# Design of a Super-Ductile Polypropylene/Polycarbonate Blend with High Heat Resistance by Using Reactive Plasticizer

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**ABSTRACT:** High-performance blend of polypropylene (PP) and polycarbonate (PC) has not been explored. The difficulty is caused by the big differences in melt viscosity (PP: low viscosity vs. PC: high viscosity) and polarity (PP: nonpolar vs. PC: polar). We put forth a new approach using a reactive plasticizer which is preferentially soluble with PC and polymerizable by organic peroxide. As the plasticizer, diallyl phthalate and triallyl cyanurate (TAC) were used. By reactive extrusion of PP/PC/plasticizer/dicumyl peroxide (e.g., 80/14/6/0.12 wt. ratio), reaction-induced phase decomposition took place in the dispersed PC particles to develop a regularly phase-separated nanostructure and the graft copolymer of PP and polymerized plasticizer was *in situ* generated at the interface. The extruded blend showed an excellent ductile behavior with about 500%-elongation at break. TAC was very effective to elevate the heat resistance. Then, a super-ductile PP/PC blend with high heat resistance was successfully developed. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 443–448, 2013

## INTRODUCTION

Polypropylene (PP) is an excellent thermoplastic with nice melt processability, chemical resistance, and mechanical properties. PP is used in a wide range of applications including packaging, automotive parts, and containers. A drawback is low heat resistance, leading to a limited range of service temperature. To overcome this drawback, some researchers proposed melt blending with thermoplastics having higher heat resistance.[1–4] One of the candidates is polycarbonate (PC). However, the high-performance PP/PC alloy has not been explored. Simple melt blending renders the blends with very poor mechanical properties. In the previous study, we tried to improve the properties by changing the operation conditions of a twin-screw extruder, barrel temperature profile, screw rotation speed, and feed rate.[5] The results showed that, even in the case of low PC content, for example, for PP/PC = 80/20 (wt. ratio), the blend showed very low tensile strength, much lower than neat PP and the additive value. It implies that the tensile property of PP is sacrificed by blending with the tougher component (PC). It seems to be owing to poor dispersion of PC particles, caused by big differences both in the melt viscosity (Figure 2) and in the polarity between PP and PC.[6,7]

In this article, we propose a new approach for the design of high-performance PP/PC blend by using a "reactive plasticizer" shown in Figure 1. A typical reactive plasticizer for PP/PC system is an allylic monomer, diallyl phthalate (DAP). DAP is miscible with PC,[8] but not miscible with PP (Appendix). Then, DAP preferentially dissolves in PC phase and reduces the melt viscosity of PC particles. Then, the mismatch in melt viscosity between PP and PC phases would be circumvented to achieve the finer dispersion. When an organic peroxide is loaded, DAP will be polymerized, branched, and then crosslinked at the late stage of melt blending. The increase in molecular weight of DAP would result in the less miscibility with PC and lead to phase separation. By the reaction-induced phase separation,[8] the heat resistance of PC would not be sacrificed. Especially, when the phase separation proceeds by the spinodal decomposition mechanism, the bicontinuous structure will be formed as shown in Figure 1. It will render the higher heat resistance as the DAP polymer possesses the higher grass transition temperature ($T_g$) ($\approx$210°C)[9] than that of PC ($\approx$140°C).

Following the above strategy, we tried to develop a high-performance PP/PC blend with high heat resistance by using the reactive plasticizer. The tensile properties were measured.
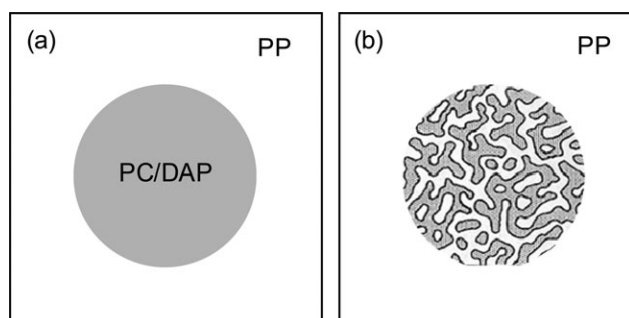
**Figure 1.** Concept of "reactive plasticizer": (a) before reaction; the lower viscosity in PC particles, plasticized by DAP would lead to the finer dispersion and (b) after reaction; a bicontinuous morphology generated by the reaction-induced phase decomposition in PC particles.

Morphology was observed by transmission electron microscopy (TEM). The structure–property relationship is discussed with the aid of dynamic mechanical analysis (DMA).

## EXPERIMENTAL

All raw materials in this study were commercially available ones. PP was obtained from Sumitomo Chemical (Tokyo, Japan): Noblen H-501 ($M_w$: 460,000, MFR: 6.8 g/10 min at 230°C/2.16 kgf). PC was from Teijin Chemicals (Tokyo, Japan): Panlite L-1225WX ($M_v$: 19,700). Two allylic monomers were used: DAP supplied by Kanto Chemical (Tokyo, Japan) and tri-allyl cyanurate (TAC) by Wako Pure Chemical Industries (Osaka, Japan). Dicumyl peroxide (DCP) was supplied from Nihon Oil and Fat (Tokyo, Japan): Percumyl D (1 min half-life period temperature: 175°C).

The melt viscosity was measured at various temperatures using a capillary flow meter, Capirograph 1D (Toyo Seiki, Tokyo, Japan).

Compositions of four component systems, PP/PC/DAP blends loaded with DCP, are summarized in Tables I and II. These were prepared as follows. PC powder was first mixed with DAP manually in a plastic bag at room temperature. The mixture was left overnight so that DAP was absorbed in PC powder. Then, DCP and PP pellets were added to the plastic bag and blended manually with the PC/DAP mixture before melt blending. Melt blending was carried out using a corotating parallel four-screw extruder, KZW-15-45MG-NH(-700) (Technovel, Oasaka, Japan) with screw diameter $D = 15$ mm and $L/D = 45$;

**Table I.** Compositions of Four-Component Systems

| Run no. | PP | PC | DAP | DCP* |
|---|---|---|---|---|
| | (wt. ratio) | | | (phr) |
| 1 | 80 | 20 | – | – |
| 2 | 80 | 18 | 2 | 0.04 |
| 3 | 80 | 16 | 4 | 0.08 |
| 4 | 80 | 14 | 6 | 0.12 |
| 5 | 80 | 14 | 6 | – |
| 6 | 80 | 14 | 6 | 0.30 |

**Table II.** Compositions of Four-Component Systems, Using TAC as Allylic Monomer

| Run no. | PP | PC | TAC | DCP |
|---|---|---|---|---|
| | (wt. ratio) | | | (phr) |
| 7 | 80 | 14 | 6 | – |
| 8 | 80 | 14 | 6 | 0.12 |
| 9 | 80 | 14 | 6 | 0.30 |

$L$ being the screw length. The screw speed was set at 200 rpm. The barrel temperature was at 250°C. The extruded strands were cooled in a water bath, pelletized, and dried in vacuum at 80°C for 12 h. Injection molding of the dried pellets was carried out by an injection machine (NP7 Real Mini, Nissei, Nagano, Japan) by setting the barrel temperature at 230°C to obtain the dumbbell specimen having stripe part of 2 mm thickness and 4 mm width (JIS-SA type) for tensile test and the bar specimen of 4 mm thick/10 mm width/80 mm length for heat deflection temperature (HDT) measurement.

The uniaxial tensile test was carried out at room temperature using a tensile tester AG-100kNG (Shimadzu, Kyoto, Japan) at a crosshead speed of 100 mm/min. HDT was estimated by a HDT tester, 6M-2 (Toyo Seiki) at flat-wise mode under a load of 0.45 MPa at a heating rate of 120 K/h. The HDT is the temperature at which the specimen distortion increases to 0.34 mm during the heating process.

Morphology was observed under a TEM (JEM-2100F, JEOL). TEM was operated at an acceleration voltage of 200 kV. For the TEM observation, the sample was picked up from the core part of molded dumbbell specimen, microtomed at −120°C to an ultra-thin section of 70 nm thick, and then stained by ruthenium te-troxide ($RuO_4$) in the gas phase at room temperature for 10 min.

To evaluate the thermal property of ternary system (without PP), PC/DAP/DCP and PC/TAC/DCP systems, DMA was performed on RSAIII (TA Instruments—Waters LLC) in a tensile mode. The storage modulus ($E'$) and the loss modulus ($E''$) were measured at a frequency of 1 Hz and heating rate of 2 K/min as a function of temperature from 35 to 230°C.

## RESULTS AND DISCUSSION

The melt viscosity of plasticized PC is shown in Figure 2 as a function of temperature at a fixed shear rate (1220 s$^{-1}$). The melt viscosity clearly decreased with increasing DAP content. All PC/DAP mixtures were transparent at all measurement temperature range. Similar results were also obtained for PC/TAC blends. Thus, these imply that DAP and TAC are soluble in PC and these act as the plasticizer. Melt viscosity of PC/DAP = 80/20 mixture is nearly equal to that of PP at 250°C (extrusion temperature), suggesting that the problem of viscosity mismatch could be solved by the plasticizing.

Figure 3 shows stress–elongation curves of the four-component alloys in Table I. Curves (c) and (d) show a nice cold drawing after the yield point like PP, keeping the stress level constant. In contrast, at curves (a) and (b), the stress after yielding point
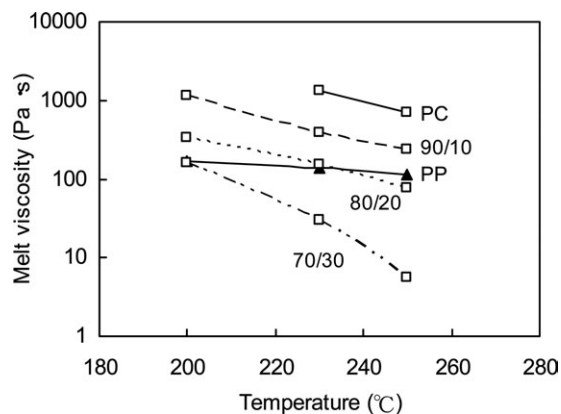
Figure 2. Melt viscosity of PP and plasticized PC as a function of temperature at a fixed shear rate (1220 s$^{-1}$).
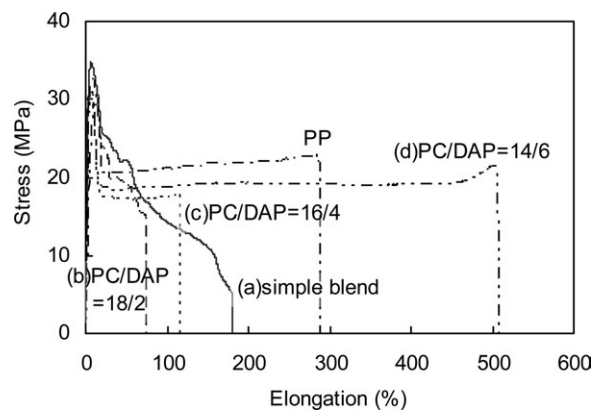


Figure 3. Stress–elongation curves of (a) simple blend (run 1)*, (b) PC/DAP = 18/2 (run 2)*, (c) PC/DAP = 16/4 (run 3)*, and (d) PC/DAP = 14/6 (run 4)*. (*) in Table I.

gradually decreases. The stress decline was caused by the delamination. A thin film delaminated from the surface broke off at the necking position and the next delaminated film broke off. After repeating several times, the whole dumbbell specimen broke. The results, curves (c) and (d), show that by adding DAP more than 4 wt % (20 wt % for PC), a nice plasticizing effect is achieved. Especially, when 6 wt % (30 wt % for PC) of DAP is loaded, the PP/PC blend shows an excellent ductile behavior with 500%-elongation at break. Such ductile behavior is expected to be attained by the size reduction with the aid of plasticizer. The improvement may owe to the enhanced interfacial strength as will be discussed later.

Figure 4 shows the TEM micrographs of the four-component systems. Symbols (a)–(d) in Figure 4 corresponds to those in

Figure 3, that is, TEM (a) in Figure 4 is for the blend of curve (a) in Figure 3, and so on. As expected, the ductile systems, (c) and (d) in Figure 3, have the finer PC particles as shown by TEM pictures (c) and (d) in Figure 4. In addition to the size effect, one should take into account of the enhanced interfacial strength, as will be discussed later.

Figure 5 is an enlarged and brighter image of Figure 4(d). Inside the PC particles, a regularly phase separated structure with periodic distance of 20 nm is clearly seen. The regular nanostructure should be generated by the reaction-induced spinodal decomposition.

Another interesting point may be the interfacial region stained more deeply. It would be assigned to the interfacial segregation.
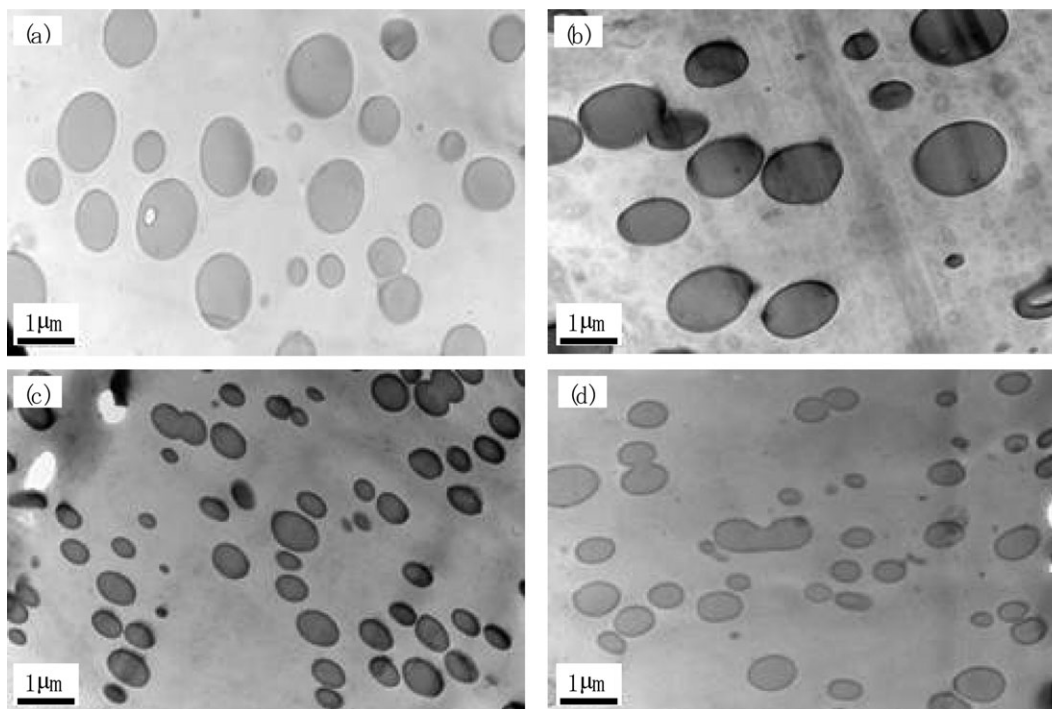


Figure 4. TEM micrographs: (a) PP/PC/DAP/DCP = 80/20/0/0, (b) PP/PC/DAP/DCP = 80/18/2/0.04, (c) PP/PC/DAP/DCP = 80/16/4/0.08, and (d) PP/PC/DAP/DCP = 80/14/6/0.12 systems.
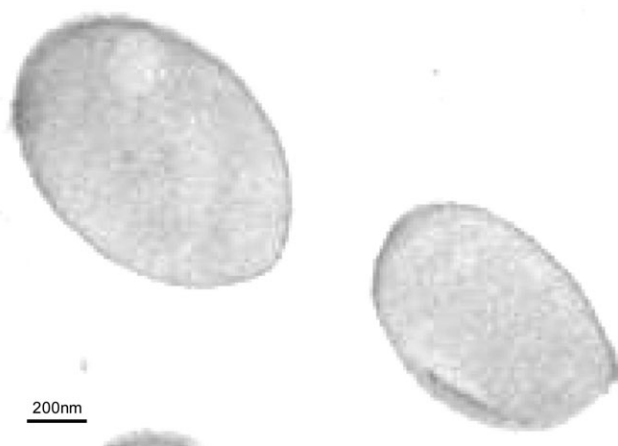
**Figure 5.** The brighter image of Figure 4(d).

That is, the polymerized DAP turned to be less miscible with PC and segregated to the interface between PC and PP. The unreacted allyl groups of the segregated polymer DAP may react with PP radicals formed by chain scission to generate PP–poly DAP graft copolymers at the interface.

Figure 6 shows the effect of DCP content on the stress–strain behavior. Without DCP (0 phr), the delamination occurred. When DCP was loaded too much (0.3 phr), the blend was very brittle. At the intermediate content of DCP, the ductile blend was prepared.

Figure 7 shows the TEM micrographs of the blends in Figure 6. When DCP was added too much, the PC particles are very large [Figure 7(c)]. The failure of the size reduction may be owing to the drastic decrease in the molecular weight of PP. The drastic chain scission by adding too much peroxide results in a serious decrease in melt viscosity of matrix, and this renders less power for the break-up of the dispersed particles during melt mixing. In contrast, without DCP the PC particles are finely dispersed [Figure 7(a)]. However, this system shows poor tensile behavior accompanied with the delamination (curve (a), [Figure 6]). The delamination may be caused by the poor interfacial adhesion without graft copolymer formation.
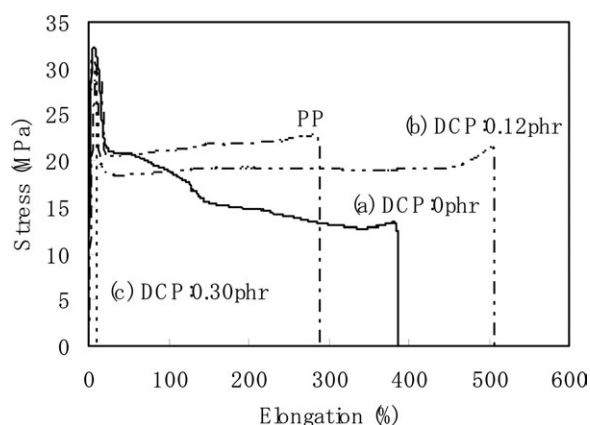


**Figure 6.** Stress–elongation curves of PP/PC/DAP/DCP = 80/14/6/$\alpha$ systems. $\alpha$ was varied: 0 phr (run 5)*, 0.12 phr (run4)*, and 0.30 phr (run6)*. (*) in Table I.
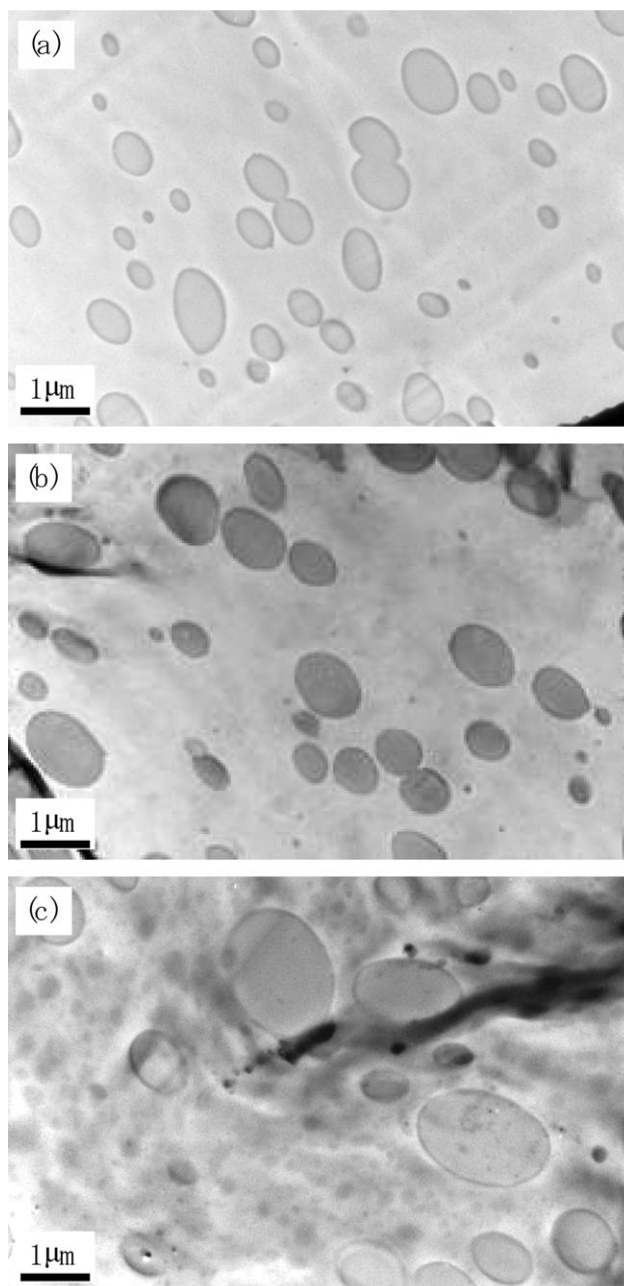


**Figure 7.** TEM micrographs: (a) PP/PC/DAP = 80/14/6 (without DCP), (b) PP/PC/DAP/DCP = 80/14/6/0.12, and (c) PP/PC/DAP/DCP = 80/14/6/0.30 systems.

To be discussed is the polymerization of DAP in PC phase really proceeds or not during reactive blending. Figure 8 shows the results of DMA analysis of PC/DAP/DCP ternary systems. Before a heat treatment at 200°C for 5 min, $T_g$ of PC/DAP mixture appears at around 40°C, showing the plasticizing effect of DAP. After the heat treatment, the $T_g$ ($E''$ peak temperature) elevates to around 110°C. It clearly suggests the increase in molecular weight of DAP, that is, the polymerization. As the $T_g$ of fully cured DAP is around 210°C,[9] the $T_g$ around 110°C implies that the polymerization and curing may not be completed in the limited heat treatment. In addition to the $E''$ peak at 110°C,
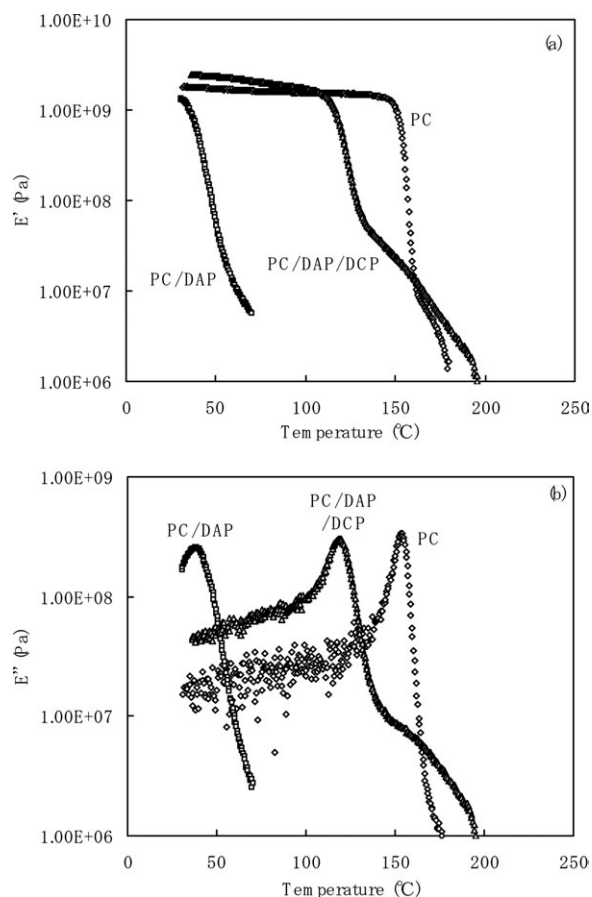
**Figure 8.** The dynamic storage modulus $E'$ and the loss modulus $E''$ as a function of temperature.



**Figure 9.** $E'$ and $E''$ of PC/TAC systems cured at 200°C for 5 min.

an $E''$ shoulder is seen around 170°C. The shoulder could be assigned to the higher $T_g$ phase which may consist of high-molecular-weight DAP polymer and PC. Thus, the DMA results may suggest the phase separation induced by the polymerization of DAP.

If DAP is replaced by the triallylic component, TAC, the higher degree of curing is expected. Actually, it is reported that TAC is more reactive than DAP.[10] Figure 9 shows the results of DMA analysis of a TAC system. Compared with DAP system, $T_g$ appears at the higher temperature. The rubbery plateau above $T_g$ is observed more clearly than the DAP system, suggesting the higher degree of curing. Also in this $E''$ curve, an $E''$ shoulder is seen around 200°C in addition to the $E''$ peak at 150°C. The result may suggest the reaction (polymerization)-induced phase separation.

Figure 10 shows the stress–elongation curves of PP/PC/TAC/DCP systems. The results are almost the same as shown in Figure 6; that is, at an appropriated amount of DCP loading, a ductile blend is nicely developed.

Figure 11 is a high-magnification TEM micrograph of the PP/PC/TAC/DCP system, exhibiting the ductile behavior (Figure 10). The regularly phase separated nanostructure is seen in PC particle. Also, the interfacial segregation is seen. Note that the
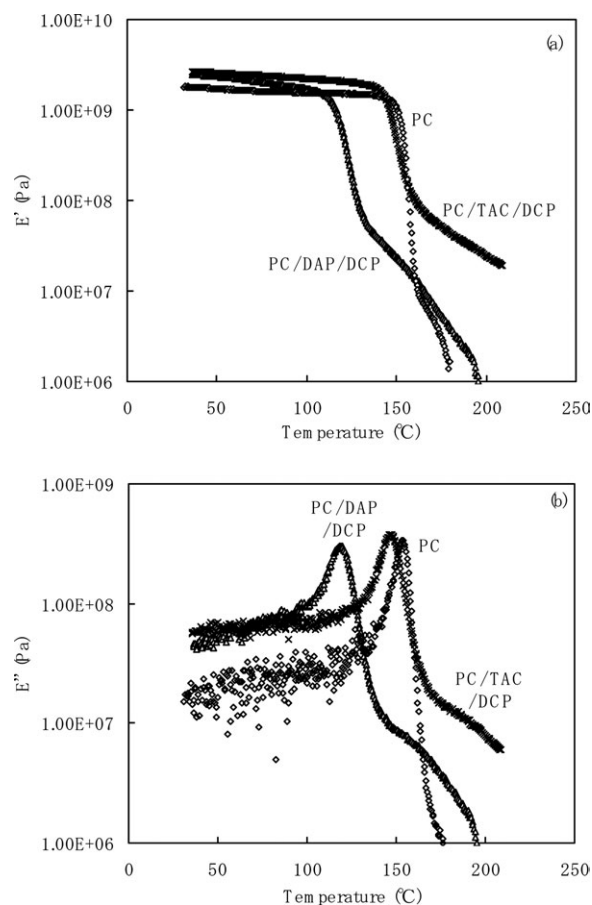
interface is not flat but it is undulated. The undulation of the interface is caused by the excess formation of graft (or block) copolymers at the interface.[11] Intermeshed structure of interface probably implies a complicated situation caused by grafting and curing.

Figure 12 shows HDT as a function of DCP content. The higher content of DCP leads to the higher HDT. The effect is significant in the case of TAC system. This is the expected result from
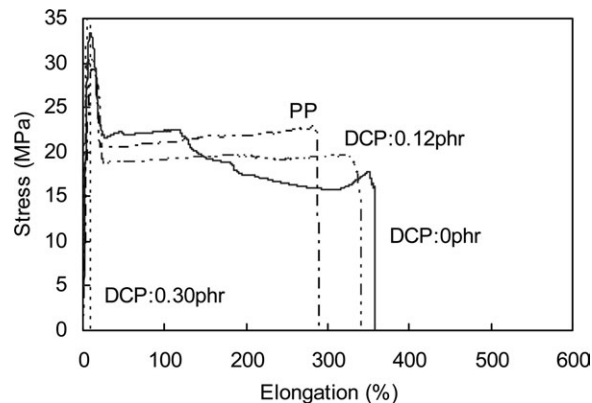


**Figure 10.** Stress–elongation curves of four-component systems using TAC as a reactive plasticizer.
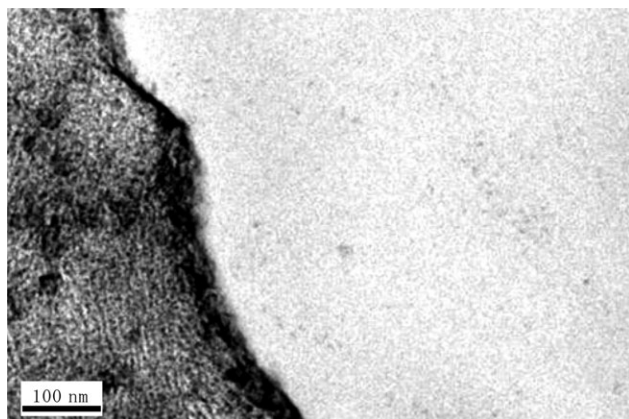
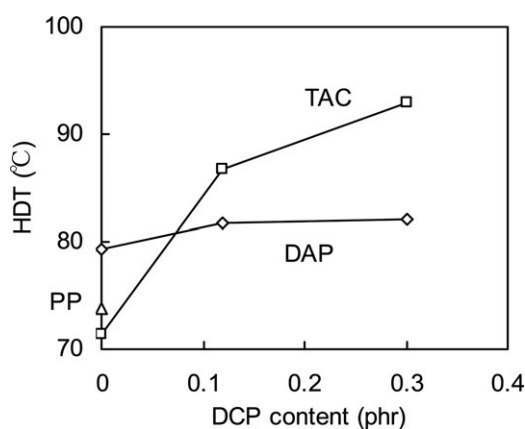**Figure 11.** TEM micrograph of PP/PC/TAC/DCP = 80/14/6/0.12 system.



**Figure 13.** Optical micrograph of PP/DAP = 70/30 blend.



**Figure 12.** HDT as a function of the content of reactive plasticizer. PP/PC/DAP(TAC)/DCP = 80/14/6/$\alpha$ systems. $\alpha$ was varied: 0, 0.12, and 0.30 phr.

## APPENDIX

Figure 13 shows an optical micrograph of the melt mixed PP/DAP = 70/30 (wt. ratio) blend. Huge particles of DAP are seen, suggesting the immiscibility. Area fraction of the dispersed particles is nearly equal to the volume fraction of charged DAP (0.25). It implies that the amount of DAP dissolved in PP phase is negligibly small. Similar result was obtained for PP/TAC blend. Thus, DAP and TAC may be highly insoluble with PP.

Figures 9 and 11. That is, the bicontinuous structure of PC and crosslinked TAC polymer in the dispersed particles (Figure 1) would lead to the higher HDT. In contrast, if the crosslinked TAC polymer is segregated as the domains in PC particles, the incorporation of TAC would not be effective so much for the HDT elevation.

## CONCLUSIONS

Thus, with the aid of the reactive plasticizer, the PC particles were finely dispersed. By the reaction-induced phase separation in PC particles, the heat resistance was nicely improved. By the reaction-induced phase separation, the polymerized plasticizer was segregated at the interface at which the graft copolymer of PP with the polymerized plasticizer seems to be generated. By the size reduction of PC particles, mentioned above, and the *in situ*-formed graft copolymer, the mechanical property may be improved to render the ductile PP/PC alloys.
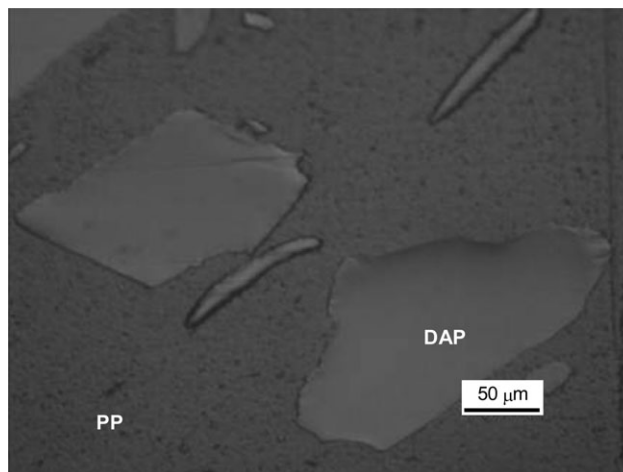
## REFERENCES

1. Borve, K. L.; Kotlar, H. K.; Gustafson, C. G. *J. Appl. Polym. Sci.* **2000**, *75*, 361.
2. Barhoumi, N.; Jaziri, M.; Massardier, V.; CassagnauP. *Polym. Eng. Sci.* **2008**, *48*, 1592.
3. Morye, S. S. *Polym. Eng. Sci.* **2005**, *45*, 1369.
4. Morye, S. S. *Polym. Eng. Sci.* **2005**, *45*, 1377.
5. Matsumoto, K.; Iwasawa, K.; Kakuwa, F.; Nishitsuji, S.; Ishibashi, J.; Inoue, T. *Proceedings of the 27th Annual Meeting of the Polymer Processing Society*, Marrakech, Morocco, May 10–14, **2011**, OP-10–1076.
6. Favis, B. D.; Therrien, D. *Polymer* **1991**, *32*, 1474.
7. Chapleau, N.; Favis, B. D.; Carreau, P. J. *Polymer* **2000**, *41*, 6695.
8. Inoue, T. *Prog. Polym. Sci.* **1995**, *20*, 119.
9. Ohtsuka, K.; Matsumoto, A.; Kimura, H. *J. Appl. Polym. Sci.* **2008**, *107*, 1517.
10. Rusli, A.Cook, W.; Liang, G. G. *Eur. Polym. J.* **2011**, *47*, 1785.
11. Inoue, T. In Polymer Blends Handbook; Utracki, L. A., Eds.; Kluwer Academic Publisher: Dordrecht, **2002**; Vol. *1*, Chapter 8, p 568.