Compatibilized Blends of PVC/PA12 and PVC/PP Containing Poly(lauryl lactam-*block*-caprolactone)

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ABSTRACT: Specially designed block copolymers have played a role as compatibilizing agents in the system of immiscible polymer blends. We applied lauryl lactam (LA)–caprolactone (CL) block copolymer [P(LA-*b*-CL)] as a compatibilizing agent for immiscible poly(vinyl chloride) (PVC) blends with various polymers. These blends possess high thermal performance and toughness. We investigated the effect of P(LA-*b*-CL) as a compatibilizing agent for immiscible PVC blends with poly(ω-lauryl lactam) [polyamide 12 (PA12)]. We also described the invention of a new compatibilizing agent system involving P(LA-*b*-CL) for PVC/polypropylene (PP) blends. The mechanical and thermal properties of (1) PVC/PA12 blend compatibilized with P(LA-*b*-CL) and (2) PVC/PP blend compatibilized with P(LA-*b*-CL)/PA12/maleic anhydride–modified PP were both enhanced. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1983–1992, 2004

Key words: compatibilization; blends; block copolymers; mechanical properties; thermal properties

INTRODUCTION

There has been great progress in the past couple of decades in the understanding of compatibilization of immiscible polymer–polymer blends. Much of this work has been based on diblock copolymers in immiscible binary polymer blends. Studies of A/B binary blends with AB block copolymers date to the late 1960s with investigation of isoprene–styrene block copolymer in the system of polyisoprene (PI) and polystyrene (PS).[1] Other similar diblock systems have been investigated as compatibilizing agents in blends of homopolymers.

Subsequently, it was found that if one of the segments of a block copolymer was miscible with a second polymer, this polymer could be compatibilized with the other homopolymer. This leads to compatibilized A/C blends with A-*block*-B when block B and polymer C are miscible. Examples of this are styrene (St)–MMA and St–caprolactone (CL) block copolymers with PS and poly(vinyl chloride) (PVC).[2]

There have also been efforts to compatibilize two different polymers C and D with A-*block*-B copolymers where block A is miscible with C and block B is miscible with D. An example is a St–MMA copolymer with poly(phenylene ether) (PPE) and St-acrylonitrile copolymer (SAN).[3]

The present article involves studies of lauryl lactam (LA)–caprolactone (CL) block copolymer [P(LA-*b*-CL)], which we developed in previous investigations.[4–6] We describe two separate studies. First, we used this block copolymer to compatibilize a blend of polyamide 12 (PA12) and PVC. It is well known that poly(ϵ-caprolactone) (PCL) is miscible with PVC.[7–13] This is a case of an A-B block copolymer compatibilizing a blend of polymers A and C. Second, we used this block copolymer to compatibilize a blend of polypropylene (PP) and PVC. This is major new innovation because PP is not miscible with either segment of this block copolymer. We achieved this as described below. It is based on the concept of compatibilizing PVC/PP blends with the ternary system of P(LA-*b*-CL)/PA12/maleic anhydride (MA)–PP. The PCL block of P(CL-*b*-LA) dissolves in the PVC phase and the PA12 block dissolves in the PA12 phase. PA12 reacts with MA–PP, which dissolves in PP. We used Ide and Hasegawa's proposal[14] that MA grafted onto PP reacts with the amine end group of commercial polyamides during mechanical blending.

The blends that we describe herein are technologically important because the addition of either PA12 or PP to PVC raises its high temperature performance characteristics.

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EXPERIMENTAL

Materials

The block copolymer used in this study as a compatibilizing agent was P(LA-*b*-CL). This block copolymer

was prepared by a reactive extrusion process from our laboratory.[4–6] The number-average molecular weights (M_n) of PA12 block and PCL block in P(LA-*b*-CL) were 39,200 and 34,700, respectively. The polydispersity (M_w/M_n) of this copolymer was 2.4.

Various polymers were used for blending with PVC in the presence of P(LA-*b*-CL) as compatibilizing agent. PA12 was obtained from Ube Industries. MA–PP (Epolene G-3003) provided from Eastman Chemical was mixed with PP provided from Equistar Chemicals. The PVC used in this study was OxyVinyls 334FG provided from PolyOne and contained 3 phr of tin-type thermal stabilizer Thermolite 31-Super obtained from Elf Atochem (now Atofina).

Blending procedure

Polymer blending was performed using a Brabender Plasti-Corder laboratory internal mixer (PL 2000) to evaluate the compatibilizing effect of P(LA-*b*-CL). This apparatus consists of a chamber, rotors, and a temperature control/torque monitoring system. The mixing is performed by tangential counter-rotating rotors, which are two 40 mm diameter rotors with centerline spacing of 40 mm distance and 47 mm rotor length. The volume capacity of the internal mixer is up to 80 mL.

The PVC blends with various polymers were prepared in a wide range of compositions with and without 10 wt % of P(LA-*b*-CL) as a compatibilizing agent. The blending was performed at temperatures under 200°C with 80–100 rpm of rotor speed using a Brabender Plasti-Corder.

Characterization of blends

The morphology of the compatibilized and noncompatibilized PVC blends with various polymers was characterized using a Hitachi S-2150 scanning electron microscope (SEM; Hitachi, Ibaraki, Japan). The blended samples were frozen in liquid nitrogen and then fractured. The fracture surfaces were coated with silver metal and then SEM images were taken for these samples.

An Instron test machine (Model 4204; Instron, Canton, MA) was used to measure mechanical properties of the PVC blends with various polymers with and without the compatibilizing system. The tensile property measurements were conducted at deformation rates of 10–50 mm/min at room temperature. The polymer sheet for tensile bar was produced by a compression-molding press (Wabash Model 20) at 195°C. The tensile bar was prepared by compression cutting of the pressed sample sheets using a tensile bar-shaped cutter (specimen type V of ASTM D638). Specimens were dried in a vacuum oven for 24 h at 45°C to remove the effect of humidity. The value of results is
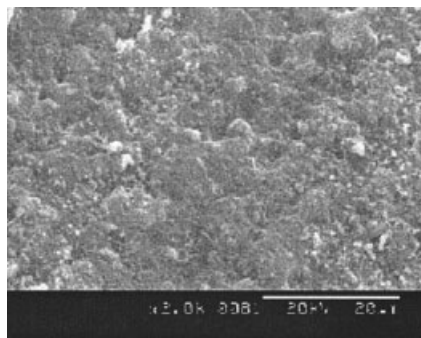
(a)
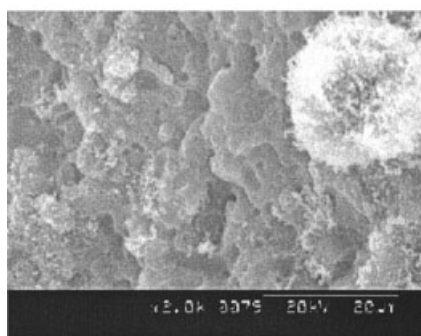
(b)

Figure 1 SEM micrographs of 4 : 1 PVC/PA12 blends: (a) compatibilized and (b) noncompatibilized with P(LA-*b*-CL).

a mean value of five tests of each sample after discarding the maximum and minimum.

The storage modulus (E') at a frequency of 1 Hz was measured as a function of temperature to evaluate high-temperature performance of PVC blends. A Rheometrics Scientific dynamic mechanical thermal analyzer (DMTA; Rheometrics, Amherst, MA) was applied in the three-point bending mode by a heating rate of 4°C/min (ASTM D 5023-94).

RESULTS

Compatibilization of the PVC/PA12 blends

Scanning electron microscopy

The morphologies of the PVC/PA12 blends with and without P(LA-*b*-CL) were studied to evaluate the effects of compatibilizer on dispersed phase size. Figure 1 shows the scanning electron microscope (SEM) image for the PVC/PA12 4 : 1 blends noncompatibilized and compatibilized with P(LA-*b*-CL). These blend systems exhibited two distinct phases because the blended polymers were generally immiscible. However, the SEM micrograph indicates that the compatibilized blend [Fig. 1(a)] has a finer morphology than
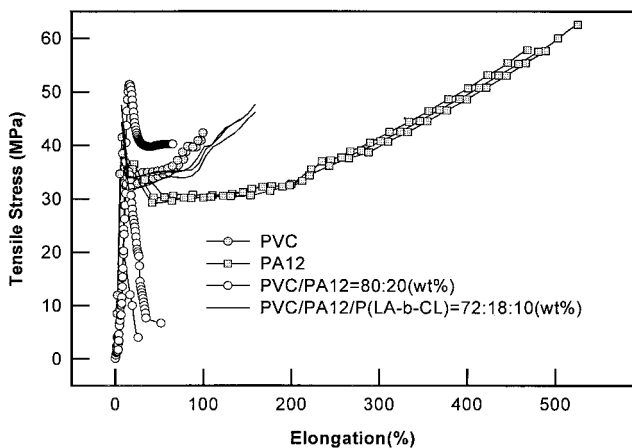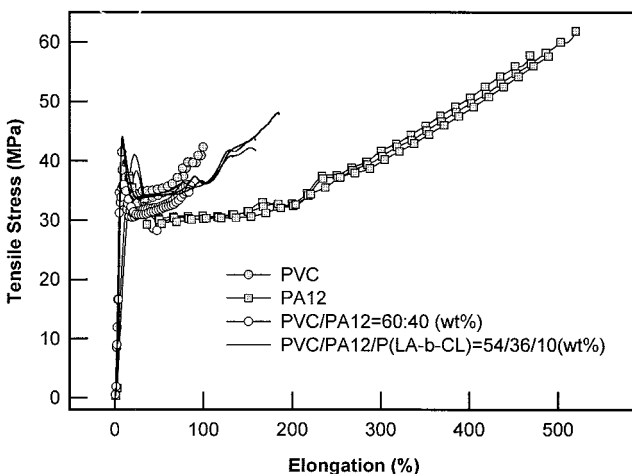
Figure 2 Engineering stress–elongation curves of the PVC/PA12 (4 : 1 wt ratio) blends with and without P(LA-*b*-CL).
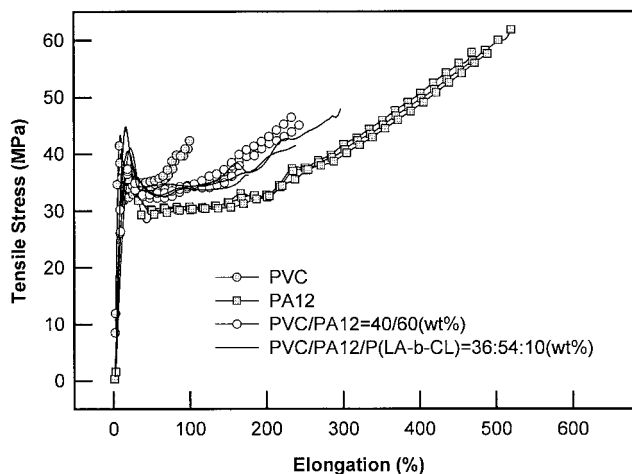

Figure 4 Engineering stress–elongation curves of the PVC/PA12 (2 : 3 wt ratio) blends with and without P(LA-*b*-CL).

that of the noncompatibilized blend [Fig. 1(b)]. The compatibilized blend has discrete phase dimensions of order 0.5 to 2 μm compared to 2 to 6 μm for the noncompatibilized blend.

Mechanical/thermal properties

The PVC including 3 phr of thermal stabilizer and PA12 were mechanically blended using Brabender Plasti-Corder at 195°C with and without 10 wt % of P(LA-*b*-CL). We carried out tensile testing to evaluate mechanical properties at room temperature. Figures 2 and 3 show the engineering stress–elongation curves for the binary PVC/PA12 blends with and without 10 wt % of P(LA-*b*-CL). PA12 has higher tensile strength and elongation than those of PVC. The binary blends of PVC and PA12 with higher PVC content (PVC-rich
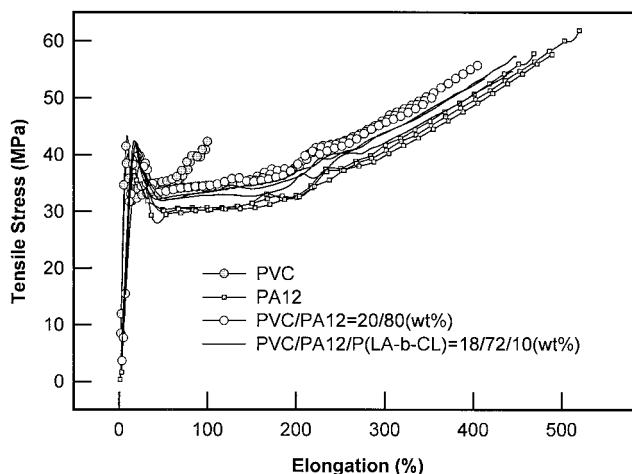
blends with 80 and 60 wt % of PVC) resulted in poor mechanical properties as shown in Figures 2 and 3. The elongation for the PVC/PA12 binary blend was far poorer than that of PVC or PA12 alone. It was reduced from 105% (PVC) and 520% (PA12) to 25% (80 : 20 PVC/PA12) and 65% (60 : 40 PVC/PA12). The PVC/PA12 binary blends with higher PVC content are more brittle. The PVC/PA12 binary blends with high PA12 content (PA12-rich blends with 60 and 80 wt % of PA12) have different mechanical characteristics compared with those of the PVC-rich blends (80 and 60 wt % of PVC). As shown in Figures 4 and 5, the PA12-rich binary blends are not brittle and exhibit ductile behavior.

The mechanical properties of the high PVC content blends were improved greatly with addition of 10 wt

Figure 3 Engineering stress–elongation curves of the PVC/PA12 (3 : 2 wt ratio) blends with and without P(LA-*b*-CL).

Figure 5 Engineering stress–elongation curves of the PVC/PA12 (1 : 4 wt ratio) blends with and without P(LA-*b*-CL).
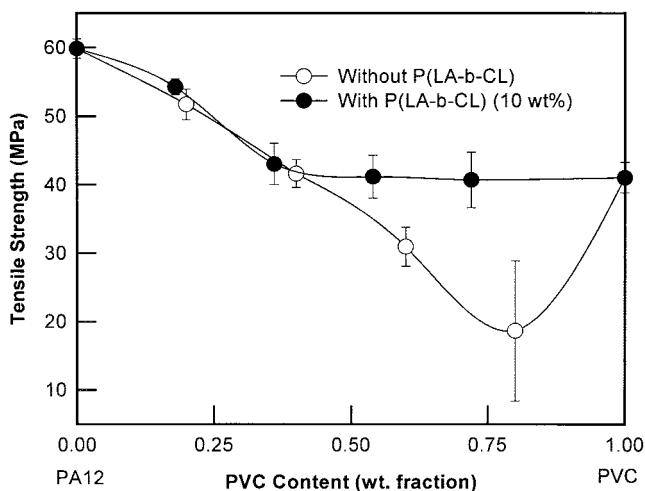
Figure 6 Plots of tensile strength of the PVC/PA12 blends with and without P(LA-*b*-CL) as a function of PVC content.

% P(LA-*b*-CL), as shown in Figures 2 and 3. The engineering stress–elongation curves of PVC/PA12/P(LA-*b*-CL) ternary blends were placed between those of PVC and PA12. The elongation to break of ternary blends containing P(LA-*b*-CL) was improved from 25% (80 : 20 PVC/PA12) and 65% (60 : 40 PVC/PA12) to 130% [72 : 18 : 10 PVC/PA12/P(LA-*b*-CL)] and 180% [54 : 36 : 10 PVC/PA12/P(LA-*b*-CL)], respectively. The mechanical properties for ternary blends containing block copolymer in PA12-rich composition also showed some improvement. The tensile strength and elongation for PVC/PA12 2 : 3 blend containing P(LA-*b*-CL) were increased from 40 MPa and 255% (PVC/PA12 binary blend) to 43 MPa and 280%, respectively. For PVC/PA12 1 : 4 blend containing P(LA-*b*-CL), the tensile strength and elongation were increased from 52 MPa and 375% (PVC/PA12 1 : 4 binary blend) to 55 MPa and 405%, respectively.

The tensile strengths for the PVC/PA12 ternary blends containing P(LA-*b*-CL) are plotted as a function of PVC content in Figure 6. For comparison, the plots of tensile strength for the PVC/PA12 binary blends are also given. The tensile strengths of PVC and PA12 were 41 and 60 MPa, whereas the tensile strengths of the PVC/PA12 binary blends by 80 : 20 and 60 : 40 wt % were 19 and 31 MPa, respectively, which indicates that binary blending of PVC and PA12 leads to poor mechanical properties. The PVC/PA12 ternary blends containing P(LA-*b*-CL) have far higher tensile strengths in PVC-rich compositions than the PVC/PA12 binary blends. The addition of P(LA-*b*-CL) (10 wt %) considerably increased the tensile strengths of 4 : 1 PVC/PA12 and 3 : 2 PVC/PA12 (PVC-rich) blends from 19 and 31 MPa to 41 and 42 MPa, respectively, but scarcely improved the tensile strengths of 2 : 3 PVC/PA12 and 1 : 4 PVC/PA12 (PA12-rich) blends, which have basically good tensile strength without addition of the block copolymer.

Figure 7 gives plots of elongation to break versus weight fraction of PVC for the PVC/PA12 binary and ternary blends containing P(LA-*b*-CL). The elongations of PVC and PA12 were about 105 and 520%, whereas those of 4 : 1 PVC/PA12 and 3 : 2 PVC/PA12 blends were about 25 and 65%, respectively. These binary blends are brittle. Addition of P(LA-*b*-CL) (10 wt %), however, increased the elongations to break of 4 : 1 PVC/PA12 and 3 : 2 PVC/PA12 blends from 25 and 65% to 130 and 180%, respectively. Particularly, the increment of elongation was remarkable in 4 : 1 PVC/PA12 blends: by addition of 10 wt % of block copolymer, a fivefold increment of elongation to break was observed. For 2 : 3 and 1 : 4 PVC/PA12 binary blends (PA12-rich), it was observed that the mechanical behavior is similar to the compatibilized blend leading to intermediate mechanical properties between PVC and PA12.

It is clear from Figures 6 and 7 that P(LA-*b*-CL) plays an important role as a compatibilizing agent in the PVC-rich blends with PA12. The values of tensile strength and elongation of the compatibilized ternary PVC/PA12/P(LA-*b*-CL) are between values of PVC and PA12. However, the values of tensile strength and elongation of the noncompatibilized binary blends are much lower than values of either PVC or PA12, confirming that their immiscibility loses inherent mechanical properties of each homopolymer.

Figure 8 gives plots of Young's modulus determined at 1% elongation versus weight fraction of PVC for the blends noncompatibilized and compatibilized with P(LA-*b*-CL). The Young's moduli of the noncompatibilized blends exhibit lower values over the entire range of compositions than those of the compatibilized blends using block copolymer. The moduli of all blends are between those of PVC and PA12. The me-
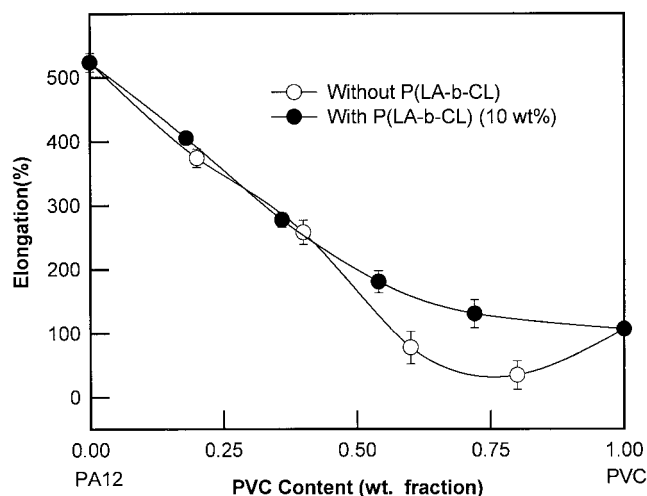
Figure 7 Plots of elongation to break of the PVC/PA12 blends with and without P(LA-*b*-CL) as a function of PVC content.
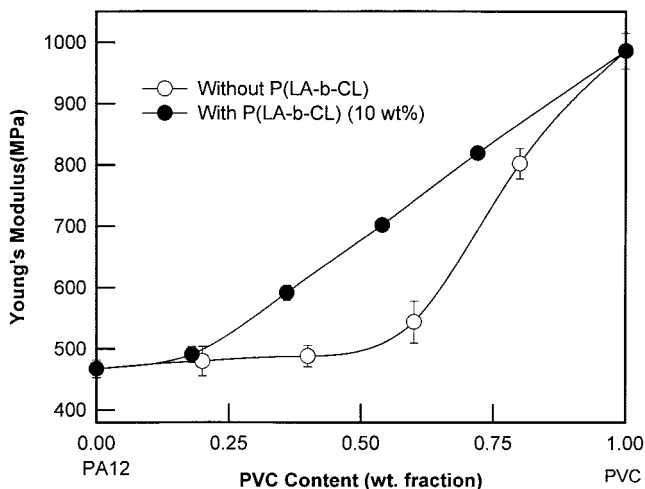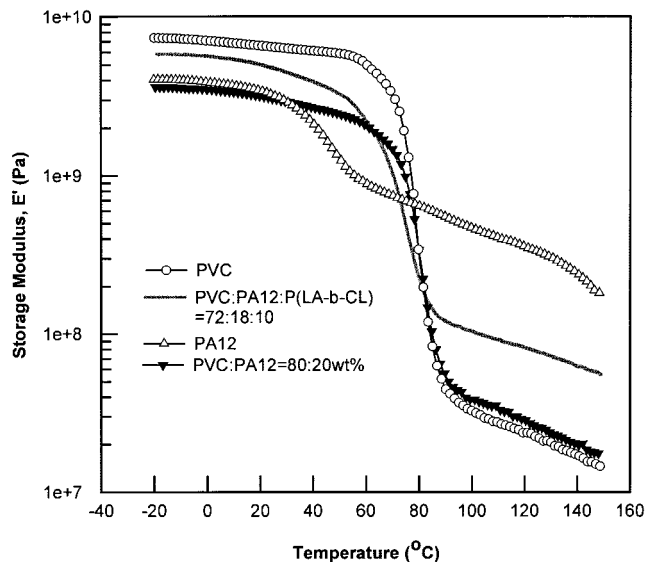
Figure 8 Plots of Young's modulus of the PVC/PA12 blends with and without P(LA-*b*-CL) as a function of PVC content.

chanical properties of the PVC/PA12 blends with and without P(LA-*b*-CL) are summarized in Table I.

We also investigated the mechanical property variation with temperature using DMTA. Figures 9 and 10 give plots of the bending storage modulus (E') versus temperature for the PVC/PA12 blends. The E' of PVC was decreased dramatically from 3500 to 35 MPa between the temperatures of 70 and 90°C, which is near the T_g, whereas the PA12 still maintained a high E' in the range of 200–800 MPa until 150°C. In Figure 9, the E' of the PVC/PA12 (80 : 20 wt %) blend without addition of P(LA-*b*-CL) shows little difference with the E' of PVC above the T_g of PVC, which indicates poor thermal performance of the binary blend. The PVC/PA12 (80 : 20 wt %) blend containing P(LA-*b*-CL) exhibits a major enhancement of the E' above the T_g of PVC. It may also be observed from Figure 9 that the E' of the PVC/PA12/P(LA-*b*-CL) ternary blend is higher

than that of PVC/PA12 binary blend at room temperature.

When we increased the weight fraction of PA12 in the PVC/PA12 binary blend to 40 wt %, the E' was slightly higher than that of PVC above its T_g, as shown in Figure 10. However, the addition of P(LA-*b*-CL) (10 wt %) in the PVC/PA12 (60 : 40 wt %) blends led to a significant improvement in the E' above the T_g of PVC.

Table II summarizes the storage moduli of the compatibilized PVC/PA12 ternary blends and PVC/PA12 binary blends at room temperature (25°C) and high
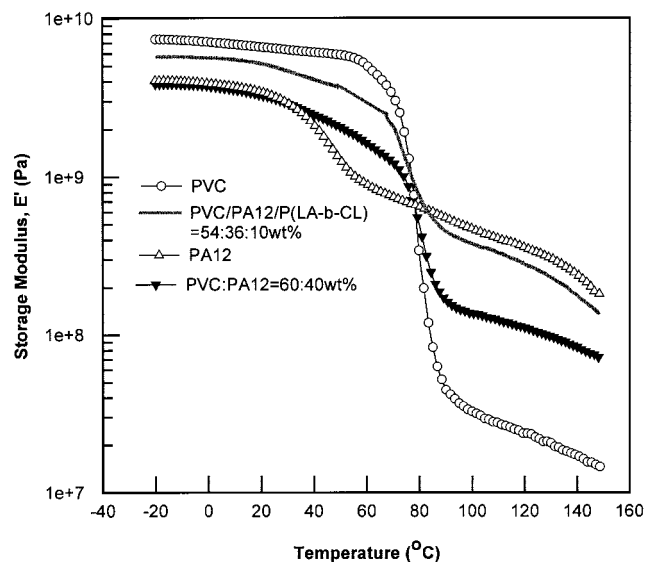

Figure 9 Dynamic mechanical behavior of the PVC/PA12 (4 : 1) blends with and without P(LA-*b*-CL) as a function of temperature.

TABLE I
Mechanical Properties of PVC, PA12, and PVC/PA12 Blends with and Without P(LA-*b*-CL)

Composition of the Blend (wt %)			Elongation to break (%)	Tensile strength (MPa)	Young's modulus (MPa)
PVC	PA12	P (LA-*b*-CL)			
100	0	0	105	41	960
80	20	0	25	19	800
72	18	10	130	41	820
60	40	0	65	31	525
54	36	10	180	42	700
40	60	0	255	40	490
36	54	10	280	43	595
20	80	0	375	52	480
18	72	10	405	55	490
0	100	0	520	60	470

Figure 10 Dynamic mechanical behavior of the PVC/PA12 (3 : 2) blends with and without P(LA-*b*-CL) as a function of temperature.

TABLE II
Storage Moduli (E') of PVC, PA12, and PVC/PA12
Blends at Room Temperature (25°C) and 120°C[a]

	E' (MPa)	
Compound (wt %)	at 25°C	at 120°C
PVC	6400	23.6
PA12	3100	360
PVC(80)/PA12(20)	3100	28.0
PVC(72)/PA12(18)/P (LA-b-CL)(10)	4700	82.4
PVC(60)/PA12(40)	3100	100
PVC(54)/PA12(36)/P (LA-b-CL)(10)	5000	275

[a] Measured by DMTA at 1 Hz of frequency and with 4°C/min of temperature increment.

temperature (120°C). The E' values of PVC and PA12 are also given for comparison. The E' of PVC at 25°C (6400 MPa) was higher than that of PA12 (3100 MPa). However, the E' of PVC at 120°C (23 MPa) was reduced by a greater degree than was the E' of PA12 (360 MPa). The E' of the compatibilized PVC/PA12 blends at 120°C was about 83 MPa for 4 : 1 ratio and 275 MPa for 3 : 2 ratio, whereas the E' of the binary blend was about 28 MPa for 4 : 1 ratio and 100 MPa for 3 : 2 ratio.

Compatibilization of PVC/PP blends

In addition to compatibilization of PVC/PA12 blends, we also sought to compatibilize PVC/polypropylene (PP) blends, with the aim of enhancing the thermal behavior of the PVC. We developed the concept of compatibilizing PVC/PP blends with the ternary system of P(LA-b-CL)/PA12/MA–PP. The PCL block of P(CL-b-LA) dissolves in the PVC phase and the PA12 block dissolves in the PA12 phase. PA12 reacts with MA–PP, according to Ide and Hasegawa's mechanism.[14] The MA–PP dissolves in PP.

We first prepared a PP-based compound of PP, MA–PP, and PA12 in the ratio of 50 : 17 : 33 wt % using an internal mixer. This is a reactive blending process for PA12 and MA–PP, which is dissolved in PP. This blending was done at the relatively high temperature of 230°C for 5 min because the reaction between the amine end group of PA12 and MA of PP preferentially occurs at this temperature. The rotor speed was 80 rpm. This compound was then blended mechanically with PVC in the presence of P(LA-b-CL). This was done at 195°C in an internal mixer for 5 min. The weight ratio of the final five-component blend was PVC(63%)/PP(13.5%)/MA–PP(4.5%)/PA12(9%)/P(LA-b-CL)(10%). This compatibilized PVC/PP blend was compared with the PVC/PP binary blend in terms of its room-temperature and elevated-temperature mechanical properties.

Scanning electron microscopy

The morphologies of the PVC/PP and compatibilized PVC/PP blends were studied to evaluate the effects of compatibilizer on the dispersed phase size.

Figure 11 shows the SEM photomicrograph for the (a) PVC(70%)/PP(30%) binary blend and (b) PVC(63%)/PP(13.5%)/MA–PP(4.5%)/PA12(9%)/P(LA-b-CL)(10%) blend. Both blend systems exhibited two distinct phases, indicating the immiscibility of the blended system. The PVC(70)/PP(30) blend has discrete phase dimensions on the order of 4 to 7 μm. The compatibilized PVC/PP blend with P(LA-b-CL)/PA12/MA–PP has smaller phase dimensions on the order of 1 to 3 μm.
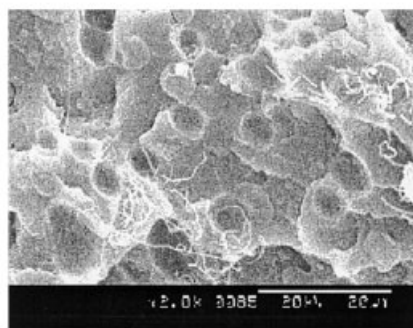
Figure 11(c) also shows the SEM photomicrograph of the PVC(70)/PP(15)/PA12(10)/MA–PP(5) blend [i.e., without P(LA-b-CL)]. The sizes of the dispersed
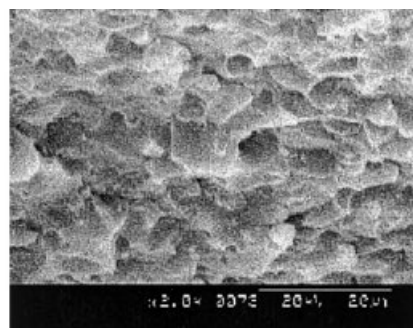
(a) PVC(70)/PP(30)
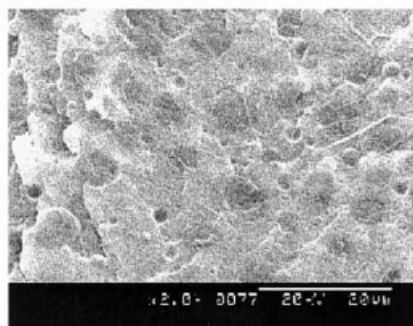
(b) PVC(63)/PP(13.5) with P(LA-b-CL)(10)/PA12(9)MA-PP(4.5)

(c) PVC(70)/PP(15) with PA12(10)/MA-PP(5)

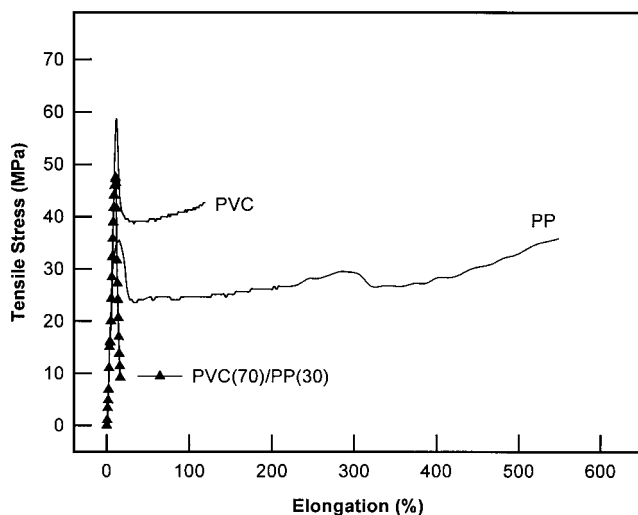**Figure 11** SEM micrographs of the PVC/PP blends with and without P(LA-b-CL)/PA12/MA–PP.

Figure 12 Engineering stress–elongation curves of PP, PVC, and PVC/PP blend.

Figure 13 Engineering stress–elongation curves of PVC/PP blends with and without ternary system of P(LA-*b*-CL)/PA12/MA–PP.

droplets were generally about 5–7 μm. With addition of P(LA-*b*-CL), the size of the dispersed domains was reduced to 1–3 μm [Fig. 11(b)].

Mechanical/thermal properties

PP has high temperature engineering performance (T_m = 170°C), whereas that of PVC is much poorer (T_g = 80°C). Figure 12 shows the engineering stress–strain curves of PVC, PP, and PVC/PP blend at room temperature. The tensile strength of PVC (42 MPa) is higher than that of PP (36 MPa). The elongation to break of PVC (100%) is lower than that of PP (550%). The mechanical behavior of the binary blend is also shown in Figure 12. It is very brittle with an elongation to break of about 3%.

The PVC/PP binary blend exhibited poor mechanical properties at room temperature, as shown in Figures 12 and 13. We carried out similar mechanical testing of compatibilized PVC/PP blend with P(LA-*b*-CL)/PA12/MA–PP.

In Figure 13 the mechanical behavior of PVC [Fig. 13(a)] and PP [Fig. 13(b)] is shown as controls. In comparison with the PVC/PP binary blend [Fig. 13(c)], the compatibilized blend [Fig. 13(d)] exhibited a significant enhancement in mechanical properties. The elongation to break of the compatibilized PVC/PP blend was about 200%, which is about two times higher than the elongation of PVC. The blending of PVC and PP with P(LA-*b*-CL)/PA12/MA–PP successfully resulted in a blend, which is superior to PVC in elongation to break. The engineering stress–elongation curve of the compatibilized PVC/PP blend is intermediate between PVC and PP.

We also carried out mechanical testing of the PVC/PP/PA12/MA–PP blend [i.e., without P(LA-*b*-CL)],
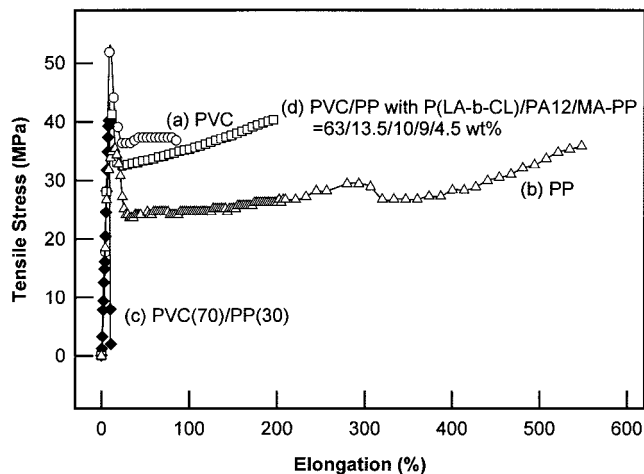
the results of which are shown in Figure 14. The PVC/PP/PA12/MA–PP blend without P(LA-*b*-CL) shows the typical behavior of an incompatible blend exhibiting poor mechanical properties. This demonstrates that P(LA-*b*-CL) plays a key role in the blend system of PVC/PP/PA12/MA–PP.

We also measured the mechanical property variation with temperature by DMTA. The E' of the compatibilized PVC/PP blend with P(LA-*b*-CL)/PA12/MA–PP was compared with the E' values of the PVC, PP, and PVC/PP blends as a function of temperature in Figure 15.

Figure 15 is a plot of E' versus temperature for the PVC/PP binary blend and compatibilized PVC/PP blend. The E' variations of PVC and PP with temperature are also given as controls. The E' of PVC de-
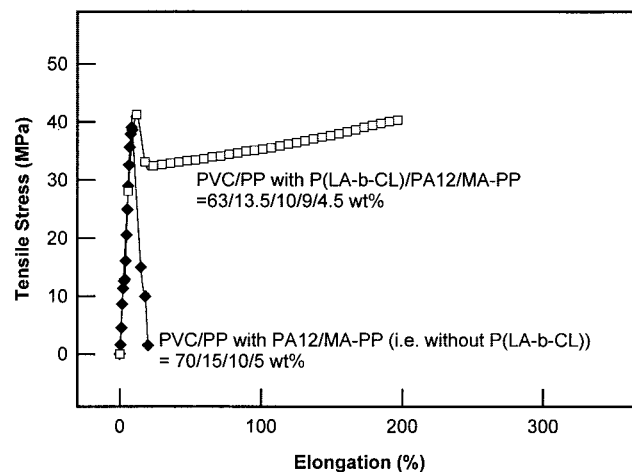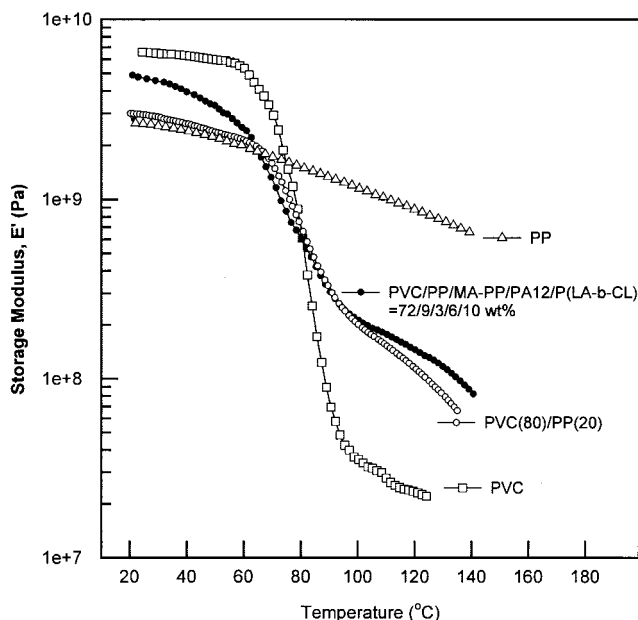

Figure 14 Engineering stress–elongation curves of PVC/PP blends with P(LA-*b*-CL)/PA12/MA–PP and with PA12/MA–PP.

Figure 15 Dynamic mechanical behavior of PVC, PP, and PVC/PP blends with and without P(LA-b-CL)/PA12/MA–PP as a function of temperature.

Figure 16 Ideal location of P(LA-b-CL) at the interface between the phases of PVC and PA12.

(LA-b-CL)(10)] at 120°C was 160 MPa, which is 50 MPa higher than that of the PVC(80)/PP(20) binary blend.

DISCUSSION

Compatibilization of the PVC/PA12 blend

Immiscible polymer blends exhibit coarse phase morphologies and poor mechanical properties, undoubtedly attributed to high interfacial tension and the lack of adhesion at the interface between the phases associated with their immiscibility. To reduce interfacial tension and improve the adhesion between separate phases, block or graft copolymers used as compatibilizing agent must be composed of the blocks or grafts that are each miscible with one of the polymer components.

We used P(LA-b-CL) as a compatibilizing agent in an immiscible blend system of PVC and PA12. This produced an A/B/(A-block-C) ternary blend. The PA12 and PCL blocks had M_n values of 39,200 and 34,700, respectively. The PCL and PA12 blocks of P(LA-b-CL) are inherently miscible with PVC and PA12, respectively. Homopolymer PVC and PCL block have a very strong thermodynamic interaction (i.e., negative interaction parameter, $\chi_{AB} \approx -0.32$). Figure 16 shows the schematic description for an ideal location of the compatibilizing agent to stabilize the interface between phases of PVC and PA12. P(LA-b-CL) would promote stability against the segregation of separate PVC/PA12 phases.

Compatibilization of the PVC/PP blend

The compatibilization of the PVC/PP blend with P(LA-b-CL) [an A/B/(C-block-D)] is more difficult because PP is not miscible with either segment of the block copolymer. We were led to develop the concept of compatibilizing PVC/PP blends with a ternary system of P(LA-b-CL)/PA12/MA–PP. MA–PP, which dissolves in PP, reacts with PA12, which dissolves in the PA12 segment of the block copolymer.
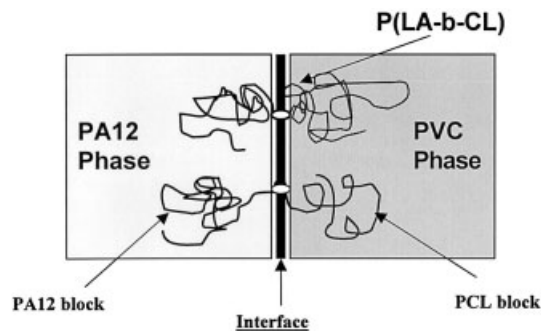
creases dramatically from 6400 MPa at 25°C to 23 MPa at 120°C, whereas PP has a value that decreases from 2800 MPa at 20°C to 700 MPa at 140°C. The E' of the binary PVC/PP blend varies from about 3000 MPa at 20°C to 55 MPa at 140°C. The five-component blend of PVC/PP/MA–PP(4.5)/PA12/P(LA-b-CL) varies from 4700 MPa at 20°C to 90 MPa at 140°C.

Table III summarizes the E' of the compatibilized PVC/PP blend and PVC/PP binary blend at room temperature (25°C) and high temperature (120°C). The E' values of the PVC and PP are also given for comparison. The E' of PVC at 25°C (6400 MPa) was higher than that of PP (2800 MPa). However, the E' of PVC at 120°C (23 MPa) was quite significantly reduced compared to that of PP (900 MPa). The E' of the compatibilized blends [PVC(72)/PP(9)/MA–PP(3)/PA12(6)/

TABLE III
Storage Moduli (E') of PVC, PP, and PVC/PP Blends with and Without P(LA-b-CL)/PA12/MA–PP at Room Temperature (25°C) and 120°C[a]

	E' (MPa)	
Compound (wt %)	at 25°C	at 120°C
PVC	6400	23
PP	2800	900
PVC (80)/PP (20)	3000	110
PVC/PP/MA–PP/PA12/P(LA-b-CL) = 72/9/3/6/10	4700	160

[a] Measured by DMTA at 1 Hz of frequency and with 4°C/min of temperature increment.

We used commercial PA12 with P(LA-*b*-CL) to compatibilize the PVC/PP blends with MA–PP. The reason we added homopolymer PA12 in our system is that one cannot expect a chemical reaction between the PA12 block of P(LA-*b*-CL) and MA-modified polymers during melt blending, as shown in the following schematic [Formula (I)]:
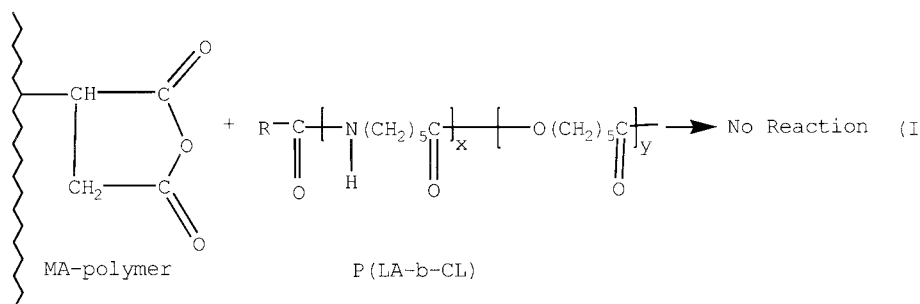
With the addition of PA12, the graft copolymer of Formula (II) is miscible with the PA12 block of P(LA-*b*-CL):
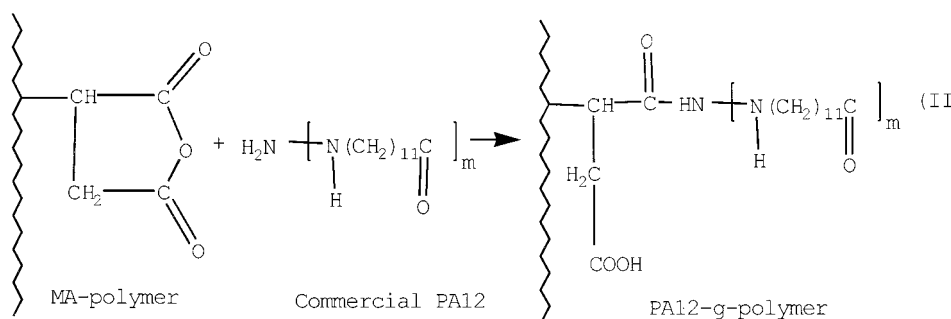
Ide and Hasegawa[14] reported a reactive blending of MA–polymer and polyamide by suggesting a reaction between the grafted MA and the amine end group of polyamide as shown in Formula (II). However, P(LA-*b*-CL) used as compatibilizing agent in this study does not contain the amine end group in the PA12 block as shown in Formula (I) because it was copolymerized using *N*-acetyl caprolactam as a coinitiator. Therefore, the reaction of MA–polymer and the PA12 unit of P(LA-*b*-CL) would not have occurred without PA12, which has an amine end group.

We thus successfully obtained the compatibilized blend by adding homopolymer PA12, which has an amine end group, in the PVC/MA–polymer/P(LA-*b*-CL) blends. Figure 17 shows a chemical description of the compatibilized PVC/PP blend with P(LA-*b*-CL)/PA12/MA–PP. The P(LA-*b*-CL)/PA12/MA–PP system plays a role as compatibilizing agent for the PVC/PP blend.

High-temperature performance

The PVC/PA12 blend compatibilized with P(LA-*b*-CL) and the PVC/PP blend compatibilized with P(LA-*b*-CL)/PA12/MA–PP exhibited a higher modulus than that of PVC and noncompatibilized blends above

T_g of PVC, as summarized in Tables II and III. We compared two compatibilized PVC/PA12 and PVC/PP blends with other thermoplastics such as poly(bisphenol A-carbonate) (PC) and poly(methyl methacrylate) (PMMA) in Table IV. PC (T_g = 150°C) has good high-temperature performance at 120°C (E' = 2000 MPa) compared with that of PP (E' = 900
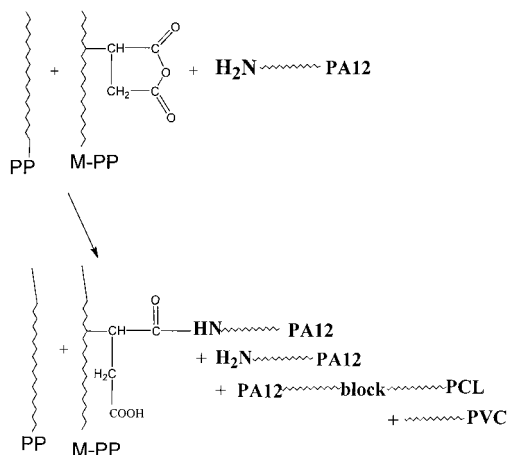
Figure 17 Chemical description of compatibilizing effect for compatibilized PVC/PP blend with P(LA-*b*-CL)/PA12/MA–PP.

TABLE IV
Comparison of Storage Moduli (E') of the Compatibilized PVC/PA12 and PVC/PP Blends with Other Thermoplastics (Order of E' Value at 120°C)[a]

Compound (wt %)	E' (MPa)	
	at 120°C	at 25°C
Poly(bisphenol A-carbonate)[b]	2000	3000
Polypropylene (PP)	900	2800
PA12	360	3100
PVC/PP/MA–PP/PA12/ P(LA-*b*-CL) = 72/9/3/6/10	160	4700
PVC/PA12/P (LA-*b*-CL) = 72/18/10	82	4700
Poly(methyl methacrylate)[b]	35	3500
PVC	23	6400

[a] Measured by DMTA at 1 Hz of frequency and with 4°C/min of temperature increment.
[b] Ref. [30], measured at 11 Hz.

MPa), PA12 ($E' = 360$ MPa), PMMA ($E' = 35$ MPa), and PVC ($E' = 23$ MPa). The E' values of compatibilized PVC(72)/PA12(18)/P(LA-*b*-CL)(10) blend and PVC(72)/PP(9)/MA–PP(3)/PA12(6)/P(LA-*b*-CL)(10) blend are 82.4 and 160 MPa, respectively, at 120°C. Both compatibilized blends have superior high-temperature performance to that of PVC and PMMA as summarized in Table IV.

For comparison with the 4 : 1 PVC/PA12 blend, the blend ratio of PVC and PP/MA–PP/PA12 was determined in 4 : 1 by weight. The storage moduli of compatibilized PVC/PA12 and PVC/PP blends are similar at room temperature. At high temperature (120°C), it was found that the E' of the compatibilized PVC/PP blend (160 MPa) is much higher than that of the compatibilized PVC/PA12 blend (82.4 MPa). This is attributed to the high E' of PP at high temperature. In comparison with E' values of PA12 and PP at 120°C in Table IV, PP exhibited a higher E' (900 MPa) than that of PA12 (360 MPa). The E' of PA12 is significantly reduced in the range between 30 and 50°C, which is around the T_g value of PA12, as shown in Figure 9.

CONCLUSIONS

We applied our LA–CL block copolymer as a compatibilizing agent for immiscible blend systems containing PVC. Our approach is based on inherent good misci-bility of PVC and PCL. We developed methods for improving high-temperature performance and toughened PVC systems by compatibilization of immiscible PVC blends. An immiscible blend of PVC and PA12 was compatibilized by P(LA-*b*-CL). The PCL block of P(LA-*b*-CL) dissolves in the PVC phase and the PA12 block dissolves in the PA12 phase. We also developed the concept of compatibilizing PVC/PP blend with a ternary system of P(LA-*b*-CL)/PA12/MA–PP. The PCL block of P(LA-*b*-CL) dissolves in the PVC phase and the PA12 block dissolves in the PA12 phase. PA12 reacts with MA–PP, which dissolves in PP.

The (i) PVC/PA12 blend compatibilized with P(LA-*b*-CL) and (ii) PVC/PP blend compatibilized with P(LA-*b*-CL)/PA12/MA–PP exhibited thermal properties superior to those of PVC with satisfactory mechanical properties. The storage moduli of these blends were much higher than the E' of PVC above the T_g of PVC. The engineering stress–elongation curves of compatibilized PVC/PA12 and PVC/PP blends were intermediate between curves of the respective components in the blend systems.

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