of LNR is in the region of 15–25%, higher than that in which the plasticiser effect will take place.

Dynamic mechanical analysis (DMA) studies of NR/HDPE (high density polyethylene) blends, also show the improvement in compatibility of the blends when LNR is added. It is found that the T_g decreases from −56°C, before adding LNR, to −59°C when 20% LNR is added to the blends.[4] The changes in T_g values show that there is an interaction between the phases in the blends.[12,13]

Because LNR was found to be most effective as a compatibilizer in NR/LLDPE blends,[3,4] here we chose the NR/LLDPE system to study the effects of various molecular weights of LNR on physical properties of the blends. We also investigated the effects of optimum molecular weight of LNR, i.e., LNR-6 (UV-irradiated for 6 h) with respect to the mixing and physical properties of the blends. Comparison studies using LNR of less effective molecular weight, i.e., LNR-16 (UV-irradiated for 16 h) as a compatibilizer have also been carried out.

EXPERIMENTAL

Materials

Natural rubber (NR) of SMR-L grade was supplied by Guthrie Corp. (M) Bhd., Malaysia. Linear low-density polyethylene (LLDPE, Dowlex type 2045) was purchased from Dow Europe S.A., Switzerland. Both materials were used as re-

ceived. LNR of various molecular weights was generated in our laboratory by photochemical oxidation of NR as previously reported.[14]

Blend Preparation

NR/LLDPE blends of the 60/40 ratio were prepared by mixing in a laboratory cam mixer (Brabender PL 2000). The capacity of the mixer was 60 g, including 15% LNR content (by dry rubber content). The mixing parameters followed were as reported earlier,[3,15] i.e., blending temperature 135°C; rotor speed 55 rpm; and blending time 15 min. NR was first discharged into the mixer 1 min before LNR. NR and LNR were allowed to mix for about 3 min before LLDPE was added. The whole process was allowed to proceed for 15 min. Subsequently, the blend was removed and compressed by a hot press for 2 min at 135°C and 8 metric ton pressure using a 1-mm spacer. The apparent shear viscosities, η_a of the blends were taken based on the torque values after 15 min of mixing.

Effects of Molecular Weights of LNR

Normally the molecular weight of polymeric material is measured by gel permeation chromatography (GPC). The technique based on the separation of molecular species according to size is believed to occur as a result of differences in the extent to which different species permeate the gel particles.[16] Thus, in this experiment, we used molecular weight distribution data from GPC as an indication of the polymeric molecular sizes in a non-ideal solution.

LNR of various molecular weights prepared as previously described was used.[14] Table I indicates

Table I   The Relationship between UV Irradiation Time and Molecular Weight of Natural Rubber Irradiated

Irradiation Time (h)	Molecular Weight		
	M_w (×10^4)	M_n (×10^4)	M_w/M_n
0	107.00	28.10	3.81
3	71.30	24.00	2.97
6	47.95	16.60	2.89
9	34.54	13.43	2.57
12	15.89	7.09	2.24
16	9.25	4.42	2.09
60	7.59	4.03	1.88

the relationship between irradiation time and molecular weights of LNR used in the experiments.

Effects of LNR Concentration

Because LNR used in the experiments was prepared in solvent, i.e., toluene, it was necessary to investigate the effects of the solvent concentration on the blends. Two kinds of LNR were investigated for this purpose, i.e., NR, which was UV irradiated for 6 h and 16 h (later known as LNR-6 and LNR-16, respectively). LNR concentrations in toluene were varied from 10–40%, with their dry rubber content fixed at 10%.

Rheological Studies

The studies were done on the plastogram of torque against time for each of the blends prepared. The apparent shear viscosities of the blends were taken based on the torque value after 15 min of mixing.

Physical Testings

The physical tests for the tensile and elongation properties were done on the dumbbell-shaped samples using an Instron Universal Testing machine model 4301 with a load cell of 1 kN at room temperature. The sample dimensions were to BS 6746 standard. The tests were carried out on seven sample pieces for each blend, and the readings were calculated from the best five samples.

Gel Content and Swelling Ratio

Gel contents were measured by the Soxhlet extraction technique using toluene as solvent. After extracting for 48 h, the sample was dried in air before keeping it in a vacuum oven at 60°C until constant weight. The test was duplicated twice for every sample, and the average value was taken. The gel content was defined as follows:

Gel content (%)

$$= \frac{\text{weight after extraction}}{\text{weight before extraction}} \times 100\%$$

For the swelling test, ASTM D 3616 was followed. Weighed samples were immersed in toluene for 24 h at room temperature. The surfaces of the swelled samples were then immediately blotted with filter paper and weighed. The swelling ratio was calculated based on the following equation:

$$\text{Swelling ratio (\%)} = \frac{W_S - W_I}{W_I} \times 100\%$$

where W_S and W_I were the weights of swelled and initial samples, respectively.

RESULTS AND DISCUSSION

Effects of Molecular Weights of LNR

Figures 1 and 2 show the effects of various molecular weights of LNR on the tensile and elongation properties of the NR/LLDPE 60/40 blends. The LNR contents used in the blends were 15%. Both kinds of molecular weight, i.e., M_w and M_n give the same effects on the properties of the blends. The lowest molecular weight of LNR used was M_w of 7.59×10^4 and M_n of 4.03×10^4, which was prepared by UV irradiation for 60 h. The LNR imparts the lowest tensile strength and elongation at break, i.e., 5.75 MPa and 500%, respectively. At that molecular weight, the LNR added to the blend does not act as a compatibilizer but acts as a plasticizer.[10] The plasticiser molecules are localized between polymeric chains, thus reducing their mutual interactions, and instead, promoting their mobility.[17]

Upon increasing the molecular weights, LNRs begin to act as compatibilizers for the blends until they reach the optimum weight at M_w of 4.8×10^5 and M_n of 1.66×10^5. The LNR with this molecular weight was generated by UV irradiation for
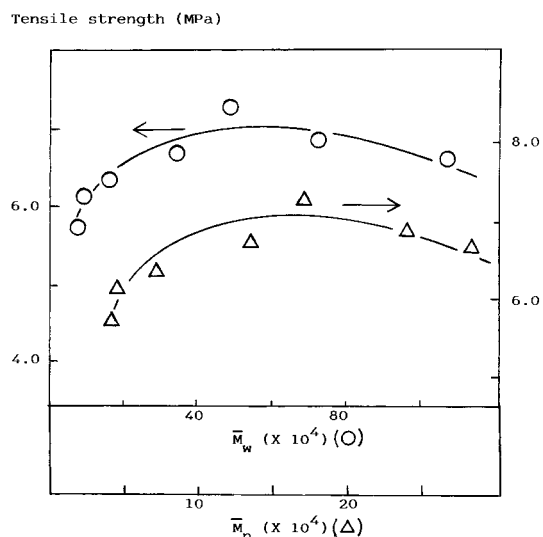

Figure 1 The effects of LNR molecular weight on the tensile strength.
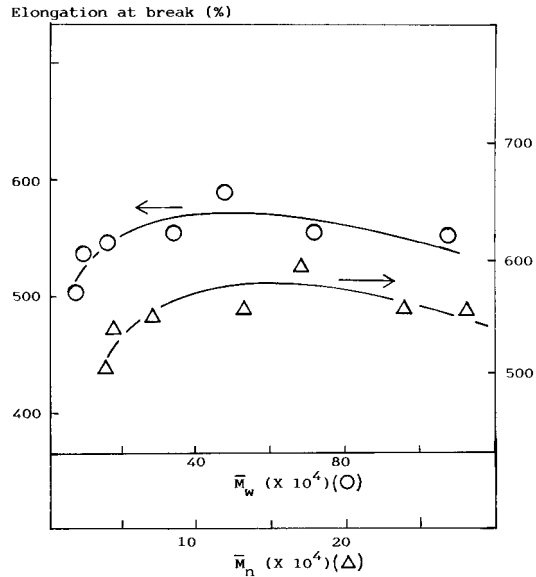
Figure 2 The effects of LNR molecular weight on the elongation at break.

6 h. The blend shows the highest tensile and elongation properties, i.e., 7.3 MPa and 592%, respectively. Upon further increasing the molecular weight, it is observed that the compatibilizing property of LNR is no longer effective. As a result, the mechanical properties of the blends decrease, as shown in Figures 1 and 2. This is due to the interactions that, being induced by LNR, are dependent on its molecular sizes, as represented by their molecular weights. Smaller molecular size LNRs have a larger interphasing area, resulting in better physical adhesion and wetting properties for the blends. Furthermore, the molecules are more mobile; therefore, they interact more easily with matrix molecules.

Pak and Jo[18] found that the compatibilizing ability of a copolymer, maleic anhydride-modified polystyrene (MPS) in the blends of polyamide 6 and polystyrene, was also dependent on its molecular weight. The high molecular weight MPSs were more effective in reducing and stabilizing the domain size of the dispersed phase than the relatively low molecular weight MPSs. According to Zhou et al.,[19] polymeric compatibilizers concentrate at the interface of the blended phases. They studied the compatibilizing ability of hydrogenated copolymers of poly(hydrogenated butadiene-methyl methacrylate) of various molecular weights for PVC/LLDPE blends. In this case, the compatibilizers need a certain size, i.e., length of polymeric chain, to firmly anchor themselves into

the phase they are penetrating. In other words, there are optimum molecular weights for the polymers to act as compatibilizers efficiently.[20,21]

Zainal and Ratnam[22] used the conversion method that was proposed by Goodrich and Porter[23] to study the blending behavior between polyvinyl chloride (PVC) and epoxidised natural rubber (ENR). Using the method, torques obtained from a Brabender mixer can be converted to standard rheological properties with the following equation:

$$\eta_a = \sigma_a/\gamma_a = K\tau_a/K'S = Q\tau_a/S \qquad (1)$$

where η_a is the apparent shear viscosity, σ_a is the apparent shear stress, γ_a is the apparent shear strain rate, τ_a is the apparent mixing torque measured, Q is the instrumental constant, and S is the angular rotor speed. S can be converted to rotor speed, R (revolutions per min, rpm) used in this work by the equation below:

$$S = 2\pi/60 \times R \qquad (2)$$

Equation (1) indicates that τ_a/S is directly proportional to the apparent shear viscosity, η_a, therefore τ_a/S can be used to represent η_a.[22,24]

Figure 3 shows the effects of the molecular weights of LNRs on the apparent shear viscosity, which is represented by τ_a/S as indicated in eq. (1). Both curves in the figure show the maximum point for the apparent shear viscosity at an M_w of
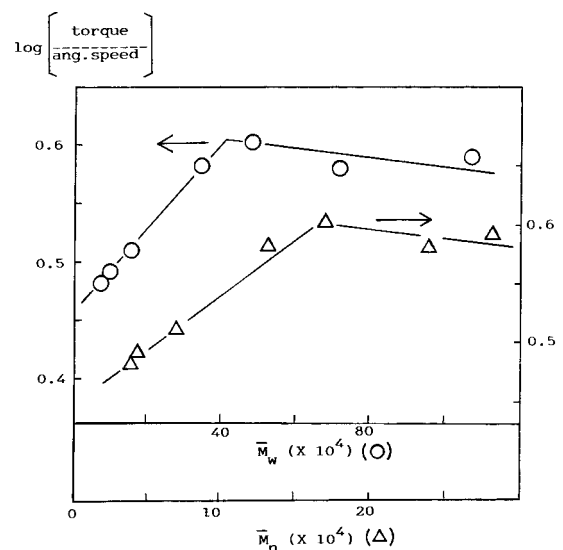

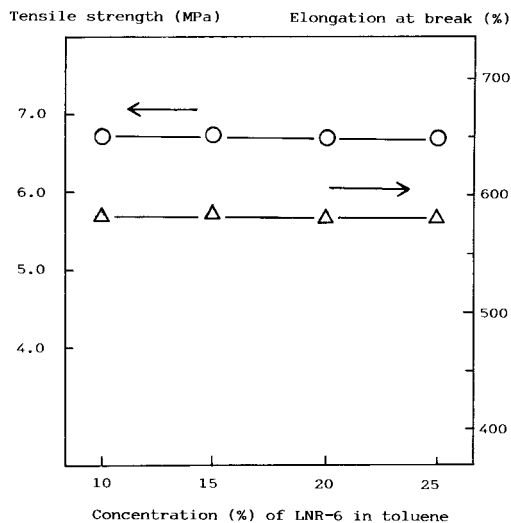**Figure 3** The effects of LNR molecular weight on the apparent shear viscosity.

Figure 4 The effects of the concentrations of LNR-6 in toluene on the mechanical properties.

4.05×10^5 and M_n of 1.65×10^5, which are about the same values as indicated in Figures 1 and 2. It is obvious that mixing improves as the molecular weights increase up to the maximum point. Beyond this point, the compatibilizing effects of LNR are no longer effective, resulting in inhomogeneous blends. Therefore, the values of τ_a/S drop.[22]

Effects of LNR Concentration

Figures 4 and 5 denote the effects of toluene as a solvent for LNR on the tensile and elongation properties of the blends. The figures show that the properties are not affected when the concentrations are varied from 10 to 40%, confirming that the solvent does not influence the properties of the blends for the range studied.

Figure 4 shows that when the concentrations of LNR-6 in toluene are increased from 10 to 25%, the tensile and elongation properties of the blends remain constant at 6.7 MPa and 580%, respectively. Meanwhile, in Figure 5, the tensile and elongation properties of the blends stay at 6.1 MPa and 533%, respectively, even though the concentrations of LNR-16 in toluene are varied from 10 to 40%. For the LNR-16, because its molecular weight is smaller, the concentration range studied is wider.

Mixing Studies

Figure 6 represents the results of mixing NR/LLDPE at a 60/40 blend ratio using LNR-6 and LNR-16 as compatibilizers. Variations in torque value for various LNR contents of LNR-6 and LNR-16 in the blends are indicated by Figures 6(a) and 6(b), respectively. Figure 6(a) shows that when NR is discharged into the mixing chamber, torque value increases instantly up to the maximum value of 27.8 Nm. This is due to shear resistance by NR before its temperature reaches the mixing temperature. When it starts to melt, its viscosity drops resulting in a decrease in torque. For the blend without LNR, LLDPE was added after 1 min of mixing. Instantly after the addition of LLDPE, the torque increases up to maximum value of 40 Nm. Subsequently, the plastic material starts to melt, reducing the torque value to an equilibrium.

The additions of LNR into the blends cause slight changes to plastogram profiles, as shown by Figure 6. The plastograms indicate the reduction of maximum torque values as the LNR contents increase. The increasing amounts of LNR added compensate for the reducing amounts of NR used to maintain the blend ratio of 60/40. The reduced amounts of NR cause the shear viscosity to drop, and in turn, reduce the torque value. The contents of the solvent, i.e., toluene, also increase with LNR; therefore, the time taken for the torque to increase again is longer.

In the case of LNR-6, torque values became stable in ca. 9 to 11 min after LLDPE was added. Thereafter, little increase in torque value was observed. According to Ibrahim et al.,[3] the increase is attributed to the effect of compatibilization by LNR-6. However, LNR-16 does not show the same
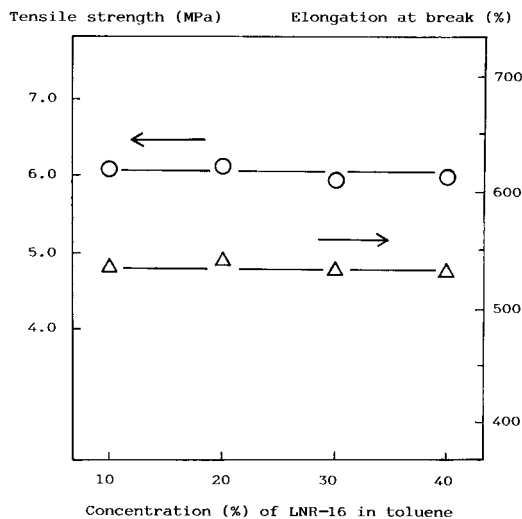

Figure 5 The effects of the concentrations of LNR-16 in toluene on the mechanical properties.
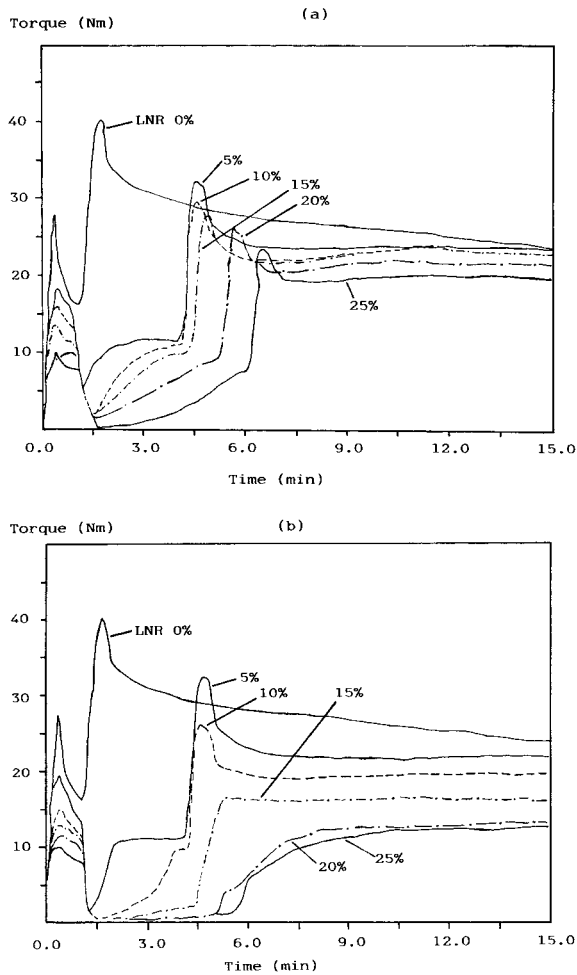
Figure 6 Variations in torque values as a result of different compositions of LNRs in the blends; (a) LNR-6 and (b) LNR-16.

Figure 7 The effects of LNRs on the mixing behavior of the blends as monitored by the conversion method.

effect, as indicated by Figure 6(b). Instead, it shows the effect of a plasticiser agent.[25,26]

To investigate further the blending behavior of the blends, the conversion method[23,24] was again applied. Figure 7 shows little increase in torque values when LNR-6 was added. The mixing between NR and LLDPE improves as the amount of LNR is increased until it reaches the optimum point at 12.75% of LNR content. Beyond this point the mixing was said to be unfused, causing the torque to drop.[22] However, LNR-16 does not show the same effects. Instead, it behaves more like a plasticizer agent, as pointed out earlier in Figure 6(b). Its fusing point could hardly be observed for the entire range of LNR-16 compositions.

Gel Formation

Gel is formed when a strong interaction between components of the blend exists. It is an indicator
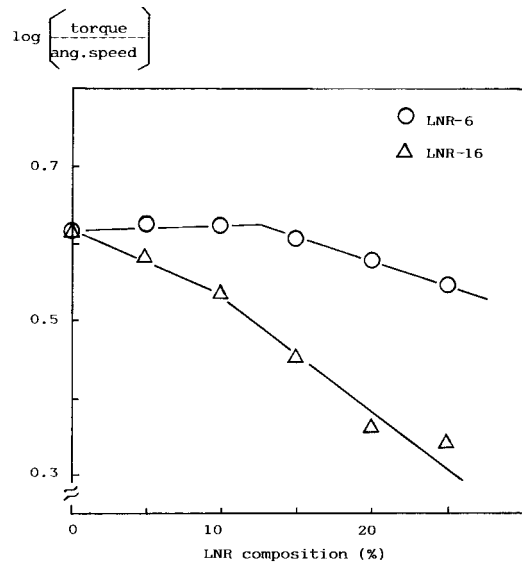
of crosslinks formed in the blend. Swelling ratio can be used as the indicator for an estimate of crosslinks in the blend.[27,28] In this case, it may not necessarily result in a thermoset network but merely in copious amounts of grafting.[29]

Figure 8 indicates the effects of LNR content on the crosslink formation of the blend. The higher gel contents reflect that LNR-6 is a more effective compatibilizer, as shown by Figure 8. In other words, LNR-6 is more effective in inducing the interfacial
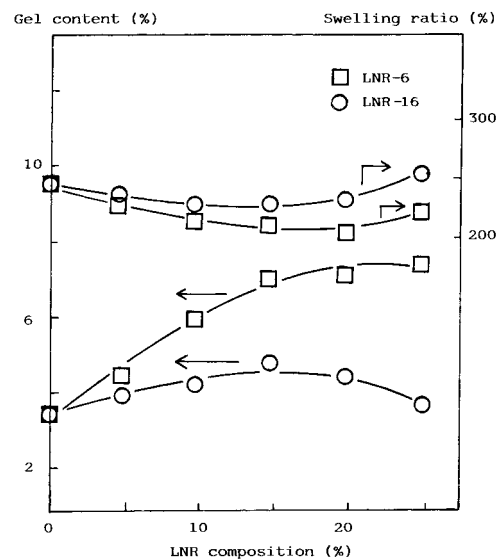

Figure 8 The effects of LNR compositions on the gel contents and swelling ratios of the blends.

interaction between the components of the blend. As also shown in Figure 8, the interaction already exists even without LNR being added, as the gel content was 3.5%. This is due to both NR and LL-DPE having very similar structures and solubility parameters, i.e., 16.5 and 16.3 MPa$^{1/2}$, respectively.[30] Therefore, the chances for both components to form interactions are better.[4] The highest gel content, i.e., 7.5%, is registered by the blend containing between 20–25% LNR-6. Higher contents of LNR-6 are ineffective in inducing more interactions between the components. However, LNR-16 does not show the same effects: the highest gel content achieved is only 4.8%.

The blends that have lower gel contents will allow more solvent to be absorbed, resulting from the uncrosslinked rubber part swelling more, as depicted in Figure 8. On the contrary, the blends that show higher gel contents will allow smaller amounts of solvent to be absorbed, thus lowering swelling ratios.[15,31] In other words, the swelling ratio curves are the inverse reflections of the gel curves.

CONCLUSIONS

It is concluded that the effectiveness of LNR as a compatibilizer in NR/LLDPE blends is closely related to its molecular size, as represented by its molecular weight. The studies show that LNR-6 with an M_w of 4.8×10^5 and M_n of 1.66×10^5 imparts the highest compatibilizing property to the NR/LLDPE 60/40 blends. The additions of LNR-6 reduce the interfacial tension, therefore improving the interactions between the phases in the blends. LNR, with the smallest molecular weight studied, i.e., LNR-60, shows some plasticizer effect to the blends. The results also confirm that, within the concentration range studied, the LNR solvent content does not influence the blend properties.

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