

Blending of Natural Rubber with Linear Low-Density Polyethylene

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SYNOPSIS

Blends of natural rubber (NR) with linear low-density polyethylene (LLDPE) were prepared by melt blending of the materials in a plasticorder mixer at various temperatures around the melting point of LLDPE and at various mixing rates. The optimum processing conditions were a temperature of about 135°C and a mixing rate of 55 rpm. The tensile properties, stress and strain, of the blend had improved significantly with the addition of liquid natural rubber (LNR) into the blend. For blends with compositions around 50% NR, about 10–15% LNR produced the most significant improvement in the physical properties. Well-dispersed plastic particles in a rubber matrix were strongly indicated in these samples. Scanning electron micrographs (SEM) of the samples also indicated an increase in the homogeneity of the mixes with the addition of LNR. A single glass transition temperature of about -55°C for the blend was observed via dynamic mechanical analysis (DMA). Interfacial linking between the NR and LLDPE phases was attributed to the presence of active groups on the polyisoprene chain of LNR, which induced the interphase reaction between the NR and LLDPE phases. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Thermoplastic properties can be incorporated into the natural rubber (NR) via blending of NR with any compatible thermoplastic such as polypropylene (PP) or polyethylene (PE). Such blends are generally termed thermoplastic natural rubber (TPNR) and the material, by the physical properties exhibited, is categorized as an elastomer lying between rubber and plastic. TPNR, which can be considered either as a rubber modified plastic or a plasticized rubber, has the advantage over NR of being processable utilizing any plastic processing machinery and at a comparatively lower temperature. NR, being a long chain natural polymer, is generally not very compatible with most synthetic polymers. However, PP and PE are the two known thermoplastics which are quite compatible, which can be rationalized as due to the similarity in the microstructures of the polymers. Blends of NR-PP¹⁻⁶ and NR-HDPE

(high-density polyethylene)^{7,8} were found to have high tensile and other physical properties. Addition of a compatibilizer into the blends further improved the physical properties exhibited.

The compatibilizer helps to induce interaction between the rubber and plastic interphase and thereby increases the homogeneity of the blend. A small molecule or a short polymer with active terminals was reported by Xanthos^{9,10} to function as a bonding agent between the distributed particles and the matrix. Investigation into the effect of liquid natural rubber (LNR) on the properties of NR-PP and NR-PE blends had been reported.^{5,8} LNR is a short-chain polymer obtained from the oxidative degradation of NR. The polyisoprene chain in LNR and NR is similar except the chain in LNR is much shorter. The LNR with some active terminals⁵ like —OH is expected to react with the plastic particles and thereby bonded the plastic particles to the NR matrix. The physical properties of the blends seem to increase significantly with the addition of LNR. These properties improved with further addition of LNR and the increment had been observed to be proportional to the LNR added. However the opti-

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mum content of LNR in the blend was found to be about 10% for the NR-PP blend⁵ whereas in the NR-HDPE blend it was about 25%.⁸

In this paper, investigation into the effect of LNR on the physical properties of NR-LLDPE blends will be discussed.

METHOD

Materials

NR of grade SMR-L was obtained from the Rubber Research Institute of Malaysia (RRIM), Commercial grade linear low-density polyethylene (LLDPE), obtained from Dow Chemicals, with density 0.916 g cm^{-3} , melt flow index (MFI) = 40 g/10 min, and $T_m = 135^\circ\text{C}$, was used without any treatment. The LNR was generated by photochemical oxidation of NR in our laboratory.

Blend Preparation

The blends were prepared by melt-blending of the components in a laboratory cam mixer (Brabender) at various temperatures and rates of mixing in accordance with the requirements of the study. Generally the LNR was added into the mixer 1 min after introducing NR. NR and LNR were allowed to mix for about 2 min before LLDPE was charged into the mixer. Once homogeneous mixing was assumed after about 15 min of mixing, the blend was removed and subsequently compressed at about 140°C and 7 kN pressure for about 2 min into a thin sheet of about 1 mm thickness from which test specimens were cut. Two compositions of NR-LLDPE blends, 50/50 and 60/40, were prepared with various compositions of LNR.

Physical Measurement

Tensile

The tensile tests were done on the dumbbell samples after 24 h of maturation time by using a Universal Testing machine, Lloyd R 2000, at 27°C in accordance with the test procedure of ASTM D638. The gauge was kept at 20 mm with a crosshead speed of 50 mm/min. From the stress-strain curves, the average stress and strain at break were calculated from at least 5 samples.

Hardness

The hardness of the samples was determined by using a hardness tester, Durometer ASTM 2240, of

shore type A (Zwick Model) on a 3-mm-thick sample. All measurements were performed at room temperature (27°C).

SEM

The morphology of the blends was investigated by scanning electron microscopy (SEM) on toluene-extracted samples with magnification of 2000 \times .

Dynamic Mechanical Analysis

The measurement were carried out using the new DMA 242, Netzch in a single cantilever deformation mode from -100 to 150°C . The oscillating frequency was 1 Hz and the scanning rate amounted to 3K/min.

RESULTS AND DISCUSSION

Generally the NR-LLDPE blends produced exhibit good thermoplastic properties, except the surface is less shiny than ordinary thermoplastics. Addition of LNR into the blend causes an enhancement of the tensile properties and the morphology of the blends. Processing of the blend gives rise to a typical fusion behavior, torque-time curve as shown in Figure 1. Peak I corresponds to the shearing torque of NR before melting. Addition of LLDPE into the melted NR at the third minute causes the torque to rise, peak II, due to melt-fusion of LLDPE. The plasticizing effect of LNR is shown by the drop in torque between peaks I and II. In samples containing LNR the torque drops to almost zero as compared to samples without LNR where the torque remains at about 10 Nm. A third rise in torque, very broad in nature, appears for samples containing LNR and the increase is higher with higher percentage of LNR. In the absence of LNR, the third peak does not appear, which strongly indicates the occurrence of a secondary curing reaction involving LNR after the first interaction between the NR and LLDPE. The increase in torque due to the second stage curing is about twice the value observed in the NR-PP or NR-HDPE systems. Apparently the interaction between the various phases is thus about twice as extensive in the NR-LLDPE blend. With more LNR added the interaction between the various phases, chemical and physical, is expected to be more extensive and result in a higher degree of material curing. The viscosity of the material will increase with respect to the level of curing and hence produces a greater torque with more LNR. The curing process

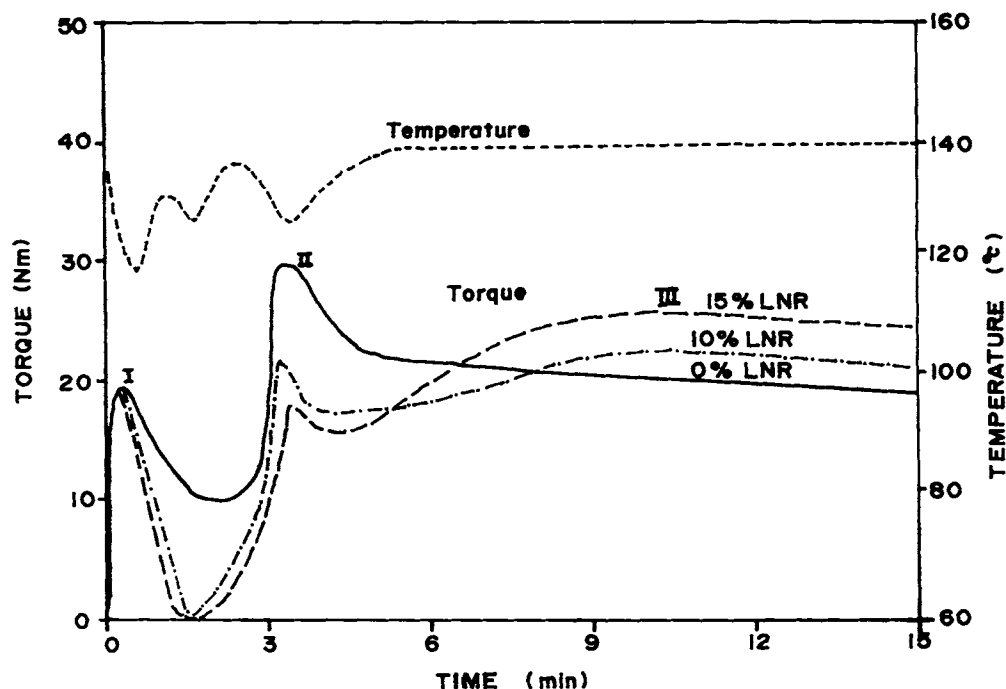


Figure 1 The variation of torque with mixing time for a 60 : 40 NR-LLDPE blends with varying composition of LNR. The temperature of processing is set at 140°C.

is dynamic in nature as shown by the slow increase in torque with processing time.

Table I shows a typical stress and strain at break of NR-LLDPE blends of composition 50 : 50 and 60 : 40 with varying concentrations of LNR. The plots of stress and strain at break against LNR concentrations are depicted in Figure 2. The stress increases with LNR concentration and reaches a maximum value of about 12 MPa at the LNR concentration around 20% for both the 50 : 50 and 60 : 40 samples. On the other hand the maximum strains of 1000% and 1300% occur at the LNR con-

centrations of 10% and 13% for the 50 : 50 and 60 : 40 blends, respectively. Thus for the best mix of the NR-LLDPE thermoplastic the LNR concentrations are about 13% and 17% for the 50 : 50 and 60 : 40 blends, respectively.

The hardness of the NR-LLDPE blends as a function of LNR concentrations is shown in Figure 3. For the 50 : 50 blend, the addition of LNR into the blend causes an increase of hardness from 87 to 90 in shore A and the increment is obtained after about 10% incorporation of LNR. The effect of LNR is more pronounced in the 60 : 40 sample where the

Table I Physical Properties of NR-LLDPE Blends with the Composition Ratios of 50 : 50 and 60 : 40

Blend Ratio	Composition of LNR (%)	Stress at Break (MPa)	Strain at Break (%)	Hardness (Shore A)
50 : 50	0	7.3	900	87
	5	9.0	1000	89
	10	10.6	1020	90
	15	11.4	970	90
	20	11.5	910	90
60 : 40	0	5.0	900	61
	5	6.0	1160	63
	10	7.6	1250	65
	15	9.8	1260	67
	20	10.6	1100	70

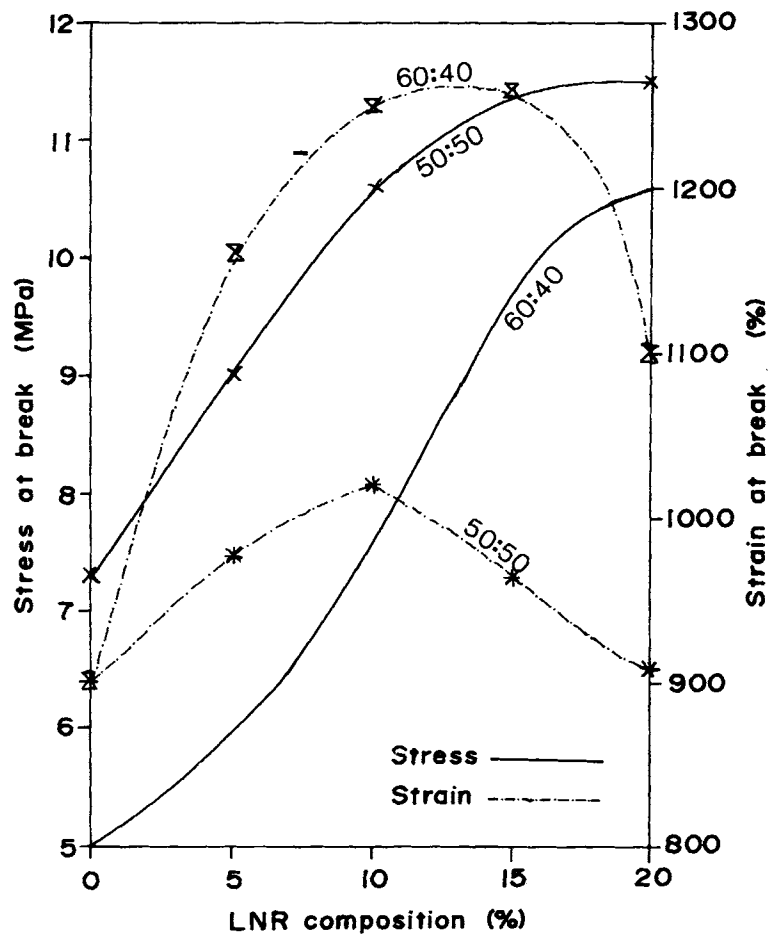


Figure 2 Tensile properties of various composition of LNR for NR-LLDPE blends.

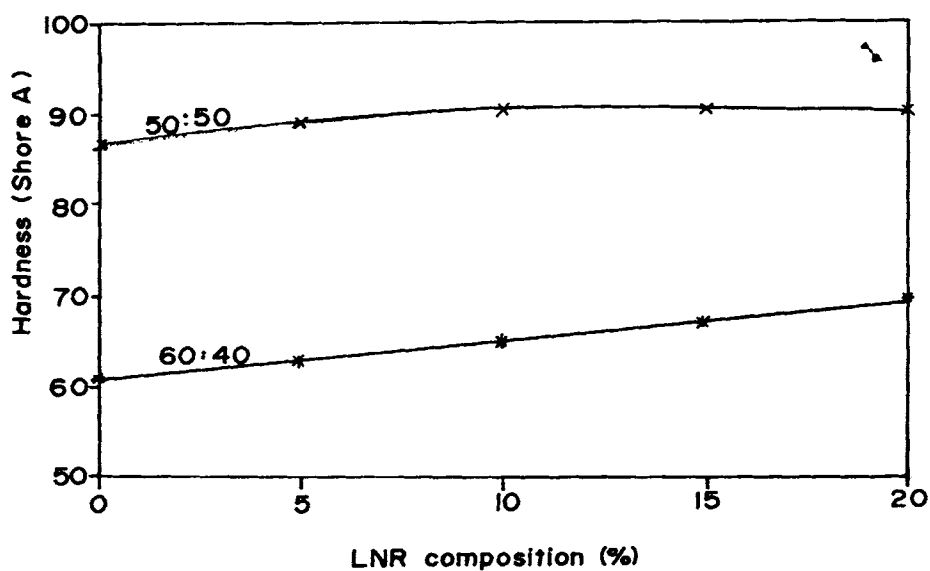


Figure 3 Hardness of the NR-LLDPE with various composition of LNR.

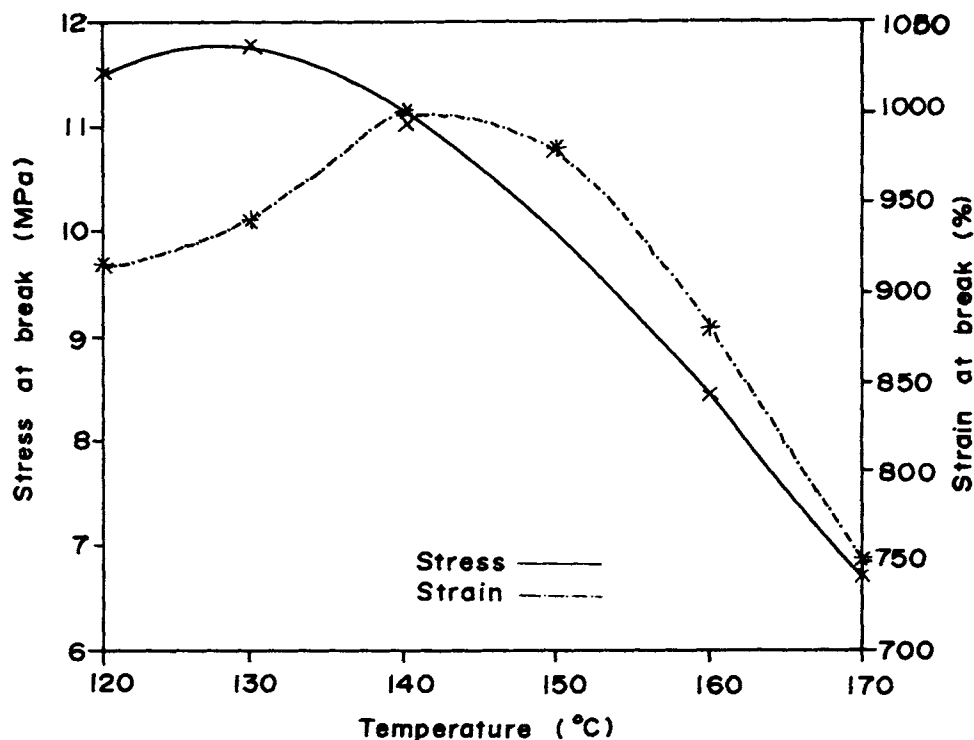


Figure 4 Tensile properties of the NR-LLDPE (50 : 50) blend at various processing temperature with mixing rate at 45 rpm.

hardness level increase from 62 to about 70 in shore A. Apparently the LNR interacts more effectively with the NR phase in the blend and thus an increase in the NR composition will result in a more significant effect of LNR. As the NR is softer than the plastic, any composition richer in NR will produce a softer elastomeric material.

The stress and strain at break of NR-LLDPE blends are comparable to NR-PP blends⁵ but slightly higher than in NR-HDPE blends.⁸ However a strain of 1300% for 60 : 40 NR-LLDPE blend seems to be the highest recorded value for any TPNR system. These observations suggest that the NR-LNR-LLDPE combination is the most compatible in comparison to other NR-thermoplastic mixes like NR-LNR-PP and NR-LNR-HDPE. Further comparison reveals that PE is more compatible to NR than PP and among the PEs, LLDPE is the most compatible.

The improved interfacial interaction most probably arises from the high degree of molecular interaction between the component polymers in the blend. From the molecular structural aspect, the basic polymeric chain of the two polymers is similar except the presence of $-\text{CH}_3$ as a side group on the PP chain. The presence of this methyl group and other side chains or copolymers in commercial

PP is probably the cause of a slight incompatibility between the NR and PP. In the PE groups the difference between the individual polymer is from the chain length and branchings. Commercially available HDPE carries groups such as $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{C}_4\text{H}_9$ etc., as side chains or branches which can hinder interaction between NR and HDPE. HDPE also has a longer chain length than LLDPE and thus reorganization of the polymer during blending and subsequent interaction with the NR chain become less effective.

The homogeneity of the blend which influences the physical properties of TPNR is determined by the way in which the polymers are mixed. The rate of mixing and the temperature at which the polymers are introduced into the blender are the two most significant parameters in blending. Figure 4 shows the variation of tensile properties, stress and strain at break, with the processing temperatures. The stress seems to decrease with temperatures and reaches a maximum around 130°C, while the strain climbs to a maximum at about 145°C and decreases thereafter. The optimum physical properties of the blend are obtained at a processing temperature of about 140°C with a mixing rate of 45 rpm.

Figure 5 shows the influence of rate of mixing on the stress and strain of TPNR. As depicted on the

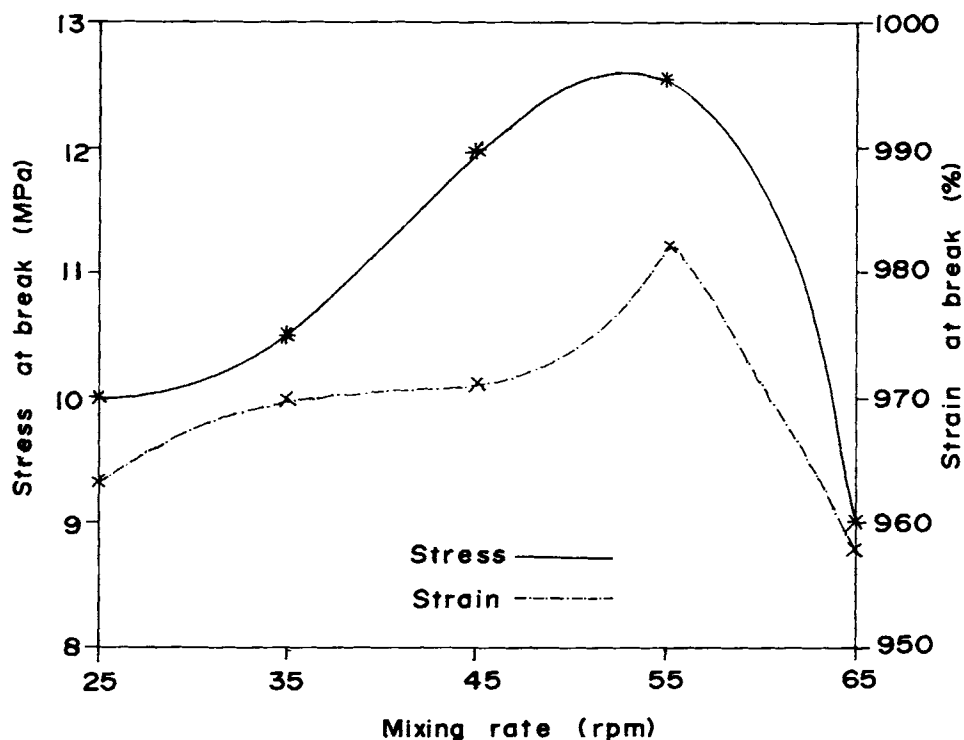


Figure 5 The effect of mixing rate on tensile properties of NR-LLDPE (50 : 50) blend at processing temperature of 140°C.

plots, the stress and strain increase with the rate of mixing and maximize at the 55 rpm mixing rate. A drop in the physical properties of TPNR is observed on further increase in the rate of mixing.

In any TPNR blend, generally the stress and strain are determined by the nature of the hard plastic and soft rubber components, respectively. The interaction between the two components leading to the homogeneity of the blend^{11,12} is also a factor that influences the physical properties of TPNR. A very homogeneous mix will yield a TPNR with excellent physical properties. The values of stress and strain recorded for samples containing LNR strongly indicate the existence of an interaction between the NR and LLDPE phases in the presence of LNR. The role of LNR in the interaction process is not very clear but it is believed to be associated with the active functional groups present on the LNR.⁵ As discussed in our previous report,¹³ the active groups present on the LNR are —OH, —OOH, and —OR. These groups are likely to induce physical and chemical interactions with the LLDPE and NR polymer chains. With LNR and NR having a similar microstructure, the diffusion of LNR into the NR phase is more probable. Thus the LNR in the blend functions both as a crosslinking agent within the NR phase and also as an in-

terphasing binder between the NR and LLDPE phases. Therefore the blend becomes more homogeneous in the presence of LNR.^{14,15}

The increase in the tensile properties and hardness with the addition of LNR can be rationalized as due to the increase in the bonding formation in the blend (Table II). Further increment in the LNR composition after the optimum value produces limited effect on the polymer interaction, but instead results in the overall increase in the NR composition leading to the formation of a soft blend which exhibits lower tensile properties. In the NR-LNR-LLDPE system the optimum composition of LNR is about 10 and 15% for the 50 : 50 and 60 : 40 NR-LLDPE blends, respectively. The blend which contains more NR is obviously able to absorb more LNR before a saturation level is reached.

The mixing temperature is found to be optimized at about the melting point of LLDPE, i.e., 135°C. At this temperature the LLDPE is in a viscous state of high viscosity and the stirring action will thus produce the maximum mixing effect¹⁶ with the other components. However, at higher temperatures, the liquid LLDPE will have a lower viscosity and thus stirring will result in lower mixing abilities of the components. Too high a processing temperature also causes the material, especially the NR, to degrade

Table II The Mechanical Properties of Natural Rubber–Polyolefin Blends

Composition Blends	Tensile Properties		Hardness (Shore)	
	Max. Stress (MPa)	Max. Strain (%)	Shore	
			Shore A	Shore D
30 : 70 (5% LNR)				
NR-LLDPE	16.6	1270	96	42
NR-HDPE	9.4	240	97	50
NR-PP	12.0	230	98	53
50 : 50 (10% LNR)				
NR-LLDPE	9.6	1070	89	34
NR-HDPE	8.8	670	93	38
NR-PP	9.0	600	94	39
70 : 30 (15% LNR)				
NR-LLDPE	6.8	1220	63	19
NR-HDPE	6.2	1080	78	23
NR-PP	7.0	950	85	30

from oxidation. At a temperature lower than 135°C the LLDPE is either not melted or partially melted and thus mixing with NR will not be conducive.

Varying the rate of mixing (stirring) also produces a similar effect as in changing the temperature. The homogeneity of the blend will be optimum at a certain mixing rate for a particular temperature. The level of mixing increases directly with the rate of stirring before the optimum rate is reached. At a temperature much higher than the melting point of LLDPE, agglomeration of like particles is highly probable during high speed mixing. As a result phase separation will set in giving rise to an inferior TPNR. A well-mixed blend is thus possible at high temperatures with low rate of mixing or vice versa.

It is thus obvious to observe at the processing temperatures of 140° and 155°C, the optimum mixing rates are 55 and 30 rpm, respectively.

The scanning electron micrograph of toluene-extracted 50 : 50 NR-LLDPE blends is shown in Figure 6. The honeycomb structure of the micrograph consists of white and dark spots. The dark spots correspond to the empty holes left behind by the NR after dissolving in toluene. The white spots represent the insoluble LLDPE and crosslinked NR physically or chemically attached to the LLDPE particles. It is apparent that the dark spots decreases in size from Figure 6(a) (0% LNR) to 6(c) (20% LNR), and the uniformity of distribution is higher in Figure 6(c) (20% LNR) than in Figure 6(a) (0%

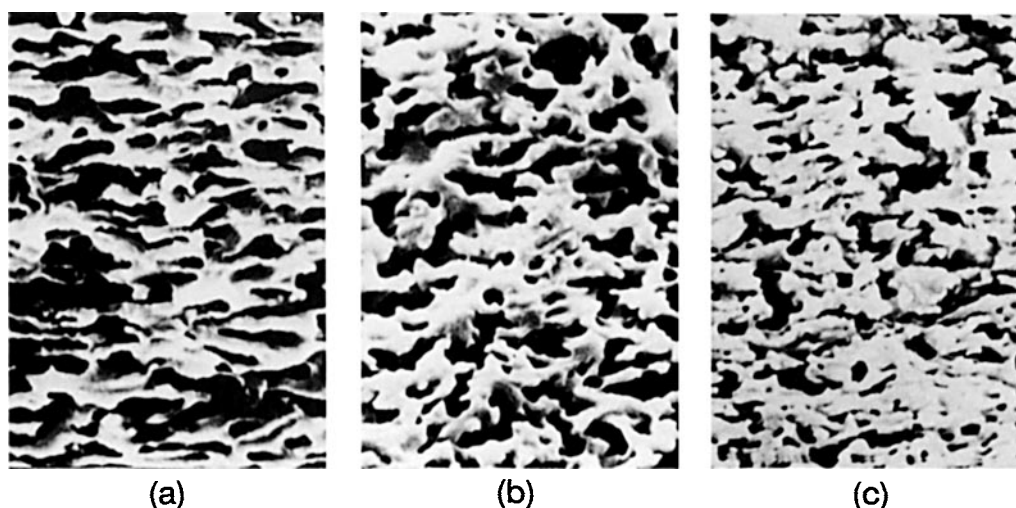


Figure 6 SEM micrographs of toluene extracted 50 : 50 NR-LLDPE blends (all magnifications are the same): (a) 0% LNR, (b) 10% LNR, and (c) 20% LNR.

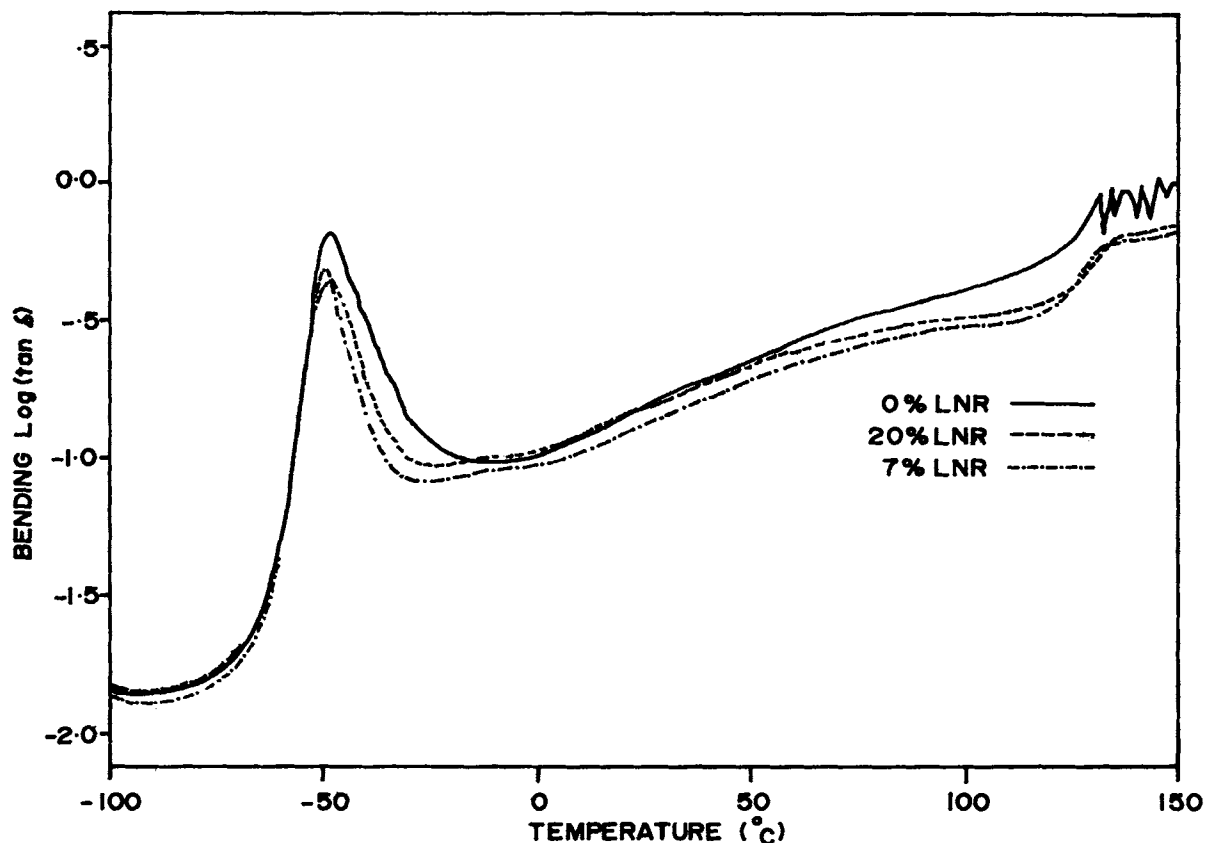


Figure 7 DMA traces of 60 : 40 NR-LLDPE blends.

LNR) and (b) (10% LNR). By examining the white or the dark spots, it clearly indicates the distribution of particles is improved with the addition of LNR. The DMA traces of the blend show a single T_g for the system as shown in Figure 7. In all the measurements the T_g s observed fall within the T_g s of NR and LLDPE and a slight variation is observed only with the various composition of LNR. As discussed before, the role of LNR as a compatibilizing agent between the NR and LLDPE is further established in this study.

CONCLUSION

The combination of NR-LNR-LLDPE forms a thermoplastic material with good physical properties. The tensile properties of stress exceeding 10 MPa and strain more than 1000% are very significant in this kind of blend. A softer TPNR is obtained with the blend richer in NR while a semirigid or hard TPNR material is produced by having more LLDPE in the blend. The role of LNR as a compatibilizer between the NR and LLDPE phases is proven in this study. The manner in which the LNR

interacts with the NR or LLDPE phase is not very clear but it strongly suggests the formation of chemical and physical bondings involving the active terminals present on the LNR polymer chain. The processing temperature and rate of mixing, rotor speed, are interdependent; a homogeneous mix is attainable with low rate of mixing at high temperatures and vice versa.

REFERENCES

1. D. S. Campbell, D. J. Elliott, and M. A. Wheelans, *NR Technol.*, **9**, 21 (1978).
2. D. J. Elliot, in *Development in Rubber Technology—3, Thermoplastic Elastomer*, A. J. Wheelan and K. S. Lee, Eds., Applied Sciences, London, 1982.
3. N. M. Mathew and A. J. Tinker, *J. Nat. Rubb. Res.*, **1**(4), 240 (1986).
4. D. J. Elliott and A. J. Tinker, in *Natural Rubber Science and Technology*, A. P. Roberts, Ed. Oxford University Press, London, 1988.
5. A. Ibrahim and A. Sahrim, *J. Material Forum*, **16**, 352 (1992).
6. D. J. Elliott, in *Thermoplastic Elastomers from Rubber-Plastic Blends*, S. K. De and A. K. Bhowmick, Eds.,

- Ellis Horwood Series in Polymer Science and Technology, New York, 1990.
7. N. R. Choudhury and A. K. Bhowmick, *J. Appl. Polym. Sci.*, **38**, 1091 (1989).
 8. A. Sahrim, A. Ibrahim, S. Che Som, S. Kohjiya, and J. R. Yoon, *J. Appl. Polym. Sci.*, **51**, 1357 (1994).
 9. M. Xanthos, *Polym. Eng. Sci.*, **28**, 1392 (1988).
 10. M. Xanthos and S. S. Dagli, *Polym. Eng. Sci.*, **31**, 929 (1991).
 11. D. R. Paul, in *Polymer Blends*, Vol. 2, D. R. Paul and S. Newman, Eds., Academic Press, New York, 1978.
 12. S. Wu, in *Polymer Blends*, Vol. 1, D. R. Paul and S. Newman, Eds., Academic Press, New York, 1978.
 13. A. Ibrahim and Z. Zuriati, *Sains Malaysiana*, **18**(2), 99 (1989).
 14. C. Qin, J. Yin, and B. Huang, *Polymer*, **31**, 663 (1990).
 15. N.r. Choudhury and A. K. Bhowmimck, *J. Mater. Sci.*, **23**, 2187 (1988).
 16. S. Al-Malaika and E. J. Amir, *J. Nat. Rubb. Res.*, **1**, 104 (1986).

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