Polym. Bull. (2011) 66:673–681
DOI 10.1007/s00289-010-0376-9

ORIGINAL PAPER

The effect of peroxide crosslinking on thermal, mechanical, and rheological properties of polycaprolactone/epoxidized natural rubber blends

Joy K. Mishra · Young-Wook Chang · Wonho Kim

Received: 4 March 2010 / Revised: 22 July 2010 / Accepted: 9 September 2010 /

Abstract Polycaprolactone (PCL)/epoxidized natural rubber (ENR) blends (PCL/ENR = 70/30, 50/50 wt/wt) were prepared by a melt mixing in an internal mixer in the presence of a small amount (0.5 and 1 phr) of dicumyl peroxide. The effect of peroxide crosslinking on thermal, mechanical, and rheological properties of the blends was investigated by means of DSC, tensile test, and small amplitude oscillating rheometer, respectively. It was revealed that peroxide crosslinking enhanced degree of crystallinity of PCL phase and its non-isothermal melt crystallization temperature. The crosslinked blends behave like a thermoplastic elastomer exhibiting high elongation-at-break and fairly good elastic recovery as well as melt processibility. From melt rheological analysis, the peroxide crosslinked blends showed more pronounced shear thinning effect and higher elasticity compared to simple blends.

Keywords PCL · ENR · Blend · Crosslinking · Mechanical properties · Rheology

Introduction

Polymer blends have been paid considerable attention for many decades as an effective and economic way to develop new polymeric materials with desirable performance properties. Recently, it was reported that the blend properties can be improved by the addition of small amount of peroxide during the melt blending or by electron beam irradiation on the blend film, which trigger the crosslinking or chain scission of the polymers. This produced a more compatible blend compared to

---

J. K. Mishra · Y.-W. Chang (✉)
Department of Chemical Engineering, Hanyang University, Ansan, Kyunggi-Do, Korea
e-mail: ywchang@hanyang.ac.kr

W. Kim
Department of Chemical Engineering, Busan National University, Busan, Korea

simple blend by strengthening interfacial adhesion between the component polymers, which improve the mechanical properties of the blends [1–8].

The non-biodegradability of the majority of the polymers is responsible for many serious environmental problems associated with their disposal. Biodegradable polymers and their blends have been concerned to overcome the environmental problems arise from the nondegradable polymers. But, elastomeric materials based on the biodegradable polymer blends are rarely reported. In our earlier communication, we reported on biodegradable elastomeric material exhibiting heat shrinkability by melt blending of polycaprolactone (PCL), one of the commercially available biodegradable plastics, and epoxidized natural rubber (ENR), a chemically modified natural rubber [9]. It was found from the study that addition of small amount of dicumyl peroxide (DCP) (1.0 phr) to the blend improved its heat shrinkability due to crosslinking. In this study, we investigated the effect of the peroxide crosslinking on thermal, mechanical, and rheological properties of the PCL/ENR blends.

Experimental

Materials and preparation of blends

Polycaprolactone was supplied by Union Carbide (TONE 787). The ENR is Epoxyprene-50 (50 mol.% epoxy group containing) purchased from Guthrie Polymer Ltd (Malaysia). DCP was procured from Aldrich.

The mixing formulations are shown in Table 1. Melt blending was carried out in Haake internal mixer at 160 °C for 8 min (within this time period mixing torque was stabilized) at a rotor speed of 60 rpm. The mixed sample was then molded (as sheet) at 180 °C for 10 min.

Characterizations

The melting temperature (T_m), heat of fusion (ΔH_m), and non-isothermal crystallization temperature (T_c) of the blend samples were determined by using differential scanning calorimeter (TA Instruments DSC 2010). Samples (10 mg) were dried completely in a vacuum oven and then used for the analysis. They were first heated from 30 to 100 °C at a rate of 10 °C min^{-1} under nitrogen atmosphere

Table 1 Blend compositions

Samples	PCL (phr)	ENR (phr)	DCP (phr)
PE5050	50	50	–
PE5050D0.5	50	50	0.5
PE5050D1.0	50	50	1.0
PE7030	70	30	–
PE7030D0.5	70	30	0.5
PE7030D1.0	70	30	1.0

and kept for 10 min at this temperature to remove prior thermal history. The samples were then cooled to −50 °C at a rate of 10 °C min^{-1} and crystallization peak temperature (T_c) was determined from the thermogram. Subsequently, the sample was reheated to 100 °C at a rate of 10 °C min^{-1} (second scan). The T_m and ΔH_m of the samples were determined from this second scan.

Tensile properties were measured using an universal testing machine (Unites Co, STM 10 E) at 25 °C at a crosshead speed 50 mm/min. At least 10 dog bone shape replica for each sample were used. Tension set was measured by stretching the specimen to 100% elongation and keeping it in that position for 10 min. The applied stress was then released and the change in length was measured after 24 h. Tension set was evaluated by the following formula

$$\text{Tension set } (\%) = (\text{Change in length}/\text{Original length}) \times 100$$

Melt rheological measurement (small amplitude oscillatory shear rheometry) was carried out by RMS 800 instrument. The dynamic oscillatory shear measurement was performed at 150 °C using a set of 25 mm parallel plate and a sample of 1–2 mm thickness. The frequency sweep was carried out at a frequency range of 0.01–100 rad/s at a strain 5%, which is within the linear viscoelastic range confirmed from strain sweep experiment.

Results and discussion

Thermal characterization of the PCL/ENR blends was carried out using DSC measurements. The heating and cooling thermograms for PCL/ENR 50/50 and 70/30 blends are shown in Figs. 1 and 2, respectively. And, the value of melting temperature (T_m), heat of fusion (ΔH_m), and associated degree of crystallinity (χ_c) as well as non-isothermal crystallization temperature (T_c) obtained from the DSC analysis are listed in Table 2. The degree of crystallinity (χ_c) of the hybrids was calculated using the heat of fusion per gram of PCL determined from DSC

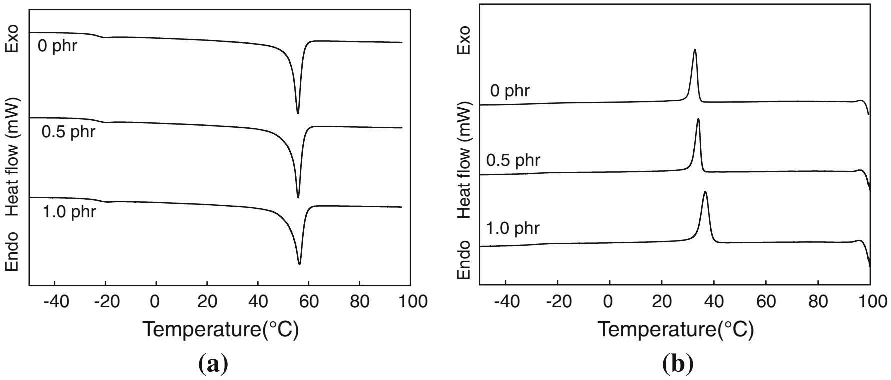


Fig. 1 DSC thermograms of PE5050 and PE5050D **a** heating scan, **b** cooling scan

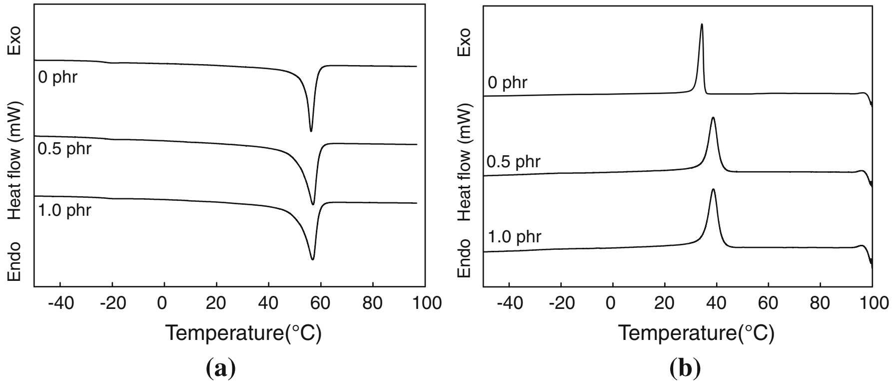


Fig. 2 DSC thermograms of PE7030 and PE7030D **a** heating scan, **b** cooling scan

measurements and the one corresponding to a 100% crystalline PCL reported by Siqueira et al. [10].

It can be seen from the second heating thermograms (Figs. 1a, 2a) that the peroxide modified blends have higher crystallinity than the simple blends, but there is marginal change in T_m for both PCL/ENR 70/30 and 50/50 blends when they are modified with peroxide. It is well known that PCL undergoes crosslinking and chain scission when a small amount of peroxide is incorporated during the melt mixing at high temperature, as depicted in Scheme 1 [1, 11]. The short chains produced by chain scission facilitate the crystallization of PCL via easy chain folding and aligning in the crystalline region, which result in the increase in its crystallinity.

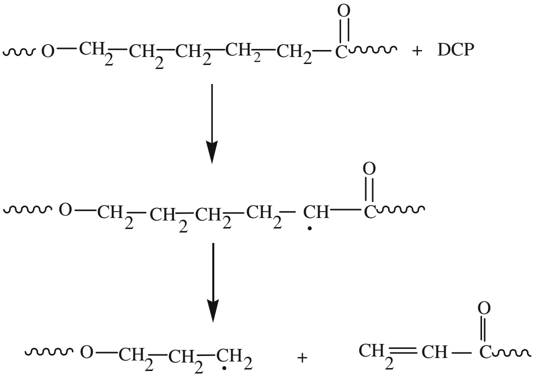
DSC cooling scans (Figs. 1b, 2b) showed that crystallization peak temperature (T_c) moved toward the high temperature for the DCP modified blends as compared to blends without DCP. For the PCL/ENR 50/50 blend, the T_c of PE5050D0.5 and PE5050D1.0 increased by 1.2 and 3.9 °C compared to that of PE5050, respectively. Such increase in the crystallization temperature was also observed in other peroxide cured semicrystalline aliphatic polyesters such as PCL, poly(butylene succinate) (PBS), and poly(butylene succinate-co-adipate) (PBAS) [11–13]. This may occur because of some substances acting as nucleating agent. So called spontaneous

Table 2 Thermal properties

Samples	T_m (°C)	ΔH_m (J/g)	χ_c	T_c (°C)
PE5050	55.7	22.2	0.283	32.8
PE5050D0.5	55.8	24.8	0.316	34.0
PE5050D1.0	56.4	26.3	0.335	36.7
PE7030	56.3	31.9	0.290	34.3
PE7030D0.5	56.9	34.0	0.309	38.7
PE7030D1.0	57.0	39.0	0.355	38.8

$\chi_c = \Delta H_m / w\Delta H_m^o$, where $\Delta H_m^o = 157$ J/g (heat of fusion for 100% crystalline PCL) and w is the weight fraction of polymer matrix in the hybrid

Scheme 1 Chain scission of PCL during crosslinking by DCP



nucleation, that is, nucleation without the intentional addition of a nucleating agent, is generally believed to be due to a foreign substances such as catalyst residues, oxidatively degraded polymer, or other processing-determined impurities whose physicochemical nature is relatively unknown. The nucleating agent should be wetted or adsorbed by the polymer and should be homogeneously dispersed in the polymer [14]. Based on this argument, it may be possible that short PCL chains, a by-product of curing reaction, or crosslink point could act as impurities that can initiate crystallization of PCL in the peroxide crosslinked PCL/ENR blends.

It can also be noted from the DSC thermograms that the melting endotherms and the crystallization exotherms of peroxide crosslinked blends are wider than the corresponding peaks of simple blends. This reflects a broad distribution of crystal sizes in the peroxide modified blends, which are supposed to be correlated with broad distribution of PCL chain length caused by chain scission during mixing in the presence of peroxide. Similar behavior was observed in electron-beam irradiated polyamide/nitrile rubber blends [6].

The tensile modulus, tensile strength, and elongation-at-break of various samples are shown in Table 3. DCP modified blends showed higher tensile strength and elongation-at-break than the simple blends. The enhancement of tensile strength and elongation-at-break in the DCP modified blends is supposed to be due to higher crystallinity of PCL phase and interchain bond between the PCL and ENR phase. The interchain bond formation is supposed to undergo during the melt blending. The

Table 3 Tensile properties

Samples	Tensile strength (MPa)	100% Tensile modulus (MPa)	Elongation-at-break (%)	Tension set (%)
PE5050	8.8 ± 0.4	3.9 ± 0.5	1500 ± 80	41
PE5050D0.5	9.1 ± 0.4	3.7 ± 0.5	1580 ± 80	26
PE5050D1.0	9.3 ± 0.5	3.4 ± 0.6	1650 ± 40	23
PE7030	18.5 ± 0.9	6.4 ± 0.4	800 ± 60	37
PE7030D0.5	20.5 ± 0.7	6.3 ± 0.4	850 ± 60	31
PE7030D1.0	23.2 ± 0.8	6.2 ± 0.3	910 ± 40	28

peroxide decomposed to $RO^\bullet$ radicals, which abstracted hydrogen from both ENR and PCL to yield free radicals. In PCL, the free radical is next to the carbonyl group, so β-scission of PCL radical occurred to yield a primary radical. The primary alkyl radicals resulting from PCL readily accessed the allylic radical of ENR to form interchain crosslinking between PCL and ENR. It can also be seen in Table 3 that there is slight decrease in tensile modulus (100% tensile modulus) for the peroxide modified blends as compared to simple blends. This is supposed to be due to the presence of short PCL chains produced by chain scission.

The tension set was measured to evaluate the effect of peroxide crosslinking on the elastic recoverability of the blends, and the results are tabulated in Table 3. It is observed that of the DCP modified blends have lower tension set value as compared to the blends without DCP, indicating that the DCP modifications improve the recoverability of the blends. It can also be seen that the blend with higher rubber content (PE5050D) showed lower tension set as compared to the blend with lower rubber content (PE7030D).

Besides mechanical properties, rheological properties in the molten state are important because they decide the applicability of various processing conditions. The melt rheological properties of the blends were investigated by the use of oscillatory rheometer. The variation of storage modulus (G') as a function of frequency (ω) of simple blends and DCP modified blends are shown in Fig. 3. It is obvious, for both PCL/ENR 50/50 and 70/30 blends, that upon DCP modification there is an increase in storage modulus, especially at low frequency region, and it is accompanied with a decrease in terminal region slope. Such lower terminal slope and higher storage modulus indicates a solid-like behavior of the peroxide modified blends, which is originated from the network structure of the blends as a consequence of the crosslinking of each phase as well as interchain crosslinking between the components in the blends. It is to be noted that, for simple blends, PE5050 have higher G' than PE7030 at entire frequency region, but upon peroxide modification, it is reversed, that is to say, the G' value of PE7030D1.0 are higher

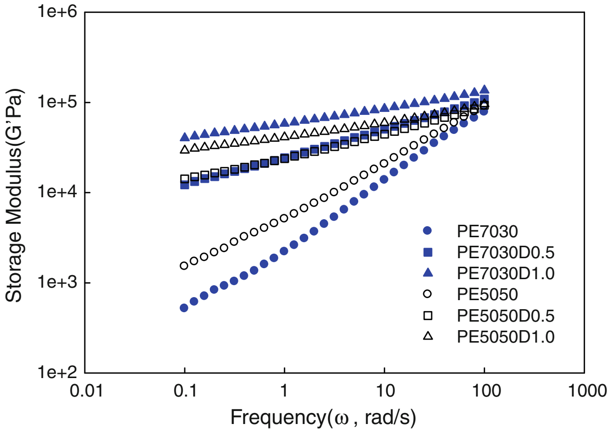


Fig. 3 Melt state storage modulus of simple blends and crosslinked blends as a function of frequency

than that of PE5050D1.0. For uncrosslinked blends, the higher G' of PE5050 than PE7030 reflects a higher elasticity of ENR rather than PCL.

Figure 4 shows the variation of complex viscosity as a function of frequency for the PCL/ENR blends with and without DCP. It can be seen that, at a given composition, the peroxide modification induced an increase in the viscosity at the low frequencies. This is due to the increased difficulty of chains disentanglement caused by the introduction of crosslinking structure in the peroxide modified samples. The simple blends as well as DCP modified blends show typical shear thinning behavior, in which viscosity decreases with the increasing frequency, which is much more pronounced for the peroxide modified blends as compared to simple blends at a given composition. In general, the shear thinning is more pronounced in the solid-like materials such as crosslinked polymer and polymer composites [15, 16]. From Fig. 4, for uncrosslinked blends, the complex viscosity of PE5050 blend is higher than that of the PE7030 blend reflecting a higher melt viscosity of ENR as compared to PCL, but for crosslinked blends, the blend with higher PCL content (PE7030D1.0) has higher viscosity than PE5050D1.0. The higher melt elasticity and melt viscosity of the PE7030D as compared to those of PE5050D, which are observed from Figs. 3 and 4, implies that the effect of crosslinking on melt flow behavior is more dominant in PCL phase rather than ENR phase.

The frequency dependences of the storage modulus (G') and loss modulus (G'') for PCL/ENR 50/50 and 70/30 blends without and with DCP (0.5 phr) are plotted in Fig. 5a and b, respectively. The figures show that, for uncrosslinked blends, loss modulus is higher than the storage modulus and beyond a certain frequency it is reversed. This indicates that up to the certain frequency the simple blends display a liquid-like behavior and exhibit solid-like behavior only when the angular frequency exceeds a critical value. On the contrary, for peroxide modified blends, storage modulus is higher than the loss modulus over the entire frequency range, clearly indicating that the crosslinked blend displays a solid-like behavior. The solid-like

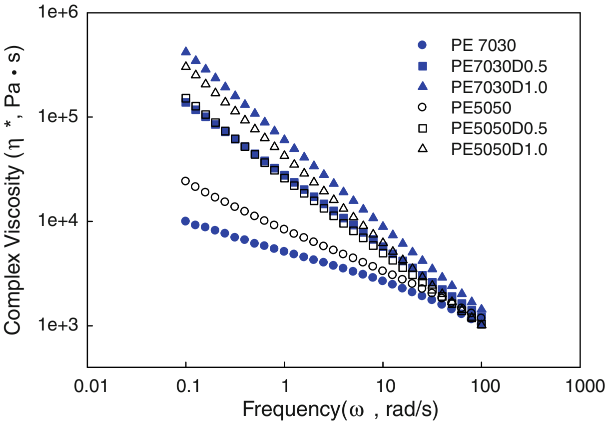


Fig. 4 Complex viscosity of simple blends and crosslinked blends as a function of frequency

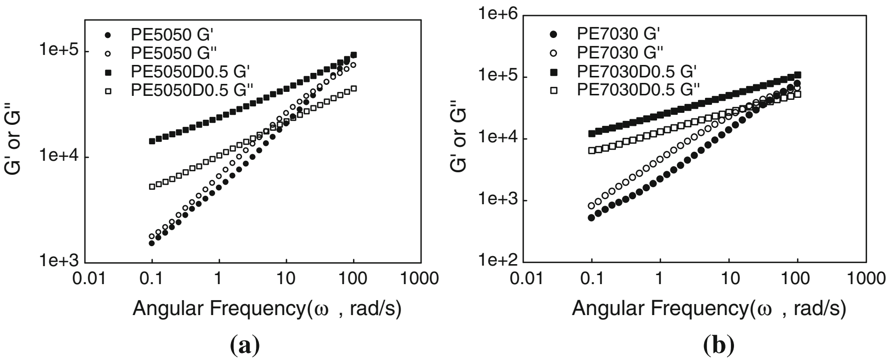


Fig. 5 Storage modulus (G', *solid symbol*) and loss modulus (G'', *open symbol*) of **a** PE5050 and PE5050D0.5, **b** PE7030 and PE7030D0.5

behavior of the peroxide modified blends in the melted state reflects the network structure induced by crosslinking.

Conclusions

New thermoplastic elastomers based on biodegradable PCL and ENR were successfully prepared by melt blending the two polymers with a small amount of DCP. The peroxide modified blends showed higher tensile strength and elongation-at-break as well as lower tension set as compared to simple blends, indicating a more elastomeric nature of the peroxide modified blend. Rheological studies revealed that the melt viscosity of the peroxide modified blend is higher as compared to simple blend in low frequency region. All polyblends show strong shear thinning behavior and the extent of shear thinning is higher in peroxide modified blends.

Acknowledgment This work was supported from Sustainable Building Research Center of Hanyang University which is supported by the SRC/ERC program of MEST (Grant R11-2005-056-04004-0).

References

1. Semba T, Kitagawa K, Ishiaku US, Hamada H (2006) The effect of crosslinking on the mechanical properties of polylactic acid/polycaprolactone blends. J Appl Polym Sci 101:1816–1825
2. Ding Z, Hu G, Wang B (2007) Effect of in-situ co-crosslinking on mechanical properties and rheology of nylon 11/EVOH/DCP composites. J Polym Res 14:511–517
3. Wang B, Ding Z, Hu G (2008) Melting behavior and isothermal crystallization kinetics of Nylon 11/EVOH/dicumyl peroxide blends. Polym Eng Sci 48:2354–2361
4. Zurina M, Ismail H, Ratnam CT (2008) Characterization of unvulcanized and dynamically vulcanized ENR-50/EVA blends. Polym-Plast Technol Eng 47:1–12
5. Wang R, Wang S, Zhang Y, Wan C, Ma P (2009) Toughening modification of PLLA/PBS blends via in-situ compatibilization. Polym Eng Sci 49:26–33
6. El-Nemr KF, Hassan MM, Ali MA (2010) Effect of electron beam irradiation on mechanical and thermal properties of waste polyamide copolymer blended with nitrile-butadiene rubber. Polym Adv Technol. doi:10.1002/pat.1497

7. Dadbin S, Frounchi M, Sabet M (2005) Studies on the properties and structure of electron-beam crosslinked low-density polyethylene/poly[ethylene-col-(vinyl acetate)] blends. Polym Int 54: 686–691
8. Kim JY, Kim OS, Kim SH, Jeon HY (2004) Effects of electron beam irradiation on poly(ethylene 2,6-naphthalate)/poly(ethylene terephthalate) blends. Polym Eng Sci 44:395–405
9. Mishra JK, Chang YW, Kim DK (2007) Green thermoplastic elastomer based on polycaprolactone/ epoxidized natural rubber blend as a heat shrinkable material. Mater Lett 61:3551–3554
10. Siqueira G, Bras J, Dufresne A (2009) Cellulose whiskers versus microfibrils: influence of the nature of the nanoparticle and its surface functionalization on the thermal and mechanical properties of nanocomposites. Biomacromolecules 10:425–432
11. Han C, Ran X, Su X, Zhang K, Liu N, Dong L (2007) Effect of peroxide crosslinking on thermal and mechanical properties of poly(ε-caprolactone). Polym Int 56:593–600
12. Kim DI, Kim WS, Lee DH, Min KE, Park LS, Kang IK, Jeon IR, Seo KH (2001) Modification of poly(butylene succinate) with peroxide: crosslinking, physical and thermal properties, and biodegradation. J Appl Polym Sci 81:1115–1124
13. Kim DI, Kang HI, Seo KH (2001) Peroxide modification of poly(butylene adipateco-succinate). J Appl Polym Sci 81:637–645
14. Zweifel H, Maier RD, Schiller M (2009) Nucleating agents for semi-crystalline polymers. Chapter 18. In: Plastics additives handbook, 6th edn. Hanser, New York
15. Sung YT, Kim CK, Lee HS, Kim JS, Yoon HG, Kim WN (2005) Effects of crystallinity and crosslinking on the thermal and rheological properties of ethylene vinyl acetate copolymer. Polymer 46:11844–11848
16. Sasmal A, Sahoo D, Nanda R, Nayak P, Nayak PL, Mishra JK, Chang YW, Yoon JY (2009) Biodegradable nanocomposites from maleated polycaprolactone/soy protein isolate blend with organoclay: preparation, characterization, and properties. Polym Comp 30:708–714