

Compatibilization of natural rubber/polyethylene blends by polyethylene-*b*-polyisoprene diblock copolymers

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Mechanical tests, differential scanning calorimetry, wide-angle X-ray diffraction, dynamic mechanical analysis and electron microscopy, as well as, to a limited extent, solid-state nuclear magnetic resonance and Fourier-transform infra-red spectroscopy, were used to investigate the morphology, crystalline behaviour, structure, compatibility and mechanical properties of natural rubber/linear low-density polyethylene/polyethylene-*b*-polyisoprene (NR/LLDPE/PE-*b*-PI) ternary blends. The mechanical properties of the blends were greatly improved by the addition of the compatibilizer PE-*b*-PI. The suggested model for ternary blends was supported by solid-state n.m.r. and FTi.r. data and the optimum surface area of PE-*b*-PI macromolecules required for the interphase was estimated.

(Keywords: compatibilization; polyethylene-*b*-polyisoprene diblock copolymer; natural rubber/linear low-density polyethylene/polyethylene-*b*-polyisoprene blends)

INTRODUCTION

Polymers can be blended to form a wide variety of composites with desirable combinations of properties. But in practice, these expected properties are not achieved because of poor adhesion of the phases created due to immiscibility in the thermodynamic sense. This situation can be remedied by using certain polymers referred to as compatibilizers¹⁻⁵, which improve the interfacial conditions between the phases. For this purpose, one usually uses a block or graft copolymer as the interfacial agent, with the segments or blocks chemically identical or similar to components A or B in a blend of A and B. Thus, the interfacial energy between the immiscible phases is reduced, ensuring finer dispersion upon mixing and higher stability against phase separation.

Block copolymers are considered as better interfacial agents than graft copolymers because of less effective penetration of the branches of the latter into homopolymer phases. For the same reason, diblock copolymers are more effective than triblocks³.

There has been no work concerning the use of a block copolymer to compatibilize polyolefin/non-polar rubber blends because of the difficulty in synthesizing a proper compatibilizer containing a polyolefin block.

We have shown previously that the mechanical properties of natural rubber/polyethylene (NR/PE) binary blends were very poor because of the limited interpenetration between NR and the amorphous fraction of PE. A compatibilizer may enhance phase adhesion in order to increase the mechanical properties of unvulcanized blends.

The synthesis of polyethylene-*b*-polyisoprene (PE-*b*-PI) diblock copolymers, with block structure similar to PE and NR respectively, has hitherto been impossible by a direct route and is now accomplished by anionic sequential copolymerization of butadiene and isoprene followed by selective hydrogenation of the former⁶.

In this work, (hydrogenated polybutadiene)-*b*-polyisoprene (HPB-*b*-PI or PE-*b*-PI) diblock copolymer was used as a compatibilizer of natural rubber/linear low-density polyethylene (NR/LLDPE) blends. Mechanical properties, compatibility, morphology, structure and transition behaviour of these blends were investigated. HPB is thought to have a branched-chain structure close to that of LLDPE among various PEs.

EXPERIMENTAL

Materials

Linear low-density polyethylene (LLDPE) was a commercial product of Union Carbide, melt index 10.2 g/10 min, $[\eta]_{\text{decalin}}^{135^\circ\text{C}} = 17.08 \text{ dl g}^{-1}$, crystallinity 38.2%.

Natural rubber (NR) had a $ML_{1+4}^{100^\circ\text{C}} = 83$, $[\eta]_{\text{toluene}}^{25^\circ\text{C}} = 5.53 \text{ dl g}^{-1}$, $\bar{M}_n = 2.58 \times 10^5$ as calculated from the viscosity equation⁷.

Synthesis and characterization of PE-*b*-PI have been described⁶, the weight ratio of PE to PI blocks of the samples used in this work being 50/50.

Preparation of samples

The ternary blends were prepared in the following steps: first LLDPE was melted at 130°C in a Brabender Plastcorder, then NR and additives were added and mixed for 3 min and finally the compatibilizer PE-*b*-PI was added and mixed for another 5 min.

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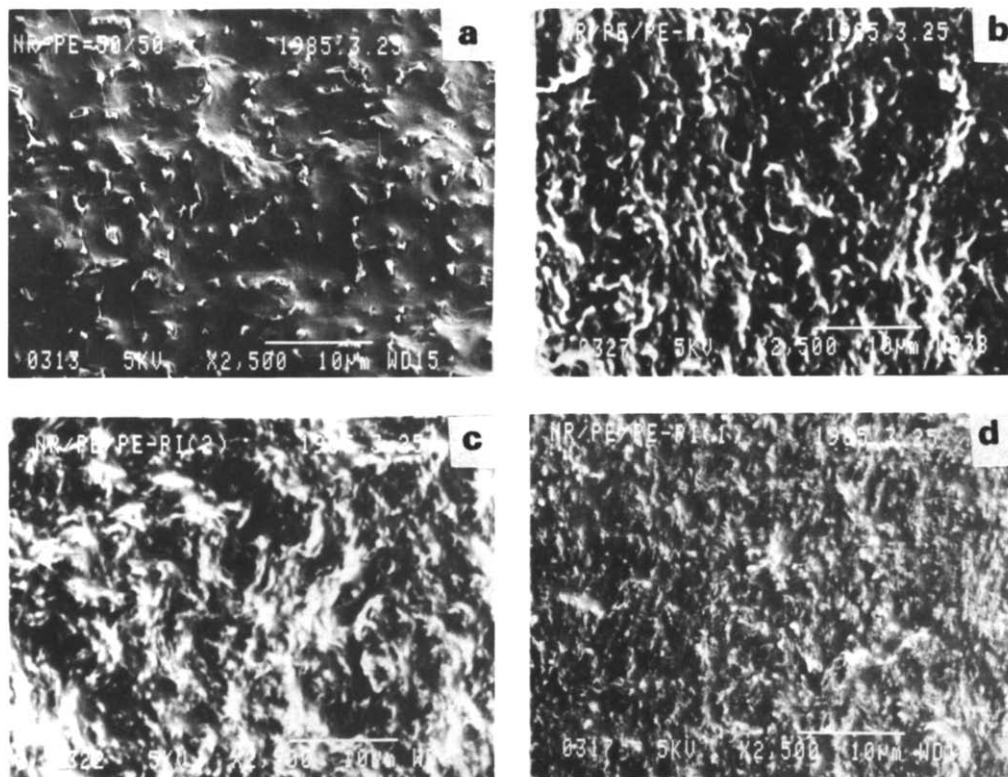


Figure 1 SEM micrographs of the blend samples. Ratios of NR/LLDPE/PE-*b*-PI (wt%) are as follows: (a) 50/50/0; (b) 45/50/5; (c) 37/50/13; (d) 37/50/13. $[\eta]_{\text{PE-}b\text{-PI}} = 18.9 \text{ dl g}^{-1}$ for B and C, 12.8 dl g^{-1} for D

Testing and observation

The measurement of mechanical properties of the blends was done in the same manner as in the previous work⁸.

WAXD⁹, d.s.c.⁹, scanning and transmission electronic microscopy (SEM and TEM)⁸ experiments were carried out under the same experimental conditions as in the previous work^{8,9}.

Dynamic mechanical properties were tested in a DDV-II-EA with a frequency of 3.5 Hz and a scanning rate of 3°C min^{-1} .

The wide-line solid-state n.m.r. experiment of blend samples was done at ambient temperature with a MSL-300PFT-NMR.

The i.r. measurement of the blends was done on a Degilab FTS-20E, using the FTi.r.-a.t.r. technique.

RESULTS AND DISCUSSION

Morphology

This study reveals the pronounced emulsifying effect of the compatibilizer PE-*b*-PI on the incompatible NR/LLDPE blends, affecting the domain size and the interface structure. SEM and TEM (OsO₄ staining) examination of the morphology of the blends containing PE-*b*-PI is shown in Figures 1 and 2.

It can be seen from SEM micrographs (Figure 1) that the morphology of the fractured surface changed greatly; the interface between NR (dark matrix) and LLDPE was clear when no PE-*b*-PI was present but became blurred on addition of the compatibilizer PE-*b*-PI. These results indicated that the compatibilizer was very effective in decreasing the interfacial tension and increasing the adhesion between the two phases.

Compared with lower-molecular-weight PE-*b*-PI (Figure 1D), on addition of a compatibilizer of higher molecular weight (Figures 1B and 1C), some apparent particles of LLDPE disappeared from the fractured surface of the blends, indicating a stronger interaction between LLDPE homopolymer and PE block in the PE-*b*-PI. Increase in molecular weight of the compatibilizer favoured the penetration of PE and PI blocks of PE-*b*-PI into the respective homopolymers.

It was also found from the dispersion of LLDPE in NR that the size of LLDPE was reduced on adding PE-*b*-PI (Figure 2) because of the emulsifying effect of the compatibilizer.

Based on the above morphological studies, a schematic representation of ternary blends could be visualized (Figure 3).

Crystalline behaviour

WAXD results showed that the crystal plane spacings d_{110} and d_{200} did not change after adding PE-*b*-PI (Table 1), indicating no change in the crystallite structure of LLDPE in the blends.

Meanwhile, the crystallite size \bar{L}_{110} of LLDPE slightly decreased in the presence of NR because of the destruction of the perfection of the LLDPE crystallites (Table 1) but slightly increased to the level of pure LLDPE after further addition of the compatibilizer (Table 1). This might be caused by the co-crystallization of LLDPE with a PE block in PE-*b*-PI. The change in \bar{L}_{200} showed a similar trend (Table 1). It is also noted that at NR/LLDPE/PE-*b*-PI=45/50/5, all the parameters in Table 1 show a maximum; this odd phenomenon cannot be easily explained based on our present knowledge. It is interesting to note in the following

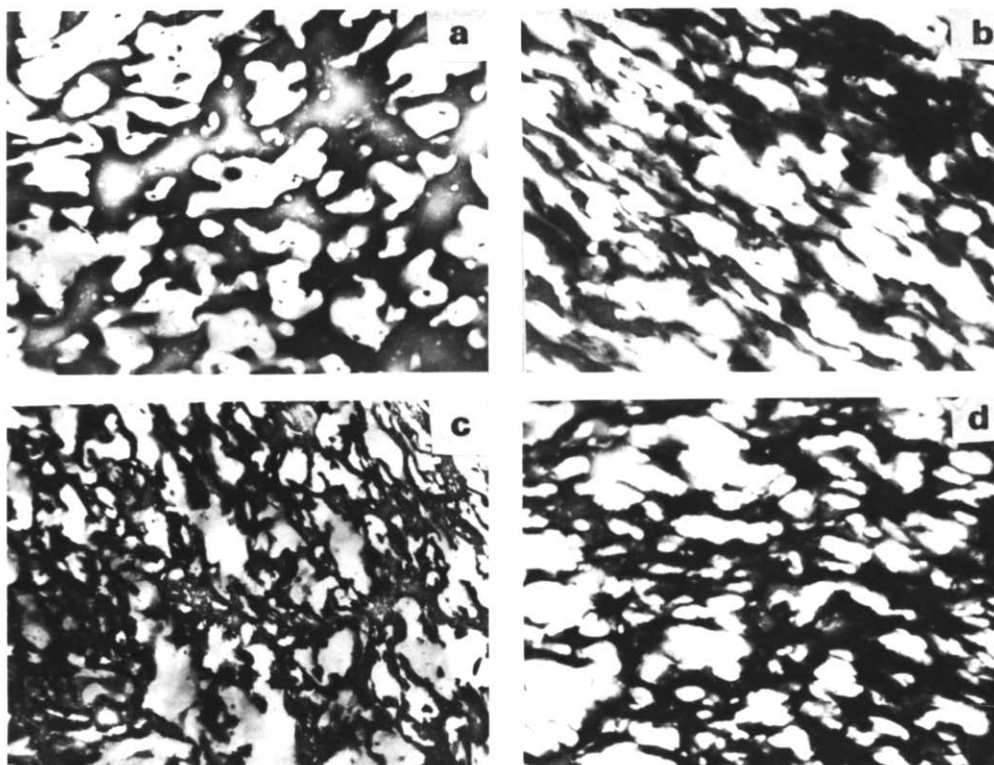


Figure 2 TEM micrographs of the blend samples. Ratios of NR/LLDPE/PE-*b*-PI (wt%) are as follows: (a) 50/50/0; (b) 45/50/5; (c) 37/50/13; (d) 37/50/13. $[\eta]_{\text{PE-}b\text{-PI}} = 18.9 \text{ dl g}^{-1}$ for B and C, 12.8 dl g^{-1} for D

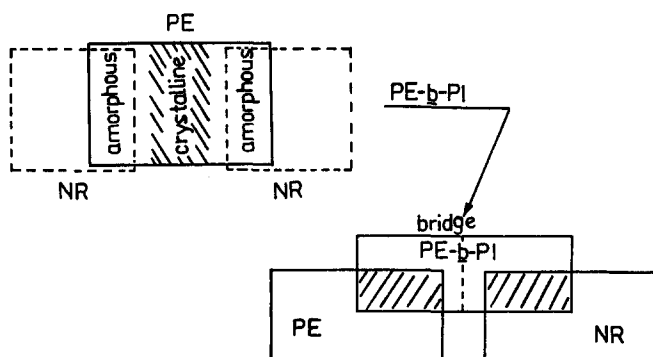


Figure 3 Change in interface between NR and LLDPE with the addition of PE-*b*-PI diblock copolymers

Table 1 WAXD results on LLDPE in NR/LLDPE-*b*-PI blends

NR/LLDPE/PE- <i>b</i> -PI	d_{110} (Å)	d_{200} (Å)	\bar{L}_{110} (Å)	\bar{L}_{200} (Å)
0/100/0	4.16	3.76	146	101
50/50/0	4.16	3.75	140	102
45/50/5	4.28	3.84	153	122
41/50/9	4.16	3.76	148	108
37/50/13	4.19	3.77	148	105
37/50/13 ^a	4.17	3.77	143	93

^a $[\eta]_{\text{PE-}b\text{-PI}} = 12.8 \text{ dl g}^{-1}$; 18.9 dl g^{-1} for other blends

discussion that optimum mechanical properties also appeared at this composition ratio.

Using d.s.c., the thermal parameters T_m and T_c and crystallinity χ_c of LLDPE in the blends were obtained (Table 2). It is obvious that T_m , T_c and χ_c , inherently characteristic of the mother component, were not affected by change in the interphase on adding the PE-*b*-PI diblock copolymer (Figure 3).

Table 2 D.s.c. results on LLDPE in NR/LLDPE/PE-*b*-PI blends

NR/LLDPE/PE- <i>b</i> -PI	T_m (°C)	T_c (°C)	χ_c (%)
0/100/0	124.9	104.3	38.2
50/50/0	125.0	106.0	39.0
45/50/5	124.8	104.3	36.2
41/50/9	124.9	103.3	38.8
37/50/13	124.8	104.3	35.7
37/50/13 ^a	124.2	103.7	38.4

^a Same as in Table 1

Dynamic mechanical behaviour

It was noted that there was no shift of T_g of NR to lower temperature on adding the compatibilizer (Figure 4). Just as reasoned above, the presence of a PE-*b*-PI 'bridge' between NR and LLDPE did not alter the chain motion of NR (Figure 3), and thus the ternary blend systems LLDPE/PE-*b*-PI/NR appeared to behave similarly to the binary blend systems LLDPE/NR in dynamic mechanical behaviour.

Mechanical properties

Usually, the addition of a compatibilizer to a blend system will enhance the mechanical properties¹⁰⁻¹⁴. The degree of compatibilization is strongly affected by the structure, molecular weight and amount of compatibilizer.

As the result of the change in morphology and interfacial adhesion, the mechanical properties of NR/LLDPE blends are greatly improved (Figures 5 and 6, Table 3) on adding PE-*b*-PI diblock compatibilizer. This enhanced compatibility, as displayed in a finer dispersion, a more blurred interface and consequently improved mechanical properties, is provoked by a change in the interfacial interaction between LLDPE and NR

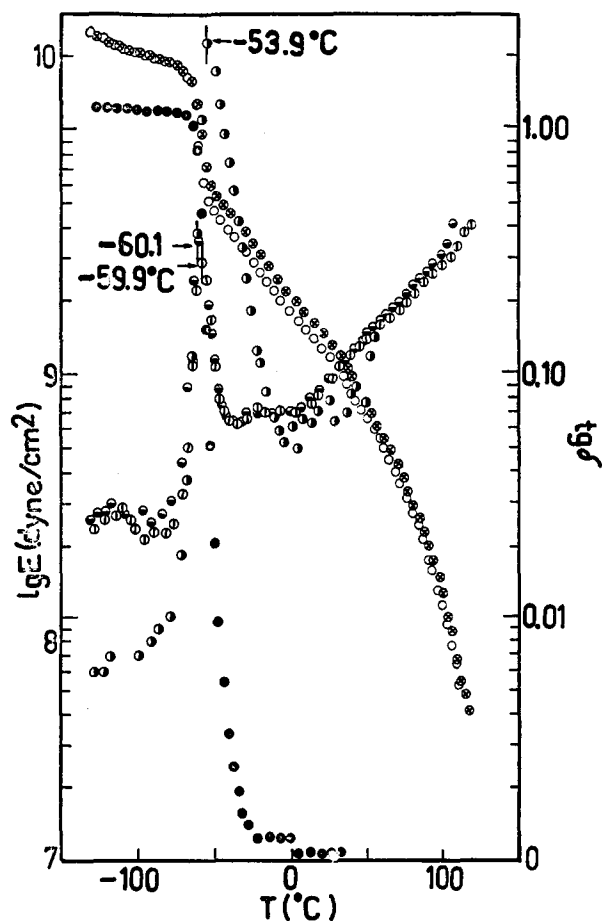


Figure 4 D.m.a. curves of the samples with different NR/LLDPE/PE-*b*-PI composition: (●, ○) 100/0/0; (○, ⊖) 50/50/0; (⊗, ⊕) 45/50/5

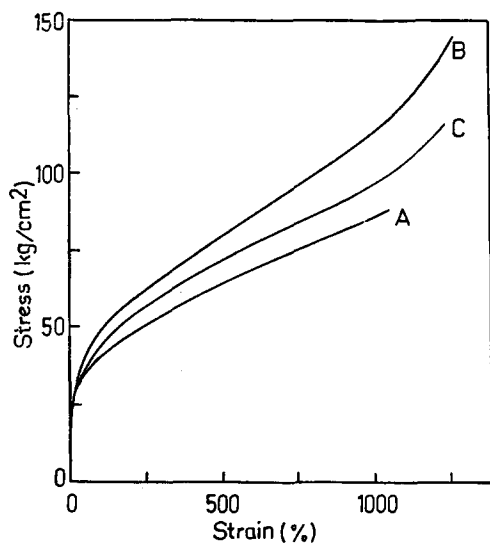


Figure 5 Stress-strain curves of the blend samples with different NR/LLDPE/PE-*b*-PI composition: A, 50/50/0; B, 45/50/5; C, 41/50/9

in the blends from physical adhesion to one with additional valence-bond bridges supplied by PE-*b*-PI (Figure 3), together with the co-crystallization of LLDPE with PE block in the copolymer.

A plot of tensile strength against the amount of PE-*b*-PI in the blends (Figure 6) indicates that optimum mechanical properties are achieved only at a proper

amount of PE-*b*-PI, an excess of which would only do harm to the mechanical properties.

Molecular weight (*M_w*) of the compatibilizer played a role in the compatibilizing effect on NR/LLDPE blends (Figure 7, Table 3). Lower-*M_w* PE-*b*-PI was not as effective as that of higher *M_w* in compatibilization. Though no effort was made to measure the *M_w* of the PE and PI blocks relative to that of the homopolymers, it is perceivable that a too short block in the copolymer is detrimental to its anchoring in the domain and matrix homopolymers, thus weakening the 'bridge' effect in the interface and hence the mechanical properties.

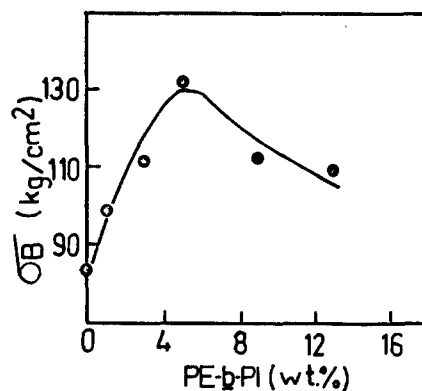


Figure 6 Variation of tensile strength with the amount of PE-*b*-PI diblock copolymer

Table 3 Mechanical properties of NR/LLDPE/PE-*b*-PI blends

NR/LLDPE/PE- <i>b</i> -PI	Tensile strength (kg cm ⁻²)	Elongation at break (%)
0/100/0	240	1387
50/50/0	84	975
49/50/1	99	965
47/50/3	112	981
45/50/5	132	1190
41/50/9	113	1089
37/50/13	110	1188
37/50/13 ^a	96	935

^a Same as in Table 1

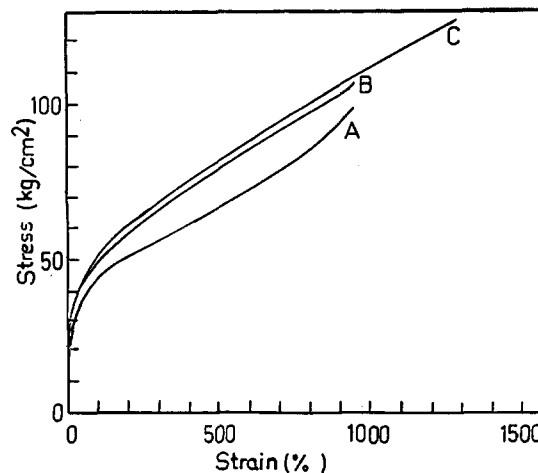


Figure 7 Effect of molecular weight of PE-*b*-PI on the mechanical properties of the blends: A, NR/LLDPE/PE-*b*-PI = 50/50/0; B, NR/LLDPE/PE-*b*-PI = 37/50/13 ($\bar{M}_n = 1.29 \times 10^5$); C, NR/LLDPE/PE-*b*-PI = 37/50/13 ($\bar{M}_n = 2.79 \times 10^5$)

Table 4 Solid-state n.m.r. results of NR/LLDPE/PE-*b*-PI blends

NR/LLDPE/PE- <i>b</i> -PI	M ₁	:	M ₂	:	M ₃
50/50/0	0.323		0.034		0.642
47/50/3	0.379		0.074		0.545
45/50/5	0.301		0.090		0.600
41/50/9	0.410		0.126		0.463

Preliminary solid-state n.m.r.* and FTi.r. study

A preliminary study of the ratio of the three phases—NR (M₃), LLDPE (M₁) and intermediate interphase (M₂)—in the blends was made using the wide-line solid-state n.m.r. technique¹⁵ (Table 4). It was found that M₂ increased with increments of PE-*b*-PI, showing the existence of the PE-*b*-PI interphase between NR and LLDPE. Without the compatibilizer, NR/LLDPE binary blends still had an interphase of 3.4%, confirming earlier inference that NR and the amorphous fraction of PE interact to offer compatibility to a limited degree¹⁶. This result agrees well with the sketched model of Figure 3.

With the FTi.r.-a.t.r. technique, the ratio of peaks height A_{835}/A_{1375} , which reflects the interaction between NR and the amorphous fraction of LLDPE in ternary blends, was investigated (Table 5). With the addition of the compatibilizer and decrease in NR component, the A_{835}/A_{1375} ratio approached that of pure NR. This result could be well explained by the rationale that direct contact between NR and LLDPE in the binary blends was intervened partly by indirect contact through the PE-*b*-PI 'bridge' (Figure 3), the direct effect of LLDPE molecules on NR molecular motion being suppressed. This result will be elaborated in a further paper¹⁷.

Calculation of surface area of PE-*b*-PI

In ternary blends, the proper amount of compatibilizer required depends on many factors, of which conformation and molecular weight are the most important. It is possible to estimate the amount of a compatibilizer with a given molecular weight M to saturate all of the interface in a blend³. In this calculation, the interfacial area per unit volume of the blend as a function of the volume fraction ϕ_A of polymer A, which is dispersed in the form of spherical particles of radius R , should be taken into consideration. The following equation was used for calculation³:

$$m = 3\phi_A M / aRN \quad (1)$$

where m is the mass ratio of block copolymer required per unit volume of the blend, a is the area of

Table 5 Change in A_{835}/A_{1375} of the blends with composition

NR/LLDPE/PE- <i>b</i> -PI	50/50/0	47/50/3	45/50/5	41/50/9	100/0/0
A_{835}/A_{1375}	1.235	1.023	0.870	0.801	0.719

compatibilizer molecules occupied at the interface, and N is Avogadro's number.

In this work, the molecular weight of compatibilizer usually used is about 2.5×10^5 , $\phi_A = \phi_{\text{LLDPE}} = 0.501$ (from a weight percentage of 0.50), and $N = 6.023 \times 10^{23}$. From the results of studies of mechanical properties, m was determined to be 0.05 (i.e. 5%). From SEM observation, R is estimated to be $1 \mu\text{m}$. Using the above values, the value of a can be roughly calculated to be about 1250 \AA . This value is between the mean-square end-to-end distance (about 10^2 \AA) and the completely stretched chain length (about 10^5 \AA), showing that the compatibilizer localized at the interface with some conformational limitation caused by its embedding into LLDPE and NR phases.

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