

Morphological Study of LLDPE-NR Reactive Blending with Maleic Anhydride

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ABSTRACT: A binary blend and ternary reactive blends of 90/10 LLDPE/NR using maleic anhydride (MA) as a reactive agent with and without dicumyl peroxide (DCP) were made at 150°C in an internal mixer. The fracture surfaces of the blends were conventionally observed by TEM and atomic force microscope, revealing that the rubber domains became smaller with the addition of MA and DCP. This suggested that the *in situ* graft copolymer (LLDPE-*g*-NR) was formed and acted as an *in situ* compatibilizer to enhance interfacial adhesion. This was further supported by FTIR results. Importantly, after removal of NR phase from the blends, the remaining LLDPE part was dissolved in hot xylene, purified by precipitation in methanol, and carefully prepared by solvent casting for TEM observation. The microstructures of the solvent-extracted LLDPE from all blends are unlike that of solvent cast- pure LLDPE,

which shows only crystalline structure. This leads to an unambiguous way to disclose the existence of an *in situ* graft copolymer. The solvent-extracted LLDPE from the blends shows mixed morphology of LLDPE crystalline structure and its *in situ* graft copolymer as nanofibrillar networks of the NR phase protruded from the amorphous region of the LLDPE matrix due to spinodal decomposition by the solvent removal. Adding MA makes more branches and fibril connections of the NR phase, whereas a thinner fibril network and more links of the NR and the LLDPE amorphous region are found in the reactive blend with MA and DCP, where the most compatibilized blend is obtained. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1914–1921, 2007

Key words: fibrillar network; natural rubber; reactive blending; polyethylene

INTRODUCTION

Polyethylene (PE) is a cheap and widely used plastic; however, its nonpolar nature makes it difficult to mix with other polymers, to reduce cost, and improve some properties. Natural rubber (NR) is one among several polymers found to be blended with PE to produce thermoplastic elastomer; for example, Ahmad and Abdullah had prepared several blends of NR with various types of PE using liquid NR as a compatibilizer.^{1–3} They found that linear low-density polyethylene (LLDPE) gave the most prominent properties due to better compatibility with NR. Other purposes of PE/NR blends are for recycling NR vulcanizate⁴ and improving mechanical properties.^{5,6} The composition of NR and PE is important for different applications. For packaging film, a high-impact film can be produced by

adding a small amount of rubber to the PE matrix.^{7–9}

Polymer blends are typically prepared by shear and solution mixing. However, this work employed reactive blending, which can be done in an internal mixer or in a twin-screw extruder. Reactive extrusion means to have a reaction occurring during extrusion and it can be carried out in various ways. There are several reagents that can react within the short residence time in the extruder; for example, in the transesterification of alcohol and acrylate or in a reaction of anhydride and amide or in a simple reaction with peroxide initiators.^{10–12} Reactive processing is an alternative way to obtain compatibilized polymer blends by direct reaction between the functional groups of two polymers to yield an *in situ* graft copolymer, which acts as an *in situ* compatibilizer. According to Cheung and Balke's work, LLDPE contains one double-bond terminal per molecule and this terminal is reactive.^{12,13} Peroxide, e.g., dicumyl peroxide (DCP), mainly introduces free radicals to facilitate the β -scission in polypropylene; however, crosslinking and end-linking are usually found for PE.^{14,15} It is difficult to control the reactions occurring with peroxide and so the amount of peroxide used should be limited to avoid gelation, which can deteriorate the properties of the blend.¹⁶

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It is known that maleic anhydride (MA) is frequently used as a reactive reagent to enhance the compatibilization of many polymer blends, especially blends containing polyamide.¹⁷ MA is often used to functionalize many polymers; e.g., NR, PE, polybutadiene, ethylene-propylene-diene monomer rubber, thermoplastic elastomer, and so on. The reactions of MA to polyolefins is usually initiated by peroxide, followed by the free radical mechanism.¹⁸ The dimer of MA is formed and decomposed to free radicals and is grafted to the polyolefin backbone. The reactions of MA with NR also occur through mechanisms like Diels-Alder and nucleophilic substitution.¹⁹ MA can react with polyolefins and rubber without peroxide, as reported by Els and McGill,²⁰ i.e., the chloroform and xylene extracted part from the blend of 49/49/2 wt % polypropylene/polyisoprene/MA (PP/IR/MA) contained more rubber bound to PP or PP-g-IR and residual gel than a simple blend of 50/50 wt % PP/IR. Therefore, it is interesting to investigate the *in situ*-formed graft copolymers that influence the compatibility of polymer blends. This brought us to do reactive blending of LLDPE and NR (at a composition of 90 and 10 wt %, respectively) with MA with and without peroxide initiator (see Scheme 1 for the possible copolymers obtained) to avoid a serious reaction by peroxide, leading to gel formation.

The existence of the products of the grafting reaction (or *in situ* compatibilizer) occurring upon reactive processing have been generally analyzed by chemical methods like Fourier transform infrared (FTIR) or NMR and by thermodynamic considerations, e.g., electron microscopy for phase separation and domain size reduction.^{17,21} However, this conventional morphological investigation of an *in situ* graft copolymer from the bulk fracture surface is sometimes difficult to evaluate due to its small amount. In this study, an alternative way to observe the *in situ* compatibilizer via TEM is introduced, i.e., by the phase separation of the polymer solution

instead of phase separation in the bulk solid. The obtained morphology is different but is so clear as to ensure that there are *in situ* graft copolymers formed during reactive processing.

EXPERIMENTAL

Materials

LLDPE was supplied by Thai Polyethylene (Rayong, Thailand). It has a melt flow index of unity, density of 0.918 g/cm³, and $M_w = 87,570$. NR of STR 5L grade was obtained from Rayong Bangkok Rubber. MA and DCP were purchased from Fluka and were used as received.

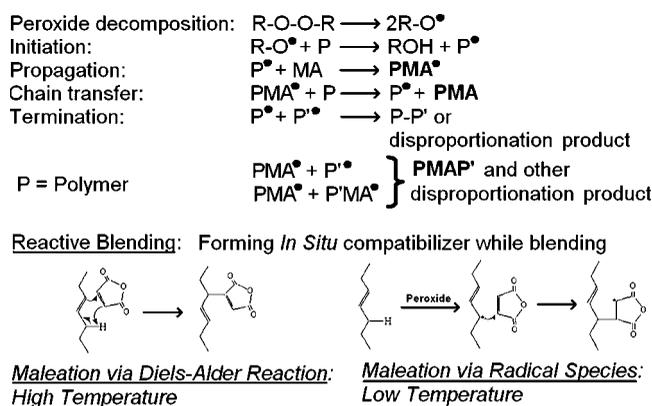
The reactive blending of LLDPE and NR were prepared by mixing in the Brabender mixer with MA as a reactive agent and DCP as an initiator. The composition of the blend was 90/10 wt % LLDPE/NR with the addition of 3 phr MA and 0.5 phr DCP.

Blending procedures

Masticated NR was mixed with [1/4] portion of MA for 5 min in the W50 Brabender mixer and was then removed from the chamber. LLDPE was then added and melted at 150°C at 50 rpm for about 3 min in Brabender mixer. Then another [3/4] portion of MA and the formerly prepared NR-MA were then added to the molten LLDPE. The mixture was mixed further for total time of 10 min and then withdrawn from the chamber. In the case of adding DCP, the procedure was changed slightly by adding peroxide right after the MA addition.

Sample preparation

The bulk sample was dissolved in acetone (a good solvent for MA) at 60°C for an hour to remove residual MA and was then filtered and washed by acetone many times. The dried insoluble part was then dissolved in chloroform for 1-h refluxing at 60°C to remove NR. This solution was then filtered, washed by chloroform many times, and dried. The soluble part (NR phase) was collected and dried. The insoluble part was refluxed in xylene at 120°C for 5 h. The hot solution was filtered through cheesecloth into an acetone flask (acetone : xylene, 1 : 2) to precipitate the LLDPE part. The precipitate was then filtered and dried. This portion was refluxed again in xylene at 128°C for 1.5 h (all samples were totally dissolved), immediately filtered by Whatman paper, and poured into methanol to reprecipitate the LLDPE part, which was dried in a vacuum oven at 40°C overnight. This portion is called *LLDPE-extraction*.



Scheme 1

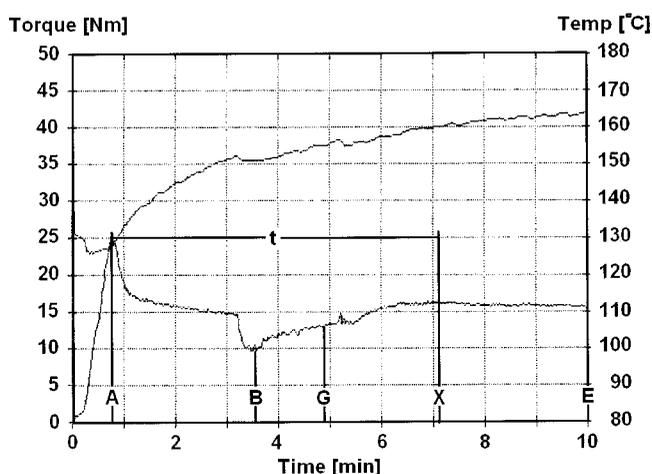


Figure 1 Torque-time-temperature profile for 90/10/3 LLDPE/NR/MA blend at 150°C (A: adding [1/4] MA to NR; B: adding LLDPE and [3/4] MA; G: reaction occurs; X: reaction finished and uniform dispersion).

Chemical structure analysis

FTIR (Bruker Equinox 55) spectroscopy was used to determine the chemical structure of the LLDPE-extracted samples in the mid-IR region from 4000 to 400 cm^{-1} .

Morphological study

The microtome-cut surfaces of the blends were observed by transmission electron microscopy (TEM, JEOL JEM-100U) at 80 kV, and atomic force microscopy (AFM) (Shimazu SPM-9500 U2 scanning probe microscope) using dynamic mode.

The LLDPE extracted part was redissolved in hot xylene at 128°C with a low concentration of about 0.5% solution. The clear solution was dropped on a glass slide, dried (in a convection oven at 75°C), and covered by polyacrylic acid. After the polyacrylic acid was removed in water, the thin film sample was stained by osmium tetroxide and used for TEM study by the JEOL JEM-100U at 80 kV.

RESULTS AND DISCUSSION

Reactive products

The reaction taking place during blending can be observed from time-temperature-torque plots as shown in Figures 1 and 2. The blends of 90/10/3 LLDPE/NR/MA and 90/10/3/0.5 LLDPE/NR/MA/DCP show an increase in torque (or viscosity) after 5 min of mixing. The reaction of MA to the polymers (without DCP) does not change the torque much but is noticeable by the increase in temperature. The torque raise is obvious after DCP was incorporated. This reveals that the reactions become

dominant in the presence of peroxide and such that the reactive products, e.g., graft or block copolymers of LLDPE-NR, could be produced as well as LLDPE-g-MA and NR-g-MA. These species can act as compatibilizers to improve the adhesion between two polymers and thus viscosity increases. Moreover, the torque may rise due to the extension of the cross-linking reaction; and if so, the gel portion will be found.^{16,20}

An initiator, like DCP, influences the improved mechanical strength; especially, for dynamic vulcanization to the rubber phase, as noted by Chodhury and Bhowmick for 70/30 wt % NR/PE blend.^{22,23} Manas et al.²⁴ found the superior curing role by DCP (less than 1 phr) to improve tensile strength in NR/PS (60/40 wt %) while the effect of the compatibilizer (liquid NR) on tensile strength is minor, i.e., to help homogenize the blend to gain more curing. On the other hand, Sajkiewicz and Phillips found that LLDPE reacted with DCP (less than 1 wt %) results in high gel formation of about 40%.²⁵ In our study, DCP can cause the above crosslinking in LLDPE and NR phases. Table I reports the gel content of the blend, with and without DCP. The gel content in the 90/10/3/0.5 blend is higher than that of the 90/10/3. The insoluble part of the samples with DCP became hard to dissolve due to the addition of LLDPE crosslinks. The increase in bound rubber content and the decrease of free MA in the blend with MA and DCP suggests better reaction between components and better compatibilization can be obtained.

The chemical structure of LLDPE was observed by FTIR, as shown in Figure 3(a). LLDPE contains car-

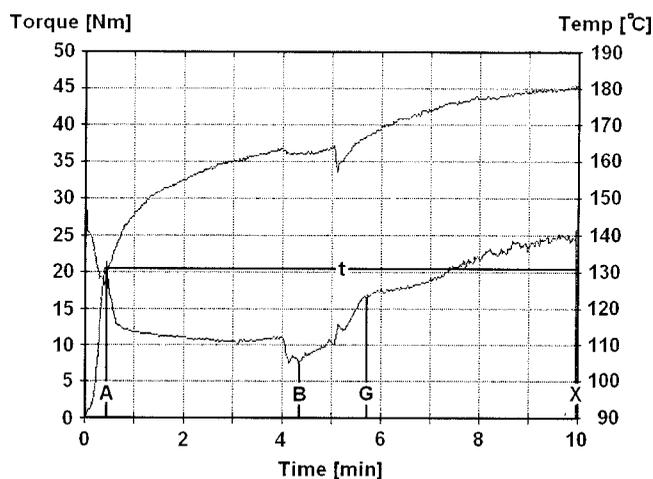


Figure 2 Torque-time-temperature profile for 90/10/3/0.5 LLDPE/NR/MA/DCP blend at 150°C (A: adding [1/4] MA to NR; B: adding LLDPE, [3/4] MA, and DCP; G: reaction occurs; X: reaction finished and uniform dispersion).

TABLE I
Content of Free MA, Extracted Rubber, and Gel in the 90/10 LLDPE/NR Blends with MA and DCP

LLDPE/NR/ MA/DCP (wt %)	% Free MA ^a	% Extracted rubber	% Gel
90/10/3	31.41	3.32	0
90/10/3/0.5	16.88	1.32	39.29

^a % Free MA is the amount of unreacted MA.

bon double-bond reactive sites, as noted by the peak at 1645 cm^{-1} , such that it is capable of reacting with MA at elevated temperature.¹³ The FTIR study for the LLDPE-extracted parts in 90/10, 90/10/3, and 90/10/3/0.5, as seen in Figure 3(b), reveals the presence of LLDPE-NR copolymers, with and without MA (NR peak characteristic is at 837 cm^{-1} and carbonyl peak of MA is at 1780 cm^{-1}). There is a tiny peak around 837 cm^{-1} in 90/10 and this peak is more obvious in the other blends. The absorption around $1771\text{--}1780\text{ cm}^{-1}$ becomes a shoulder for the 90/10/3 blend, representing smaller content of MA-grafted products than those in the 90/10/3/0.5 blend.

Morphological study by AFM from bulk surfaces of the blends

Figure 4(a–d) shows the AFM micrographs of the cut surface from the bulk solids of the pure LLDPE and the 90/10 blend series. It is relevant that the surface of the pure LLDPE is the smoothest, with fringes of crystal, whereas that of the 90/10 LLDPE/NR is the coarsest and shows some deep holes. Those deep holes correspond to the NR region, which is much softer than the LLDPE phase so that it is deformed easier than the LLDPE matrix. The rubber phase in the LLDPE/NR is more aggregated and thus poorer distributed than that in the LLDPE/NR/MA. Moreover, AFM micrographs illustrate clearly that the 90/10/3 LLDPE/NR/MA has a relatively rougher surface than the 90/10/3/0.5 LLDPE/NR/MA/DCP. The finer structure (less roughness) of the latter indicates better role of the *in situ* compatibilizer to homogenize the blend.²⁰ The rough surface of the blends is comparable to that found by Sanchez-Valdes et al. who showed an AFM micrograph of an extruded 15% LLDPE-*g*-MA film with an average roughness of 317.5 nm .²⁶ The same trend is also found in several polymer blends by SEM study, where a finer structure is found for blends having compatibilizers.^{24–27} More compatibilizer produces a finer structure.^{20,28} Moreover, due to a significant amount of gel in the 90/10/3/0.5 blend, the very tiny particles or grits (submicron size) distributed in the matrix are revealed.

TEM analysis of microtomb-cut bulk 90/10 LLDPE/NR blends

TEM micrographs of the bulk blends were prepared at 24,000 times magnification. Figure 5 shows bulk 90/10 LLDPE/NR with a wide distribution of NR domain size (the dark part stained by OsO_4) from very small particles to large long bands of NR, suggesting poor compatibility. Figure 6 reveals the more homogeneous well-distributed NR domains with narrower size distribution in the LLDPE matrix for a 90/10/3 LLDPE/NR/MA blend. This reveals that without DCP, MA is capable to compatibilize LLDPE and NR blend.²⁰ Moreover, the NR domains are much finer for a 90/10/3/0.5 LLDPE/NR/MA/DCP blend, indicating the reduced interfacial tension and better compatibilization (see Fig. 7).

TEM analysis of solvent-cast LLDPE extracted part

To investigate the reaction of LLDPE and NR with MA using DCP as an initiator to form the *in situ* LLDPE-*g*-NR copolymer, a series of solvent extractions and purification was employed to separate the LLDPE part out of the blend. Using the solvent casting technique to prepare the sample for TEM,

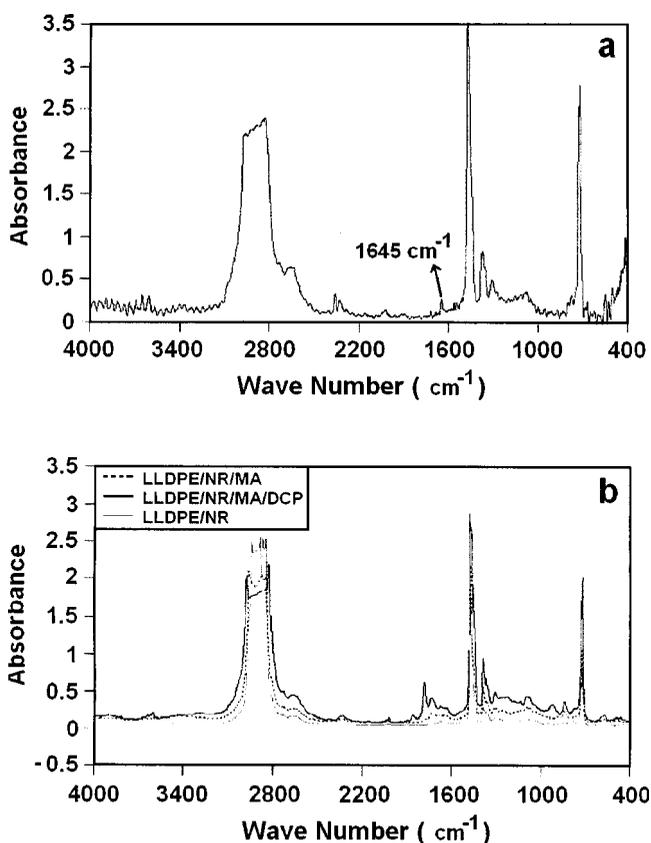


Figure 3 FTIR spectra for (a) pure LLDPE, (b) LLDPE-extracted parts of 90/10, 90/10/3, and 90/10/3/0.5 LLDPE/NR/MA/DCP blends.

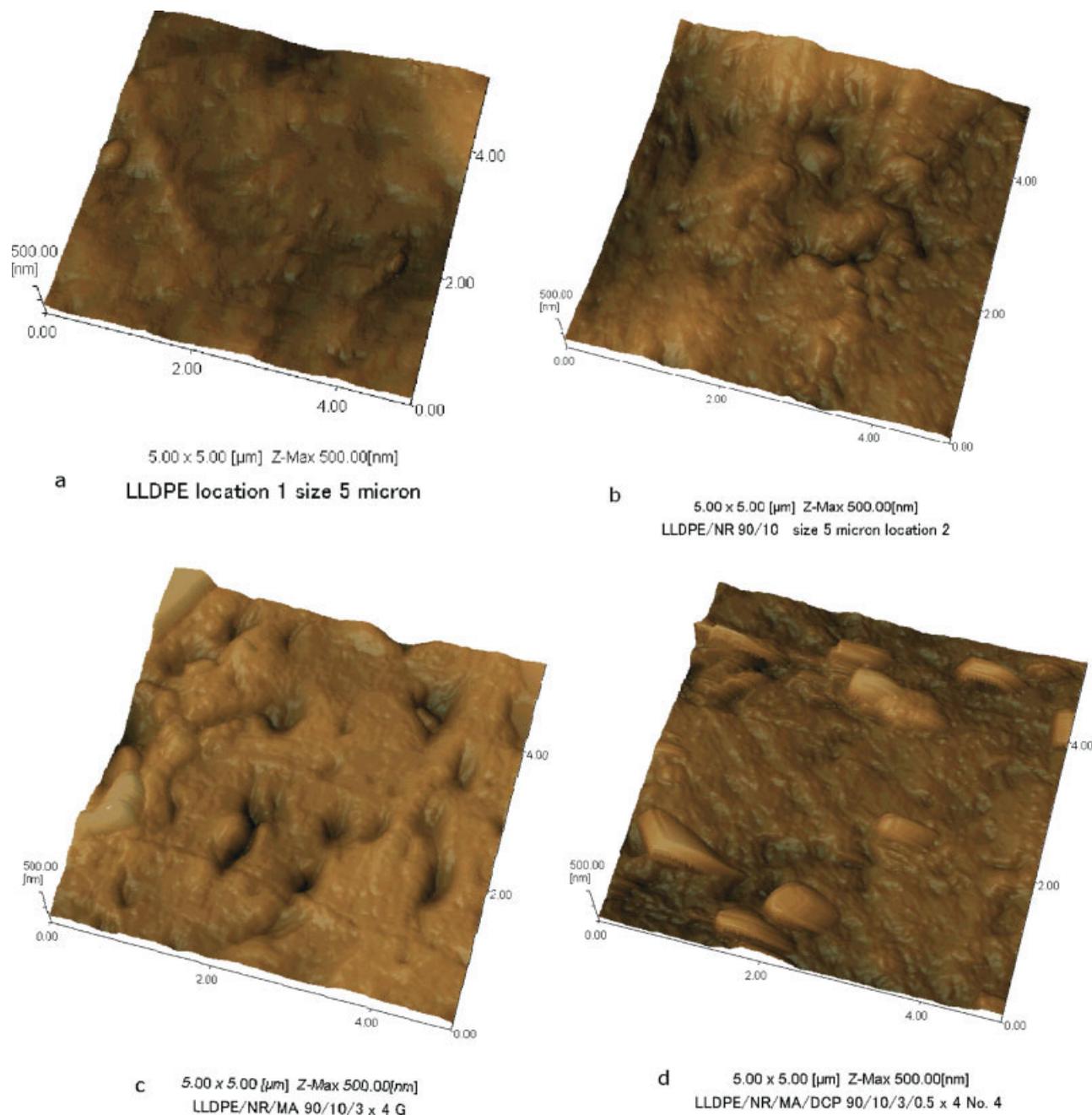


Figure 4 AFM images from ultrathin microtomb-cut surfaces of compressed crude samples: (a) pure LLDPE, (b) 90/10 LLDPE/NR, (c) 90/10/3 LLDPE/NR/MA, and (d) 90/10/3/0.5 LLDPE/NR/MA/DCP blends.

instead of microtome cutting, the morphology due to phase separation after solvent removal is obtained. Importantly, the *in situ* copolymers remaining in the LLDPE-extracted parts can be disclosed. Figure 8 shows the crystalline morphology of pure LLDPE with OsO_4 staining. The dark region corresponds to the amorphous phase in LLDPE.

Figures 9–11 exhibit TEM morphologies of the LLDPE extracted part from 90/10/0/0, 90/10/3/0, and 90/10/3/0.5 LLDPE/NR/MA/DCP blends, in that order. The magnification is about 30,000 times,

covering an area of 5–6 μm in length × 3–4 μm in width. After drying, the films from all LLDPE-extracted solutions exhibit the demixing nanofibrillar network together with the LLDPE crystalline. The width of the fibrils in 90/10/3/0.5 LLDPE/NR/MA/DCP is roughly about 33–66 nm, or nanofibrils, whereas that of the 90/10/3 LLDPE/NR/MA blend is relatively higher, i.e., 33–100 nm. The fibrillar network connecting external domains is dark, thus resembling the presence of NR. It is interesting that all “solvent-cast LLDPE-extracted” samples show a

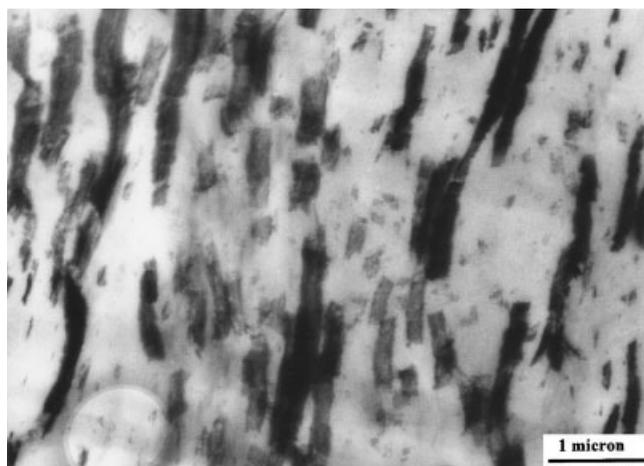


Figure 5 TEM micrograph of the crude 90/10 LLDPE/NR blend from compression molding.

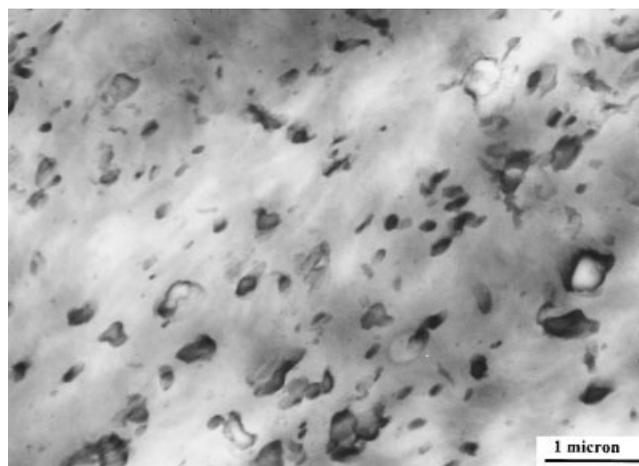


Figure 7 TEM micrograph of the crude 90/10/3/0.5 LLDPE/NR/MA/DCP blend from compression molding.

unique phase separation morphology that is different from the morphology due to phase separation from melt mixing (Figs. 5–7). Similar morphology as in Figures 9–11 is known to be obtained from the fast cooling of polymer solution (binary system) or thermally induced phase separation. The spinodal decomposition occurs upon cooling or solvent removal so that polymer-rich phase composition is coincident with the glass-transition composition, such that the polymer-rich phase is vitrified and left with a foam-like structure, i.e., voids (due to solvent removal) and polymeric (NR) connected fragments or fibrils. In our case, this morphological relic of spinodal decomposition has not been in the sample prepared from the LLDPE solution (Fig. 8), due to precipitation and fast crystallization of LLDPE. It is also very interesting that one can see the interface regions between NR and LLDPE located at the grain boundaries of LLDPE.

The NR nanofibrillar network has its ends anchored in the amorphous regions of LLDPE matrix; this ensures the presence of the *in situ* copolymer LLDPE-*g*-NR. On the other hand, some crystalline region of the LLDPE is destroyed due to the presence of NR. Interestingly, Figures 9–11 show that binary melt mixing can induce the formation of the graft copolymer; in other words, it is suggested that without the initiator, mechanical shearing can produce enough NR macroradicals responsible to react with PE chains to form an *in situ* copolymer. However, its effectiveness to compatibilize the blend is less than those formed by ternary reactive blends, especially when initiator is used like LLDPE/NR/MA/DCP blend (Figs. 5–7).

The texture and characteristic of *in situ* copolymers in those blends, therefore, can be compared and related to the effectiveness of compatibilization. The comparison can be considered according to the fibril-

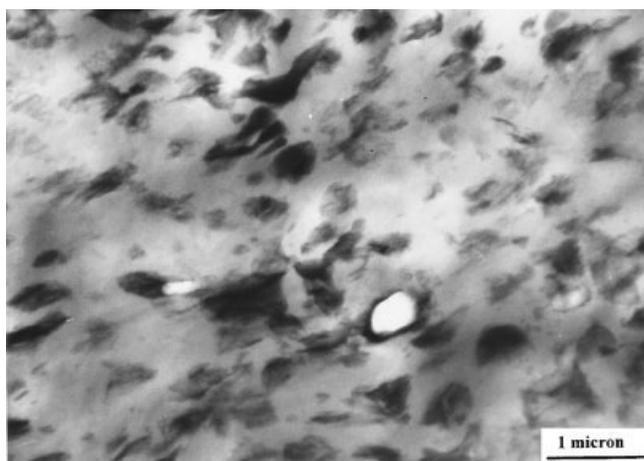


Figure 6 TEM micrograph of the crude 90/10/3 LLDPE/NR/MA blend from compression molding.

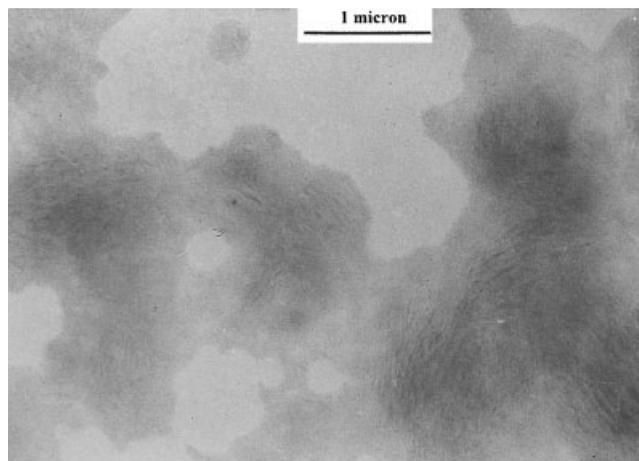


Figure 8 TEM micrograph of pure reprecipitated LLDPE prepared by solution drying.

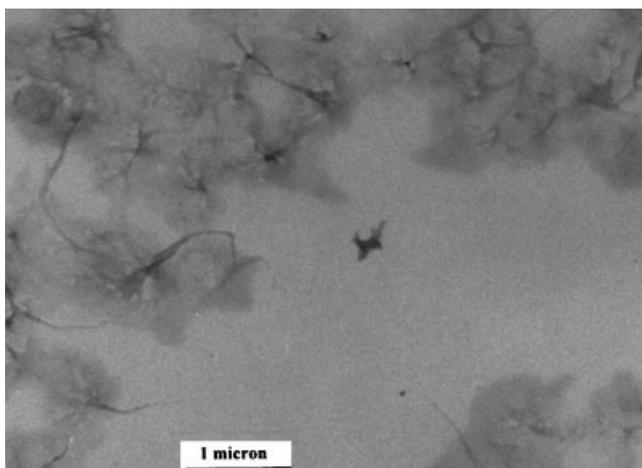


Figure 9 TEM micrographs of LLDPE-extracted part from solution drying of the 90/10 LLDPE/NR blend.

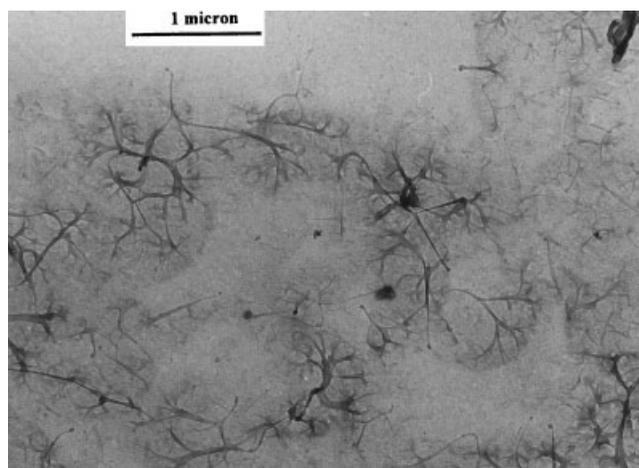


Figure 11 TEM micrographs of LLDPE-extracted part from solution drying of the 90/10/3/0.5 LLDPE/NR/MA/DCP blend.

lar density protruded from the LLDPE amorphous regions to each NR domain and to the extent of the fibrillar network connecting the NR domains. The copolymer in the binary blend (Fig. 9) resides as separated small NR domains and there are only limited numbers of fibrils connecting the domains, but with many dangling fibrils. This structure is poor in compatibilization; in other words, the less the extent of interdomain connection (short fibrils), the less the compatibility. For LLDPE/NR/MA (Fig. 10), the fibrillar networks are extended to link between domains and cover all amorphous regions (denser). And the size of fibrils is relatively large. There are some long fibrils, with many branches, connecting domains. When DCP is added (Fig. 11), more numbers of fine fibrils are extended to link between domains, and also there are more branches anchored near the grain boundaries of the amorphous LLDPE

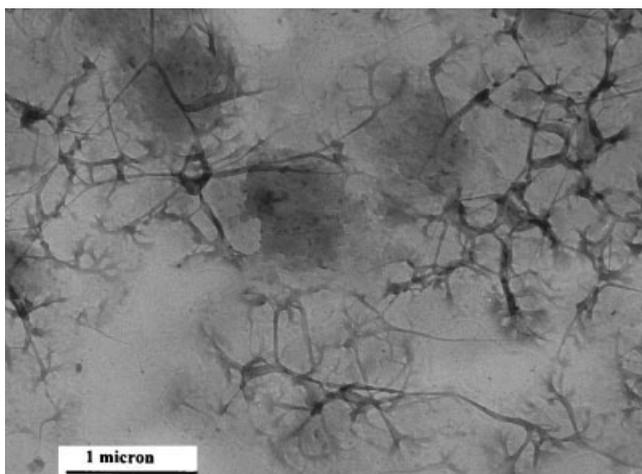


Figure 10 TEM micrographs of LLDPE-extracted part from solution drying of the 90/10/3 LLDPE/NR/MA blend.

region. In the presence of DCP, a more uniform distribution of fine fibrils with more links to the LLDPE phase than those found in LLDPE/NR/MA blend is obtained. This tells that the reactive blending provides more reactive sites or more intense reaction of LLDPE and NR to form the *in situ* copolymer that is sufficient and effective for compatibilization. This further suggests that the interfacial adhesion becomes stronger.

In addition, this work also shows that a polymer nanofibrillar network (foam-like structure) can be prepared by solvent removal to allow phase separation of the copolymer.

CONCLUSIONS

In situ compatibilizers obtained from the reactive blending of LLDPE/NR using MA and DCP as an active agent and initiator are ensured by conventional characterization techniques: e.g., the increase in torque and temperature during reactive blending, especially when DCP was added; FTIR for grafted MA products; and AFM to disclose the topology and size of the NR phase and its distribution in the blends. TEM micrographs from microtomb-cut bulk solid show similar results to those found in AFM, i.e., the finer and more uniform domains of NR in the LLDPE/NR/MA/DCP blend than in the LLDPE/NR/MA and LLDPE/NR blends, respectively. The blend of LLDPE/NR shows the biggest domains with wide-size distribution. This work successfully shows that the *in situ* compatibilizer, e.g., LLDPE-g-NR, has indeed occurred due to reactive blending and revealed by using solvent extractions and the solution preparation technique to induce phase separation during solvent removal. TEM

micrographs obtained from the solution technique disclose the *in situ* copolymers that remain in the LLDPE extract and can be found whether the initiator (DCP) is added or not. The morphology after phase separation due to solvent removal contains both the structures of LLDPE crystalline and LLDPE-g-NR copolymer, which is a fibrillar network of the NR phase having fibrillar ends anchored in the amorphous LLDPE matrix. This suggests that the *in situ* copolymer is capable of promoting good interfacial adhesion. Additionally, the copolymer with fine fibrils and more links between domains plays an important role in inducing compatible blends.

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