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PROPERTIES OF LOW DENSITY POLYETHYLENE/POLYPROPYLENE BLENDS

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ABSTRACT

The role of di-cumyl peroxide (DCP) as compatibilizer in low density Polyethylene/Polypropylene (LDPE/PP) blends has been explored. Mixtures with varying LDPE/PP ratio were prepared in a Brabender plasticorder and tested for their mechanical properties and calorimetric response. Then peroxide was added at concentrations up to 0.5%, and the mechanical properties of the these new blends were measured. Also, the mixing torque, melt flow index and gel content of the above products were recorded as a function of peroxide concentration. It was found that the incorporation of DCP restricts the thermoplastic characteristics of the melt, which was primarily attributed to branching which occurs in LDPE. This results in an enhancement in the adhesive bonding between the two polymers mainly due to chain entanglements. This was further supported by the fact that mechanical properties of the treated blend were significantly improved.

INTRODUCTION

Polymeric blends and alloys have attracted the interest of many researchers, as they appear to be promising materials with a broad spectrum of applications. Surprisingly, polyblends often present far better properties compared to those of their components and therefore, they display great versatility.

The synergistic effect which occurs in the mixtures of two or more polymers, is the basis for a series of new materials. For instance, the rubber toughened polymers contain small particles of elastomers dispersed into a plastic matrix. This combination displays unique properties in terms of impact strength [1].

Polymer blends have also been studied in the framework of recycling since waste materials usually contain polyolefins and vinyl polymers, and their miscibility is of great importance. It should be noted that miscibility is associated with the solubility of the components to each other, whereas compatibility is rather estimated via the overall mechanical response of the heterogeneous mixture [2].

Recent reports on polymeric blends include the effect of polypropylene contamination on the properties of recycled high density polyethylene [3] and the development of the related modeling [4]. Blends based on polyolefins containing filers or reinforcements, have also been studied [5-8]. Many parameters must be taken into consideration when predicting compatibility of the components of a blend. Such parameters are molecular weight and molecular weight distribution, rheological properties, morphology and mechanical properties [9]. However, it is common practice to use additives which are specified for improving miscibility of the components of the blend, the so called compatibilizers [10]. These additives are either chemicals acting at the interface or low molecular weight copolymers, which contain the suitable units and groups capable of promoting compatibility among the polymers of a certain mixture which otherwise would not display a synergistic effect [11, 12]. Thus, copolymers of maleic anhydride have been reported [13] along with alkyl carboxyl-substituted polyolefins [14], ethylene-co-vinyl acetate and ethylene-co-acrylic copolymers [15]. Other attempts focus on the mixing techniques and the content of compatibilizer [16, 17].

In this work, a reactive compatibilizer for blends of polyolefins was studied as an attempt to develop new means for improving properties of polymeric blends. A crosslinker, bis-α,α-dimethyl benzyl peroxide or di-cumyl peroxide (DCP), extensively used in the past for the crosslinking of polyolefins was investigated for its effect on the properties of low density polyethylene/polypropylene (LDPE/PP) mixtures when reacted with their melts. DCP has been studied during the last years and was proposed as a crosslinking agent for low density polyethylene [18-25]. Based on these data, it seemed worthy exploring the possibilities of improving properties of LDPE/PP mixtures after a crosslinking reaction which was reasonable to influence the chain interactions between the two polymers and therefore, to promote compatibility of the components of the blend.

EXPERIMENTAL

Materials

LDPE, with the trade name Alcudia, was supplied by Repsol Quimica, Spain. The density of the polymer was 0.917 g/ml and its melt flow index 7 g/10min. Similarly, the PP, supplied by Appryl (Spain), had a density of 0.905 g/ml and a melt flow index of 6 g/10min. The di-cumyl peroxide (Merck, Germany) was 98% pure.

Preparation of the Blend

A Brabender plasticorder was employed as the internal mixer for preparing the blends. The plasticorder is capable of indicating and recording the mixing torque of the melt and was adjusted at the following working parameters: temperature of mixing head: 200°C, speed: 20 rpm, time: 20 minutes. A hydraulic press equipped with the suitable molds was used for molding the mixtures obtained from the plasticorder into rectangular sheets with 3 mm thickness. Molding was carried out at 200°C and 100 atm for 5 minutes. Tensile specimens were cut from the above sheets according to ASTM D-638, with a suitable die (Zwick, Germany).

Characterization and Testing of Samples

The melt flow index of the prepared specimens was determined with a Tinius Olsen rheometer, type MFD, according to ASTM D 1238, at 190°C and 2.16 Kg load. The gel content of the blends containing DCP was determined by Soxhlet extraction with boiling toluene, for 4 hours. The procedure is described in detail in Reference 26 and provides us with information about the extent of crosslinking. The heat of fusion for the obtained blends was determined by Differential Scanning Calorimetry, using a Perkin-Elmer (Switzerland) apparatus, type DSC 4. Samples of about 10mg were used and the scan was carried out in the range 50 to 200°C at a heating rate of 10°C/min. Finally, the tensile properties of the LDPE/PP specimens were measured in a Zwick (Germany) tensometer according to ASTM D 638.

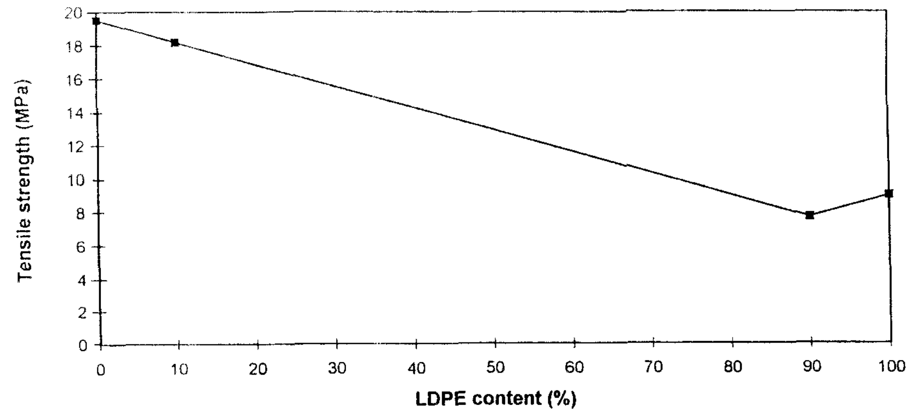


Figure 1. The tensile strength of LDPE/PP blends as a function of LDPE content.

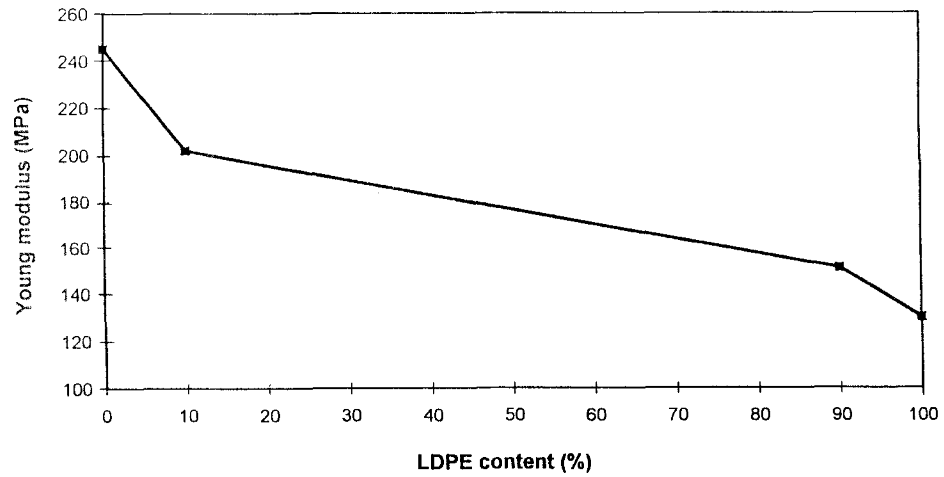


Figure 2. The Young modulus of specimens LDPE/PP blends versus LDPE content.

RESULTS AND DISCUSSION

The properties of LDPE/PP blends were first examined in terms of their mechanical and calorimetric response. The tensile strength, modulus and elongation at break as a function of LDPE content in the mixture, are shown in Figures 1, 2, and 3, respectively. From the curves of Figures 1 and 2, it can be seen that the

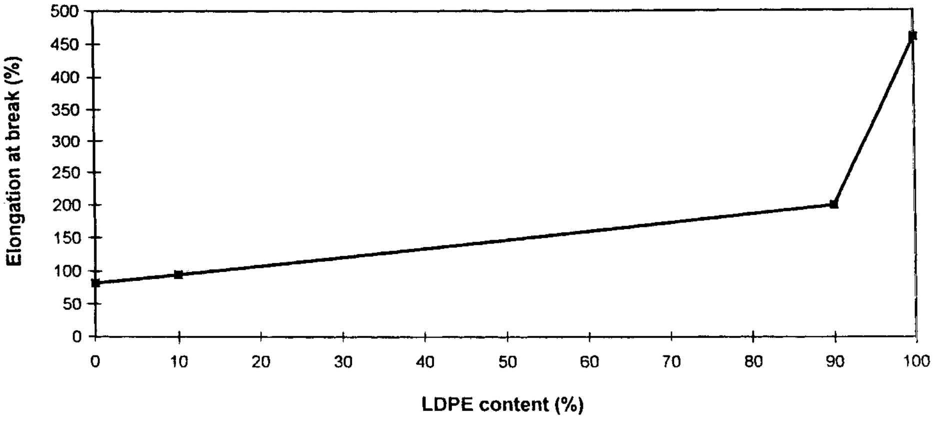


Figure 3. The percent elongation of specimens of LDPE/PP blends as a function of LDPE content.

increase of LDPE concentration in the blend causes a linear decrease in strength and modulus. Taking into account the values of these properties for pure PP and LDPE, this blend behavior seems reasonable. On the other hand, Figure 3 shows a sharp decrease of the elongation at break in mixtures containing 10% PP, compared to that of the pure LDPE. This can be attributed to the fact that a big difference in elongation between the two components of the blend, as shown in Figure 3, in combination with the poor interfacial characteristics causes debonding and therefore, the specimen breaks before its complete deformation. This is consistent with the changes of fusion heat with the blend consistency presented in Figure 4. It is again clear that the incorporation of 10% PP into the blend leads to a sharp decrease of the melting endotherm observed at fusion. This suggests that incorporation of PP into a partially crystalline polymer such as LDPE, probably causes interference in the crystallites which are dispersed in a continuous amorphous phase. Therefore, the crystallinity of LDPE is reduced, despite the expected increase due to the higher crystallinity of PP.

When di-cumyl peroxide is incorporated into the mixture of LDPE/PP during its melt blending, it decomposes to free peroxide radicals (RO•) and, therefore, chemical reactions take place leading to branching or crosslinking and chain scission (Figure 5, a and b, respectively). The overall effect of those possible processes is an increase in the mixing torque, shown in Figure 6. This torque increase, with a peroxide concentration, is accompanied with an increase of the

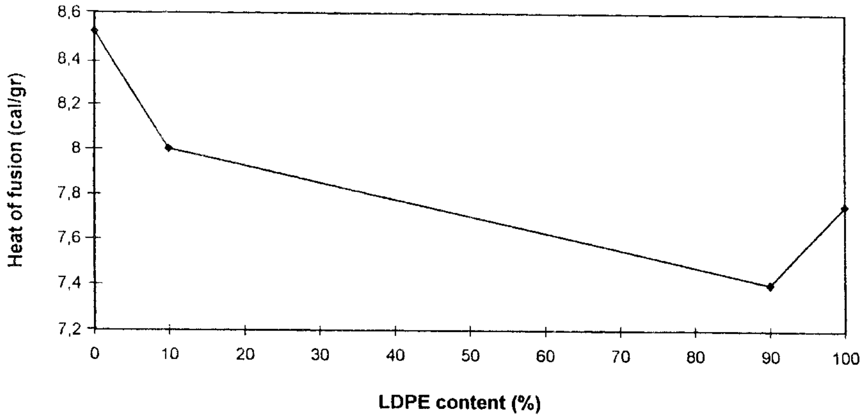
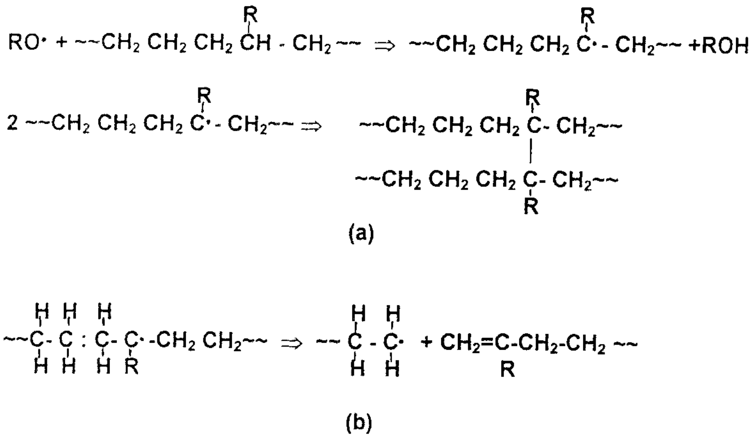


Figure 4. The fusion heat of LDPE/PP blends as a function of LDPE content.



$$RO^{\bullet} + \sim\sim CH_2\,CH_2\,CH_2\,\overset{R}{\overset{|}{C}}H - CH_2\sim\sim \Rightarrow \sim\sim CH_2\,CH_2\,CH_2\,\overset{R}{\overset{|}{C}}{}^{\bullet} - CH_2\sim\sim + ROH$$

$$2\sim\sim CH_2\,CH_2\,CH_2\,\overset{R}{\overset{|}{C}}{}^{\bullet} - CH_2\sim\sim \Rightarrow \begin{array}{l} \sim\sim CH_2\,CH_2\,CH_2\,\overset{R}{\overset{|}{C}} - CH_2\sim\sim \\ \qquad\qquad\qquad\quad | \\ \sim\sim CH_2\,CH_2\,CH_2\,\underset{R}{\underset{|}{C}} - CH_2\sim\sim \end{array}$$

(a)

$$\sim\sim \underset{H}{\overset{H}{C}} - \underset{H}{\overset{H}{C}} : \underset{H}{\overset{H}{C}} - \underset{R}{\overset{H}{C}}{}^{\bullet} - CH_2\,CH_2\sim\sim \Rightarrow \sim\sim \underset{H}{\overset{H}{C}} - \underset{H}{\overset{H}{C}}{}^{\bullet} + CH_2{=}\underset{R}{C} - CH_2 - CH_2\sim\sim$$

(b)

Figure 5. Chemical reactions initiated by DCP free radicals in polyolefin melts. (a) branching or crosslinking (b) chain scission.

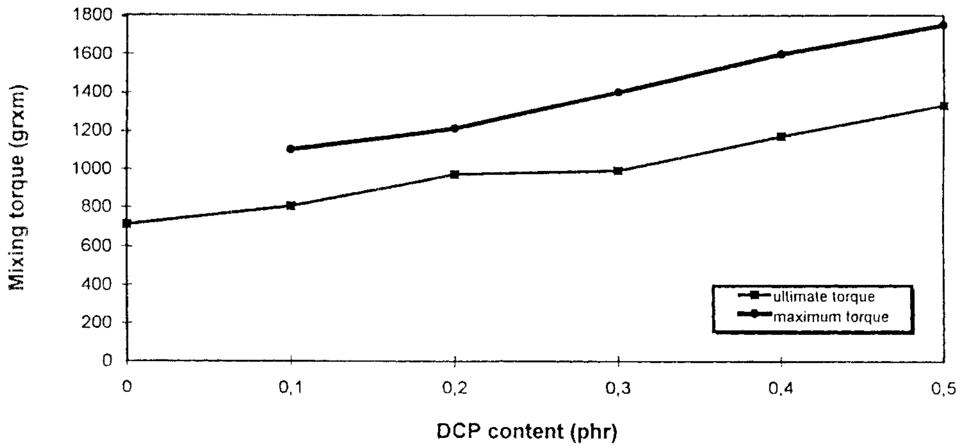


Figure 6. The mixing torque versus peroxide concentration for 90/10 LDPE/PP blend.

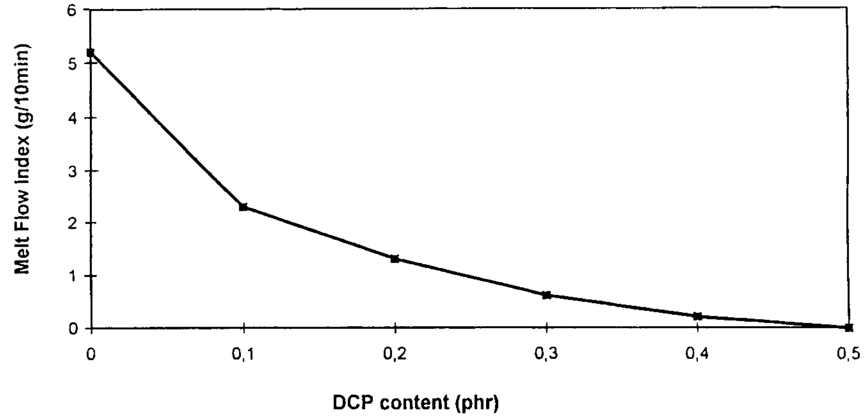


Figure 7. The Melt Flow Index as a function of DCP concentration for 90/10 LDPE/PP blend.

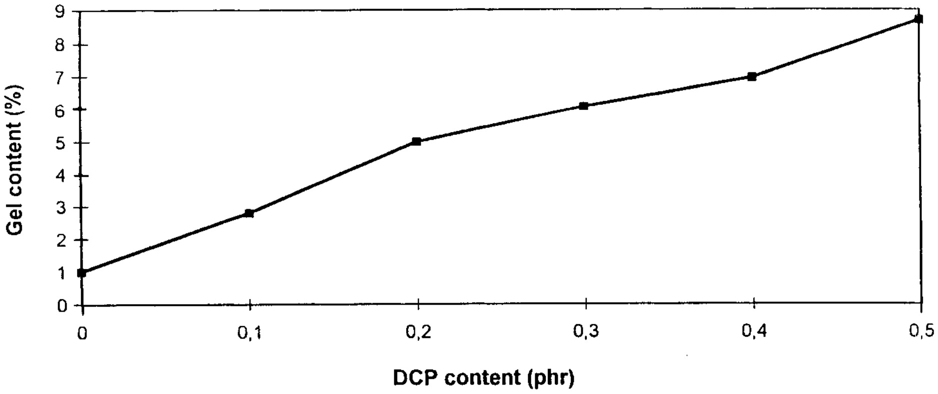


Figure 8. The gel content of 90/10 LDPE/PP blend treated with DCP.

average molecular which corresponds to the blend. Similarly, this effect is also observed by the melt flow index measurements in blends treated with various amounts of peroxide. Figure 7 illustrates a parabolic decrease of the capability of the blend to flow, as the peroxide concentration increases up to 0.5%. It should be noted that the zero flow which is shown to correspond to the blend containing 0.5% peroxide is not associated with a lack of thermoplastic characteristics of the sample, but is due to the temperature and pressure conditions that are set in the test method.

Further information about the effect of peroxide on the melt is obtained by extraction experiments which determine the gel content, as the percentage of

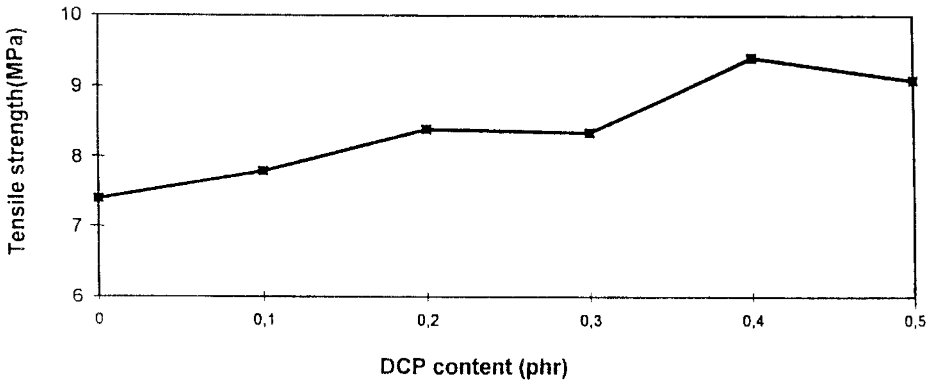


Figure 9. The tensile strength of 90/10 LDPE/PP blends as a function of DCP concentration.

insoluble matter after extraction of a sample in boiling toluene for 4 hours (see Figure 8). It is clear that almost a linear dependence of the gel content on the peroxide concentration is established, and the ultimate degree of crosslinking remains low, not exceeding 9%. The above results show that some chemical interaction takes place and since the formation of copolymer between polyethylene and polypropylene is not likely to happen [27], it is believed that branching and chain scission are the main chemical reactions in the melt.

As to the mechanical properties of blends treated with peroxide, their tensile strength, elongation and modulus are plotted versus the concentration of DCP in Figures 9, 10 and 11, respectively. The curve of Figure 9 clearly shows that the presence of the peroxide improves the strength of the blend and this effect tends to be linear with DCP concentration. Similarly, the elongation shows an increase as the percentage of peroxide increases, with the exception of the area around 0.3% ,where a decrease is recorded. This is presented in Figure 10 and was attributed to the fact of reduced results repeatability when the elongation is measured, which was already reported in the related literature [28]. As the tensile strength and elongation increase both with the peroxide concentration in specimens of the treated blend, it seemed reasonable that the Young modulus of the same specimens remains almost constant as the content of peroxide increases (Figure 11). Based on the above results, we can conclude that di-cumyl peroxide significantly improves the mechanical properties of the blend LDPE/PP of a ratio 90/10. It is also worth mentioning that the tensile

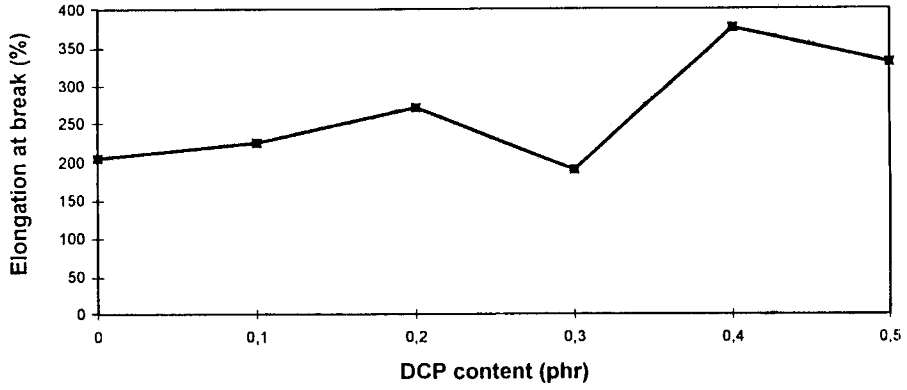


Figure 10. The elongation of 90/10 LDPE/PP blends as a function of DCP concentration.

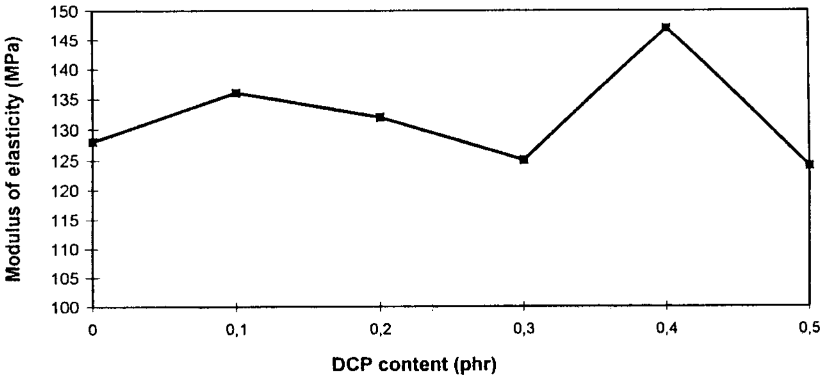


Figure 11. The Young Modulus of 90/10 LDPE/PP blends as a function of DCP concentration.

strength for peroxide concentration above 0.3% exceeds even that of the pure LPDE. This cannot be attributed to the creation of interchain bonding between the two components of the blend, but it is rather the result of the better adhesion between the two polymers due to anchorage via branching and chain entanglements. This latter fact is very important in plastic waste recycling, where impurities of polypropylene up to 10% in a stock of LDPE could be tolerated, provided that proper treatment with peroxide takes place.

CONCLUSIONS

From the above results, the following conclusions can be drawn: Dicumyl peroxide was found to be a suitable agent for promoting compatibility between the components of LDPE/PP blends. Its main function seemed to be interchain reactions within the LDPE phase, which results in branching, and network formation to a small extent. The overall effect of peroxide is the restriction of thermoplastic characteristics of the blend accompanied with significant improvement of mechanical properties which suggests better compatibility.

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