

Crosslinking of HDPE during Reactive Extrusion: Rheology, Thermal, and Mechanical Properties

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SYNOPSIS

The effect of peroxide and coagent, alone and together, on the crosslinking of HDPE during melt extrusion was studied. The melt flow index decreased rapidly with peroxide (1,3-bis(*t*-butylperoxy-isopropyl) benzene), and smoothly with trimethylolpropanetriacrylate (TMPTA), but showed a small increase with parabenzoquinone (PBQ).

Melt viscosity of 0.3 phr peroxide-treated PE responded elastically, whereas that of 0.3 phr TMPTA showed yield behavior. T_m (crystalline melting temperature) and T_c (crystallization temperature) increased with peroxide, T_m decreased, and T_c increased with TMPTA. ΔH_f (heat of fusion) increased at 0.05 phr followed by a sharp drop, more with peroxide and less with TMPTA. Hardness and preyield properties increased with TMPTA, and peroxide (except hardness) with the loss of elongation at break. The most significant improvement was obtained with impact strength, over 5 times with peroxide and 7 times with TMPTA.

When the TMPTA was used in combination with peroxide, more reduction in MI, followed by a further increase of hardness, modulus, and strength, was obtained, but impact strength was decreased below that of TMPTA alone. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Postreactor modification of polyethylene (PE) by controlled crosslinking and degradation has recently become a practical method to satisfy the growing variety of specific applications.¹ However, depending on the crosslinking process and conditions, the property change upon crosslinking is diverse. Following the earlier works,²⁻⁷ environmental stress cracking resistance, useful upper temperature limit, and strength are generally improved by introducing proper crosslinkings in PE.

PE is crosslinked in three different ways,^{8,9} that is, by high radiation, thermochemical, and moisture crosslinks. Among these, the thermochemical method is done with an added chemical, typically a peroxide. The reaction is generally carried out in

melt state and crosslinkings occur at random locations.⁸ When the crosslinking is done in an extruder, the resins are subject to shear and thermal degradation, which deteriorate the physical properties in general.

For peroxide crosslinking, additional chemicals, called coagents, are sometimes added to improve the crosslinking efficiency by preventing unwanted side reactions, such as chain scission and disproportionation.¹⁰ Typically, these coagents are reactive multifunctional monomers, and the most frequently employed ones include methacrylates and allyl compounds.

This article describes tests of the crosslinking ability of trimethylolpropanetriacrylate (TMPTA) and parabenzoquinone (PBQ) during extrusion of high density polyethylene (HDPE) in a twin screw extruder, and a comparison was made with peroxide (1,3-bis(*t*-butylperoxy-isopropyl) benzene) in regard to rheological, thermal, and mechanical properties. The effect of the coagent in the peroxide system was also tested with TMPTA.

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EXPERIMENTAL

The HDPE used in this experiment was an injection molding grade (M850, Korea Petrochemicals) with number average mol wt, $M_n = 18,600$, weight average mol wt, $M_w = 96,600$, and melt flow index, MI (2.16 kg, 190°C) = 4.8 g/10 min.

Peroxide and coagents used were 1,3-bis(*t*-butylperoxy-isopropyl) benzene, trimethylolpropane-triacrylate (TMPTA), and parabenzoquinone (PBQ). The first grade of the reagents was used without further purification.

Crosslinking was done in a twin screw extruder, with $L/D = 30$, and $D = 2.5$ cm at 230°C. Peroxide and coagent concentrations were 0.05 ~ 0.3 phr when they were used alone. The effects of coagent in the peroxide system were tested with 0.01 ~ 0.05 phr of peroxide, and with 0.1 ~ 0.3 phr of TMPTA.

Thermal properties were measured from a differential scanning calorimetry (DSC, du Pont 1090). Samples were first heated to 200°C at 20°C/min and then were cooled to room temperature. The crystallization temperature (T_c) was recorded. Crystalline melting temperature (T_m), and heat of fusion (ΔH_f) were measured during the second heating cycle.

MI of the extrudate and the injection-molded specimen was measured at 190°C, 2.16 kg of loading using a Monsanto capillary rheometer according to ASTM D1238-657. Rheometric Dynamic Spectrometer (RDS-II) with a cone-and-plate fixture was used to measure the rheological properties at 230°C, 10% strain level. Discs, measuring 2.5 cm in diameter, were compression-molded to prepare the RDS sample.

Specimens for mechanical tests were injection-molded at 230°C, and tests were made following the standard procedure in ASTM. Tensile tests (ASTM D638) were made on an Instron using an $\frac{1}{4}$ in. specimen with crosshead speed, 50 mm/min, and Izod impact test (D256) with a notched $\frac{1}{8}$ in. specimen. Flexural modulus and hardness (Rockwell) were measured following ASTM D790, and D785, respectively. The above tests were done at room temperature, and at least 5 runs were made to report the average.

RESULTS AND DISCUSSION

Rheological Properties

It is now accepted that in the process of reactive extrusion of PE degradation, as well as crosslinking,

should occur simultaneously,¹ but because of the stability of the formed polymeric radical, crosslinking seems to be the dominant reaction at ordinary conditions. However, at temperatures higher than 270°C, degradation becomes prominent for PE. The present extrusion temperature of 230°C should minimize the degradation.

Figure 1 shows that MI is decreasing rapidly with peroxide concentration up to 0.1 phr and then starts to approach zero. A similar tendency is seen with TMPTA, but MI decreases slowly with its concentration. On the contrary, MI is rather slightly increased with PBQ, and it is independent on concentration. It seems that PBQ does not exert effect on the crosslinking of PE, and the increased MI should come from the thermal and/or shear degradation of PE during extrusion. It can be seen that MI is slightly decreased by injection molding for peroxide and TMPTA, indicative of further crosslinking during injection molding.

The complex viscosity of virgin and crosslinked PE at 230°C is shown in Figure 2. It is noted that the tendency with which the viscosity increases or decreases is similar to the tendency with which the MI decreases and increases. However, another aspect is revealed in Figure 2. The viscosity function of the 0.3 phr peroxide-treated samples is nearly a straight line, which is typical of elastomeric materials.^{11,12} This implies that with 0.3 phr peroxide, the polymers may lightly be crosslinked in three dimensions in such a way that they respond elastically in melt state. The more elastic than viscous nature of the 0.3 phr peroxide-treated PE melt is also seen

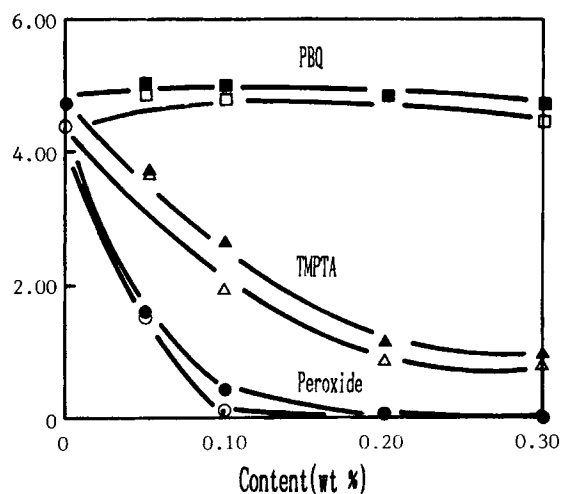


Figure 1 Melt flow index vs. peroxide or coagent concentration. (filled symbol) pellet, (open symbol) injection molded specimen.

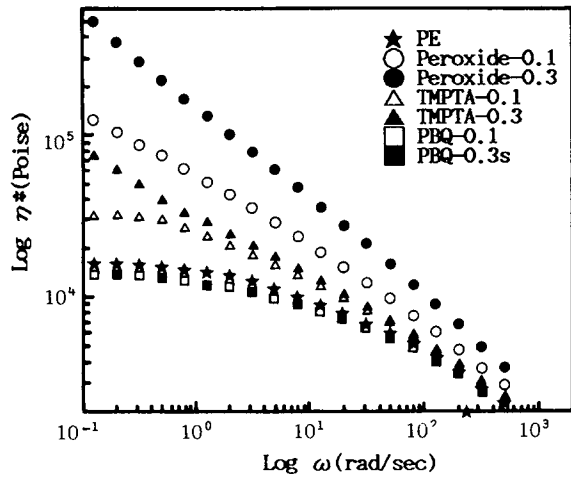


Figure 2 Complex viscosity of untreated and peroxide or coagent-treated PE's.

in Figure 3, where storage modulus (G') is slightly larger than loss modulus (G'') throughout the frequency range tested (the frequency range is not shown, but it is the same as in Fig. 2). This result may be favorably compared with others, showing G'' higher than G' at low frequencies. At the low frequencies, the deformation is mainly viscous and, hence, the value of G'' is larger than G' for the typical thermoplastics, and the opposite is typical for elastomeric materials.

The viscosity function of the 0.3 phr TMPTA-treated sample shows a yield that is unusual for homopolymer melt (Fig. 2). A yield is often observed in immiscible polymer blends and suspensions when the interactions between dispersed phases are

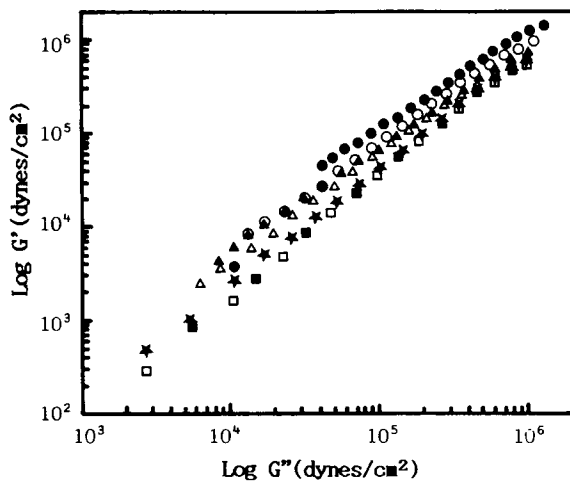


Figure 3 Storage modulus vs. loss modulus of untreated and peroxide or coagent-treated PE's (same caption as in Fig. 2).

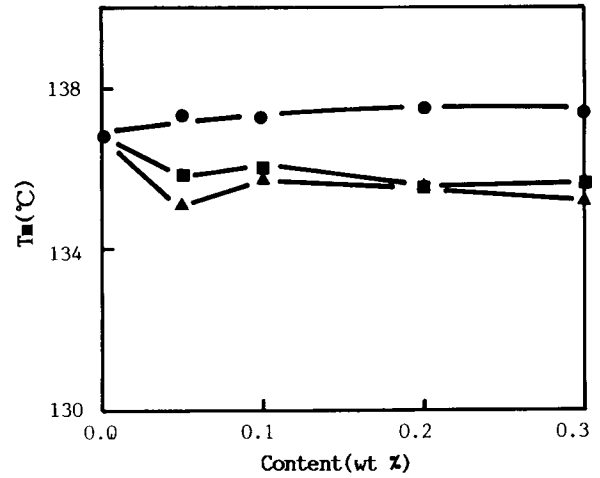


Figure 4 Crystalline melting temperature of peroxide or coagent-treated PE's (same caption as in Fig. 1).

strong, or when the concentration of the dispersed component is high enough to form agglomerates.¹³⁻¹⁵ In view of this, it may be inferred that the crosslinking is insignificant to form a three dimensional network through the mass, and it is sufficient to form a dispersed domain to form heterogeneity. With 0.1 phr TMPTA, crosslinking may be insufficient to induce yield, but sufficient to approximately double the Newtonian viscosity of PE. Viscosity is reduced with PBQ, indicating thermal degradation, perhaps in the absence of crosslinking.

Thermal Properties

T_m , T_c , and ΔH_f of the crosslinked PE are shown in Figures 4 to 6. T_m is decreased with TMPTA, and

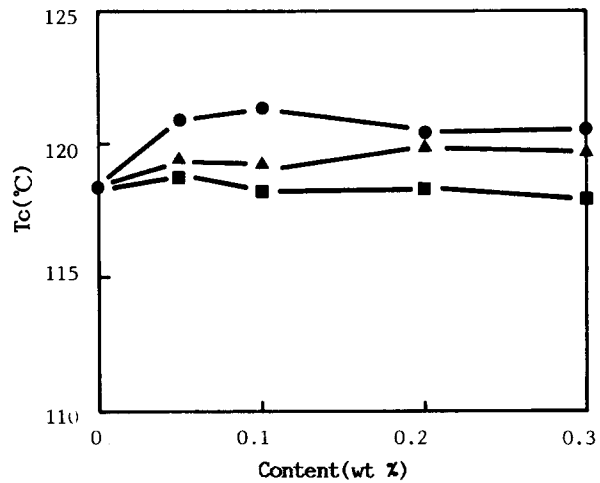


Figure 5 Crystalline temperature of peroxide or coagent-treated PE's (same caption as in Fig. 1).

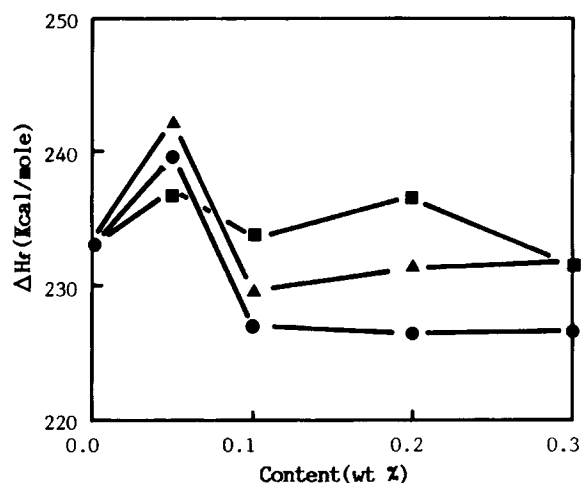


Figure 6 Heat of fusion of peroxide or coagent-treated PEs (same caption as in Fig. 1).

increased with peroxide. T_c is increased with 0.05 phr peroxide, whereafter the level stays almost constant, and T_c shows an increasing tendency with TMPTA. ΔH_f is increased at 0.05 phr peroxide and TMPTA, and drops at 0.1 phr, more with peroxide and less with TMPTA, beyond which the level is more or less maintained.

In a peroxide system, the dominant reaction is crosslinking, and T_m^3 and T_c would increase due to the restricted chain mobility. In Figures 4–6, the increase of T_m is smaller than the increase of T_c , leading to a reduced degree of supercooling (ΔT). In addition, the crosslink acts as a local defect,⁸ and this, together with the reduced ΔT , would lead to the reduction in total crystallinity,¹⁶ except at 0.05

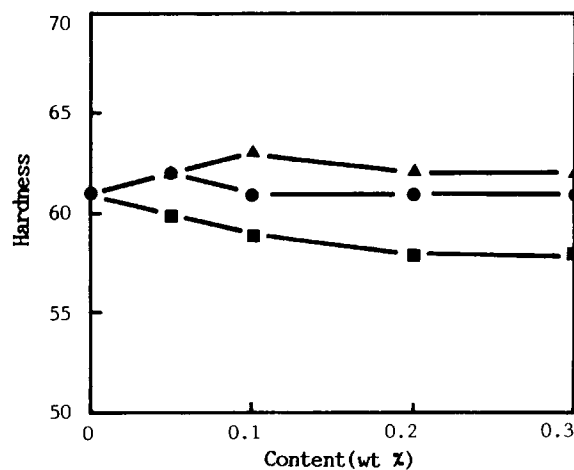


Figure 7 Hardness of peroxide or coagent-treated PEs (same caption as in Fig. 1).

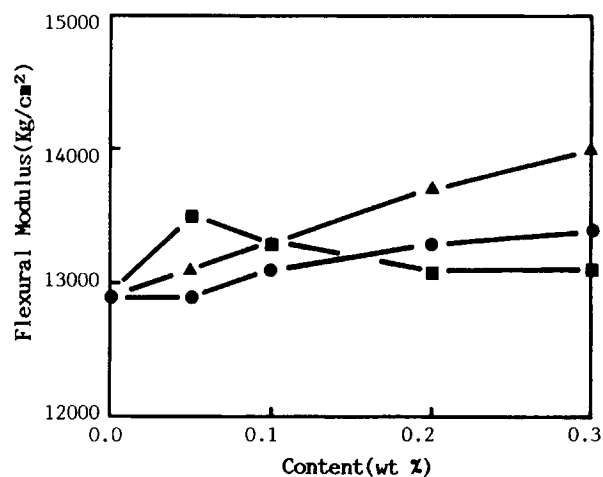


Figure 8 Flexural modulus of peroxide or coagent-treated PEs (same caption as in Fig. 1).

phr peroxide and coagent. The decrease of ΔH_f with TMPTA is smaller than the decrease with peroxide, which probably is due to the smaller crosslinking density with TMPTA. The variation of thermal properties with PBQ is insignificant.

Mechanical Properties

Hardness (Fig. 7) is slightly increased with TMPTA, and decreased with PBQ, and almost invariable with peroxide. Flexural moduli (Fig. 8) increase more with TMPTA and less with peroxide. Modulus variation with PBQ shows maximum at 0.05 phr. Yield strength (Fig. 9) increases with peroxide (more) and TMPTA (less) in a sigmoidal fashion. Elongation

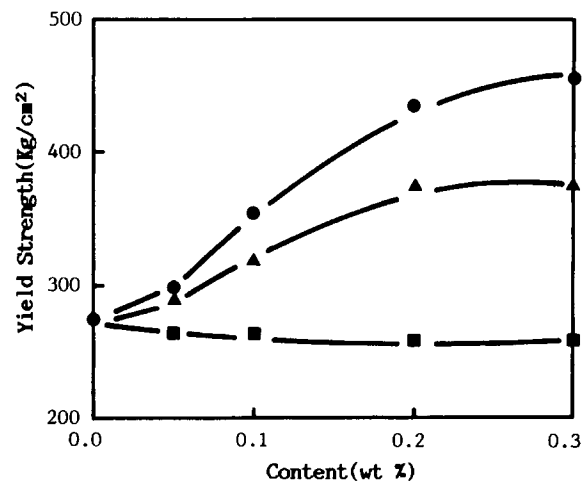


Figure 9 Yield strength of peroxide or coagent-treated PEs (same caption as in Fig. 1).

Table I Effect of Coagent on Peroxide Crosslinking of HDPE

Peroxide (phr)	TMPTA (phr)	MI (g/10 min)	Hardness (R)	IZOD (kg × cm/cm)	Flexural Modulus (kg/cm ²)	Yield Strength (kg/cm ²)	Elongation at Break (%)
—	—	4.74	61	14.8	12900	275	600 <
0.05	—	1.62	62	57.6	12900	300	20
—	0.3	0.95	62	108.4	14000	375	30
0.05	0.3	0.037	64	77.0	14400	420	30
0.01	0.1	1.78	62	90.8	13400	350	30
0.01	0.2	0.98	63	103.2	14100	390	20
0.02	0.1	0.49	61	101.1	13400	355	20
0.02	0.2	0.13	62	101.6	14200	385	20

at break (Fig. 10) drops to approach zero at 0.05 phr peroxide, and 0.1 phr TMPTA, and it is also reduced with PBQ.

The most significant improvement of mechanical properties upon peroxide or coagent treatment is seen with impact strength (Fig. 11). The notched impact strength is increased over 5 times with 0.1 phr peroxide, and over 7 times with 0.2 phr TMPTA, and it is invariable with PBQ. It should also be noted that the impact strength shows a maximum in the peroxide and TMPTA system. Upon introducing crosslinks, impact strength increases, due to the increased amorphous domain and crosslink density, providing resistance to crack propagation. However, with excessive crosslinking, the materials become brittle and lose ductility. The fact that TMPTA yielded a greater impact maximum at a higher content than the peroxide should imply that a different type of morphology is obtained. It was noted earlier

that T_m is increased with peroxide, but slightly decreased with TMPTA, which would reflect smaller crystal size for TMPTA. In PE, smaller crystal size and narrower mol wt distribution gives greater impact strength.^{17,18}

Effect of TMPTA in the Peroxide System

The primary objective in adding coagent to the peroxide crosslinking is to augment the crosslinking efficiency by preventing unwanted side reactions.¹⁰ In this work, the effect of coagent (TMPTA) in the peroxide system is shown in Table I. Independent addition of 0.05 phr peroxide, and 0.3 phr TMPTA, yielded MI of 1.62 and 0.95 (g/10 min), respectively. When these two reagents were added together, the MI approached zero (0.037). Hardness, flexural modulus, and yield strength follow essentially identical tendencies with MI, that is, more reduction in

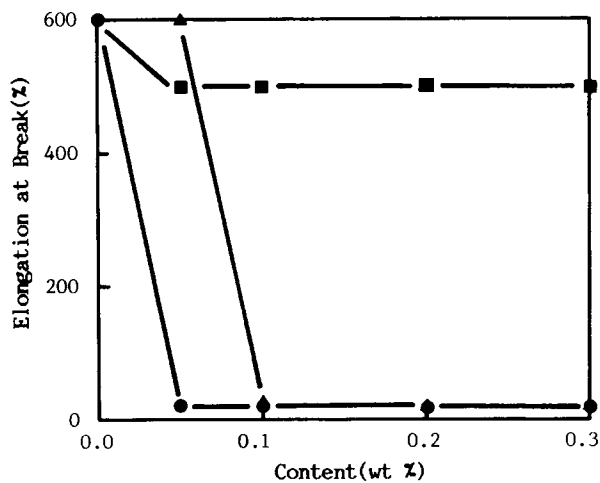


Figure 10 Elongation at break of peroxide or coagent-treated PEs (same caption as in Fig. 1).

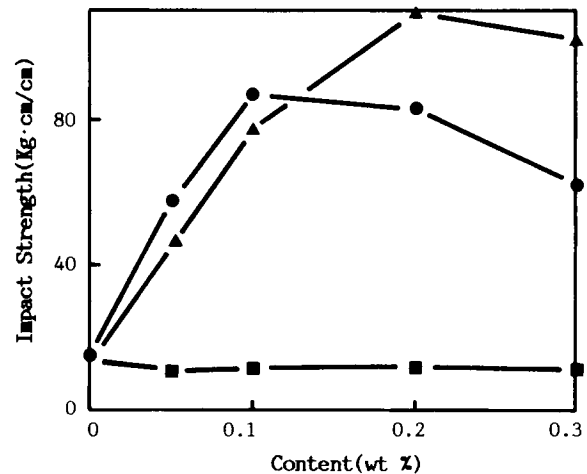


Figure 11 Notched Izod impact strength peroxide or coagent-treated PEs (same caption as in Fig. 1).

MI in the peroxide-coagent system is accompanied by more increase in modulus and strength. However, the maximum impact strength was obtained with TMPTA alone. However, with the addition of coagent, better impact improvement is obtained at lower peroxide concentration.

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Received May 12, 1992

Accepted July 27, 1992