Synthesis of a Graft Copolymer from an Ozonized Polycarbonate and Its Application as a Compatibilizer

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ABSTRACT: The polycarbonate (PC)/polystyrene (PS) blend is an immiscible system. The use of copolymers as compatibilizers in blends is one approach that is being developed within the larger field of polymer alloys. In this study, PC was ozonized to create peroxides and hydroperoxides on the polymer chain. These functional groups under heating conditions were used to initiate the radical polymerization of styrene (vinyl monomers) to give graft copolymers. The first part of this study was dedicated to the examination of the kinetics of the styrene polymerization initiated by an ozonized PC. However, the structure of the graft copolymers was confirmed by IR spectroscopy, and the molecular weight of the PS graft chain was determined by gel permeation chromatography. The compatibilized bends were prepared by melt blending in an internal mixer. The morphologies of the PC/PS/graft copolymer blend were examined by transmission electron microscopy and were finer than those of an uncompatibilized blend. The tensile properties of these blends were also investigated. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

It is well known that styrene polymers [polystyrene (PS)] and engineering plastics, such as polycarbonate (PC), occupy a large part of the plastics market and are some of the most recycled polymer materials.[1,2] PC has a distinguished role in this context because it is extensively used in engineering applications; this is due to its relatively high toughness under certain conditions and its excellent chemical resistance.[3] PS has been used all over the world because of its excellent physical properties and low production costs.[4] Earlier studies have shown that PS degrades under exposure to sunlight in air through two distinct processes: photolysis and oxidation.[5] Usually, these plastics are used or recycled in blends.[6] It is hard to separate these plastics from recycled materials.[7] Moreover, the immiscible polymer blends show a large interfacial tension in the melt, which makes it difficult to disperse the components properly and results in poor mechanical properties.[8] For this reason, it is important to find experimental conditions for mixing different plastics without a loss of mechanical properties. Combining different plastics with the help of a compatibilizer is a convenient way of upgrading the properties of recycled materials.[9] Various compatibilization methods have been reported.[10–14] One of most popular

methods is to add a third component that can act as an interfacial agent at the interface. A block or graft copolymer is generally used as the third component.[14]

Polymer oxidation by ozone has been used for the past few years because of dual interest in the addition of new heat-sensitive functional groups (peroxides and hydroperoxides) and for scission molecular chains.[15,16] Ozone process is a simple and a rapid method: a gaseous mixture of ozone and oxygen goes through a fluidized bed of polymer powder. The temperature, ozone concentration, and exposition time are the main parameters that regulate the reaction. The ozonized polymers are able to initiate the radical polymerization of a vinyl monomer.[16]

Fahimi et al.[17] showed the possibility of breaking down the network of peroxide crosslinked polymers to obtain new products with thermoplastic properties.[15] However, they grafted vinylic monomers and obtained new materials and emulsions. Landler and Lebel[18] used an ozone flow on PS and succeeded in grafting vinylic monomers. This method was used later by Polednick et al.[19] on propylene. Sarraf et al.[20] and Robin et al.[21] focused their research on polyethylene (PE), which also gave grafted products with various monomers, such as methacrylate,

Table I. Experimental Conditions of the Ozonization Reaction

PC concentration (g/L)	Temperature (°C)	Gaseous flow of O_2/O_3 (L/h)	Ozone concentration (mg/L)	Ozonization time (min)	Content of initiators (assay by DPPH; mol/g of ozonized polymer)
30	60	32	75	30	1.7×10^{-5}
30	60	32	75	90	4.2×10^{-5}

glycidylmethacrylate, and styrene. The content of initiators brought about by the ozonized polymers is a fundamental parameter in controlling polymerization reactions. The different methods of titration described in the literature have used ferrous ions, iodine, or free radicals, such as 2,2-diphenyl-1-picrylhydrazil (DPPH),[15,20,21] often as polymerization inhibitors. Bawn and Ellish[22] employed this molecule to measure the decomposition rate of initiators such as *tert*-butyl peroxide and 2,2′-azobisisobutyronitrile. PC has a distinguished role in this context because it is used extensively in engineering applications.[3] PC copolymers have not been studied very much with ozonization. Moreover, a study of the theoretical approach is an important key to the problem entailed by the polymerization of vinyl monomers initiated by macroradicals (ozonized polymers). In this article, we emphasize the fundamental approach and establish the kinetic characteristics of the radical polymerization reaction initiated by an ozonized PC (macroinitiator). On the other hand, studies were carried out on the characterization and properties of the PC–PS graft copolymer synthesized. Moreover, the new graft copolymer was investigated as a compatibilizer in a PC/PS blend operated in a solvent-free process under molten medium conditions.

EXPERIMENTAL

Materials

PC and PS were provided by DSM Engineering Plastics Europe (TE Heerlen, The Netherlands) from electrical and electronic equipment. Both materials were characterized, and the obtained results for melt flow index (MFI), density, and vicat softening temperature (VST) were as follows: PC MFI (230°C/5 kg) = 6.06, density = 1.2 g/cm³, and VST = 139.2°C and PS MFI (230°C/5 kg) = 20.45, density = 1.05 g/cm³, and VST = 95.3°C. Styrene was provided by Sigma-Aldrich. 2,2-Diphenyl-1-picrylhydrazyl (95% free radicals) was purchased from Aldrich.

Ozonization

PC (250 g) was exposed under an O_2/O_3 mixture. We studied the exposure at 60°C. The gaseous flow was 32 L/h, and the ozone concentration was 75 mg/L of gaseous mixture. The reaction time was varied from 30 to 90 min according to the desired content of the initiators (Table I).

Initiator Content

An ozonized PC sample (250 mg) was dissolved in a solution of DPPH (0.6 g/L). The solution was saturated with argon for 45 min, and the reactor was placed in a thermostated oil bath at 110°C for 10 min. The reactor was quickly cooled with cold water, and the polymer was precipitated. After 30 min, the solution was filtered through a fine filter (0.45 μm of porosity) and was determined by colorimetry at 520 nm. We thus obtained

the residual DPPH concentration. A blank determination was made under the same conditions without polymer to obtain the concentration. To determine the decomposition rate constant (k_d), the blank determination was made at different temperatures and reaction times.

Polymerization

Ozonized PC and styrene were introduced in a reactor equipped with a thermometer, a condenser, and a gas entry. The solution was saturated with argon for 30 min. The slight argon flow was maintained. After the desired reaction time, the reactor was cooled with cold water, and the polymer was precipitated. The PC and formed PS were filtered, dried, and weighed. The quantity of converted monomers and the concentration of unreacted monomers ([M]) were deduced.

Characterization of the Graft Copolymer

The chemical structure of the graft copolymers was characterized by a PerkinElmer 983 IR spectroscope (Santa Clara, California). Sample films cast from CH_2Cl_2 were used for the measurement.

Molecular Weight Determination of the Graft Chains

One hundred milliliters of a 1% (w/v) solution of copolymer graft in dichloromethane was mixed with 100 mL of 40% (w/v) aqueous sodium hydroxide. The immiscible mixture was stirred vigorously for 12 h. After the reaction, the organic layer was separated and washed sequentially with distilled water. When the organic layer was subsequently reduced to dryness, no residue was found. The degradation products of the PC were transferred quantitatively to the aqueous phase as the sodium salt of bisphenol. The number-average molecular weight (M_n) of the PS graft chain was estimated by gel permeation chromatography (GPC).

Melt Blending

PC, PS, and the PC/PS/graft copolymer blends were melt-blended at composition of 75% PC/25% PS by weight by variation of amount of graft copolymer. These blends were prepared in a Haake Buchler internal mixer (Sattle Brook, New Jersey). The mixer was operated for 15 min at 85 rpm and 250°C.

Thermogravimetric Analysis (TGA) Measurements

TGA was carried out with a TGA Q500 instrument (Eschborn, Germany). The heating was carried out in the temperature range from room temperature to 400°C at heating rate of 10°C/min under a nitrogen gas atmosphere.

Transmission Electron Microscopy (TEM) Analysis

Specimens were stained in a 2% solution of OsO_4 for 48 h, and ultrathin slices were cut with a Reichert-Jung ultracut microtome at room temperature. The apparent particle diameter was determined by digitization of the TEM photomicrographs. The weight-average particle diameter of the dispersed phase was
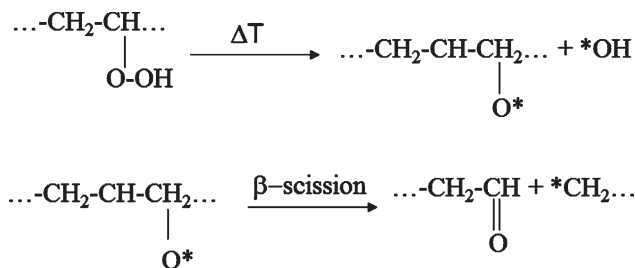
Figure 1. Thermal decomposition of peroxides and hydroperoxides.

calculated from the analysis of 300–500 particles with an image analysis software program.

Mechanical Testing

The mechanical properties were determined by means of a universal tensile testing machine from Instron (Norwood, MA, USA). Five individual dumbbell-shaped specimens were cut out from the sheets with a steel die of standard width (6.2 mm). The values were determined at a crosshead speed of 10 mm/min on a rubber tensile testing machine.

RESULTS AND DISCUSSION

Kinetics of the Radical Polymerization by an Ozonized PC

The reaction between PC and ozone generates peroxides and hydroperoxides on the polymer chains. The quantity of initiators is one of the necessary parameters for controlling radical polymerizations. Many researchers[20–22] have used a free radical, such as DPPH, to determine the amount of peroxides and hydroperoxides created by the ozonized polymers. The two main parameters to destroy all of the initiators were the temperature and the time.

After 10 min at 110°C, the DPPH concentration remained constant; this indicated that there was no more creation of free radicals in the solution. This method presupposed that DPPH caught the radicals originating from the decomposition of peroxides and hydroperoxides (Figure 1). This recombination of one DPPH mole could neutralize 1 mol of free radicals:

$$R—O—O—R' + 2X \rightarrow R—OX + XO—R'$$
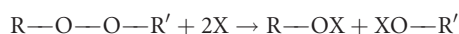
where X is a free-radical inhibitor, such as DPPH.

Table II. Decomposition Rate of Some Ozonized Polymers Obtained by the Colorimetric Determination of Residual DPPH[a]

Reference	Ozonized polymer and decomposition rate (K_d)	Half-time at 20°C (h)	Half-time at 110°C (min)
Sarraf et al.[20]	PE, Ln $K_d = 10.6 - 52,500/RT$	9.9	3.8
Fahimi et al.[17]	Crosslinked EVA wastes, Ln $K_d = 11.8 - 52,000/RT$	34.4	7.5

[a]Temperature range = 60–90°C. Extrapolation to half-time at 20 and 110°C. EVA, ethylene vinyl acetate.

Experimental conditions:
Ozonized PC=2g, Styrene=25g, Content of initiators=1.73x10^{-5} mol (O-O)/g of PC, T=100°C, M_0 = initial monomer concentration
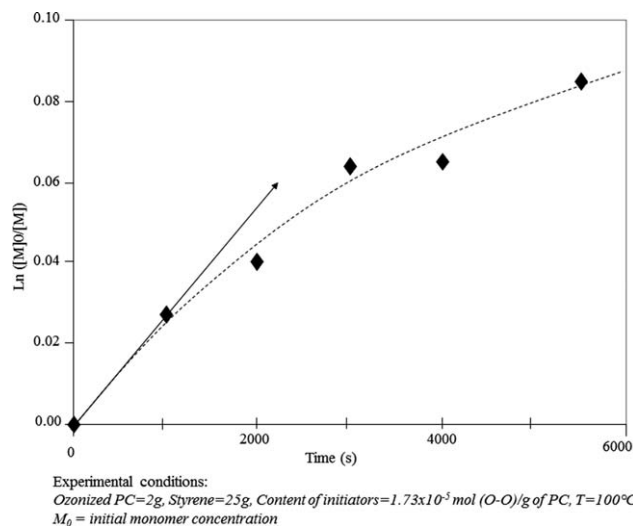
Figure 2. Example of calculation of the fk_d product.

k_d is one of the most important constants in a radical polymerization because it controls the time of reaction. One of the best methods for measuring the decomposition of macroinitiators is DPPH determination. Sarraf, Fahimi, and coworkers[17,20] observed a decomposition rate of the first order in agreement with the theory of the radical decomposition (Table II). Because the reaction was too rapid, they fixed the temperature between 60 and 90°C. Moreover, the decomposition rate measured on the ozonized polymers was very fast for peroxides and hydroperoxides; this implied that these initiators might not have been very stable at room temperature. Sarraf et al.[20] observed a 10% decrease in the initiator content of an ozonized PE kept for 2 weeks at room temperature. Fahimi et al.[17] also noticed a 12% decrease in the content of initiators of ozonized wastes stored for 1 month at room temperature.

This method of initiator assay to ozonized PC was applied. The DPPH concentration remained constant after 10 min at 110°C. This time seemed to be enough to destroy all of the initiators created by ozonized PC. Their decomposition rate was very
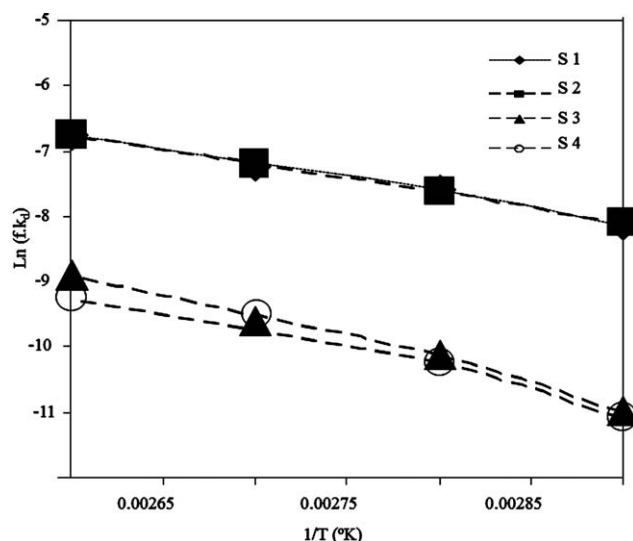

Figure 3. Arrhenius diagram for the fk_d product.

Table III. Values Obtained for the Original Slope and Calculated Values of fk_d

Initial styrene/PC weight ratio		$[I]_0$ ($\times 1000$; mol/L)	Temperature (°C)	$Ln(fk_d)$
3/2	S1	25.37	65	−8.12
			80	−7.58
			100	−6.75
	S2	10.27	65	−8.09
			80	−7.61
			100	−6.77
25/2	S3	3.05	65	−10.98
			80	−10.12
			100	−8.90
	S4	1.23	65	−11.07
			80	−10.27
			100	−9.25

$[I]_0$, initial initiator concentration.

rapid, with a half-lifetime no longer than 90 s at 110°C. It was noticed that the content of initiators remained constant in the case of an ozonized PC sample stored for 6 months at 4°C away from light and humidity. Moreover, the ozonized polymer through its ability to initiate a polymerization was studied. The kinetics of radical polymerization is known, and it was possible to determine the decrease in the monomer concentration as follows:

$$-\frac{d[M]}{dt} = \sqrt{\frac{K_p^2}{K_{te}}} \times \sqrt{f \times K_d} \times [M] \times \sqrt{[I]_0} \times e^{(-K_d \times t/2)} \quad (1)$$

After integration, we had

$$\ln([M_0/M]) = 2\sqrt{\frac{K_p^2}{K_{te}}} \times \sqrt{f/K_d} \times \sqrt{I_0} \times \left(1 - e^{-K_d \times t/2}\right) \quad (2)$$

where M_0 is the initial monomer concentration (mol/L), M is the monomer concentration (mol/L) at time t (s), f is the initiator efficiency, K_d is the initiator decomposition rate constant (s^{-1}), K_{te} is the termination rate constant (L mol^{-1} s^{-1}), K_p is the propagation rate constant (L mol^{-1} s^{-1}), and I_0 is the initial initiator concentration (mol/L) determined by DPPH.

The parameter fK_d was obtained by the drawing of $\ln([M_0/M])$ as a function of time (Figure 2).

The initial slope at $t = 0$ is given as follows:

$$\left\langle\frac{d\ln(M_0/M)}{dt}\right\rangle_0 = \sqrt{\frac{K_p^2}{K_{te}}} \times \sqrt{f \times K_d} \times \sqrt{I_0} \quad (3)$$

According to eq. (2), the curve showed a decrease of the polymerization rate because the initiator concentration decreased rapidly. When the conversion ratio was about 13%, we observed an inversion in the curvature, and this could be explain by the Trommsdorff effect. The values used for K_p and K_{te} were taken from the literature:[15]

$$K_p = 2.2 \times 10^7 \times e^{(-32.6 \times 10^3/RT)}$$

$$K_t = 1.3 \times 10^9 \times e^{(-10 \times 10^3/RT)}$$

where R is the universal gaz constant 8.31 J mol^{-1} °$^{-1}$ and T is the temperature (K).

The reaction was done under an argon gaseous flow in a reactor. [M] was determined by the weighing of the formed polymer after precipitation. The following points should be taken into consideration:

- The content of the initiator brought about by the ozonized PC was determined by the DPPH method.
- The total conversion rate was measured, that is, monomers incorporated as grafts and also homopolymers originating from hydroperoxides.

The decomposition rates of peroxides and hydroperoxides usually respect the Arrhenius law.[15,20] Figure 3 and Table III show the variation of $\ln(fk_d)$ as a function of $1/T$ (with T in degrees Kelvin). The straight lines obtained were not superposed. The main difference between these experimentations arose from the weight ratio (of monomer to ozonized PC).

With the straight lines in Figure 2 all being parallel, it was easy to calculate the average slope (E_a activation energy/R) of the Arrhenius law as follows:

$$Ln(fk_d) = 6.72 - 46,500/RT$$

$$E_a = 46.5 \pm 2\,\text{kJ/mol}$$

$$Ln\,A = 6.72$$

Table IV. Activation Energies and Arrhenius Coefficient Values of the Decomposition Rates of Initiators Brought About by the Ozonized Polymers

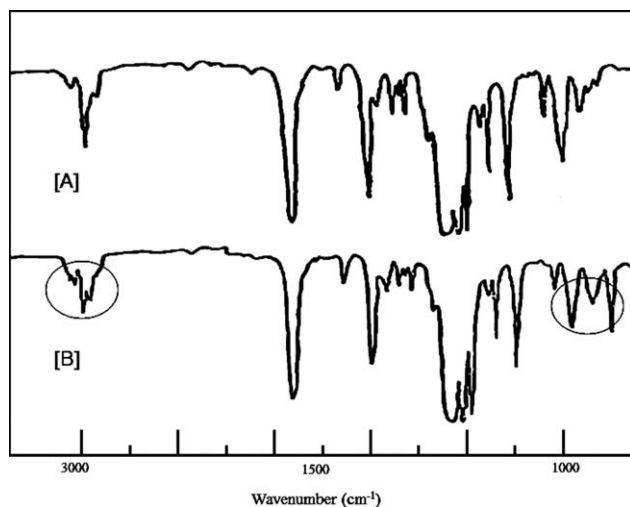| Reference	Ozonized polymer	Method of assay	Activation energy (kJ/mol)	Arrhenius coefficient: Ln A
Polymer Handbook[24]	Usual peroxides and hydroperoxides		120–150	27.6–36.8
Sarraf et al.[20]	PE	DPPH	52.5	10.6
Serdani et al.[25]	PVDF	DPPH	39.0	5.80
Our results of fk_d	PC	Polymerization rate of styrene	46.5	6.72

PVDF, polyvinylidene difluoride.

Figure 4. FTIR spectra of (A) PC and (B) PC/St copolymer.

where A is the Arrhenius constant. These results were compared to values from the literature (Table IV). The result showed a very low A of the ozonized PC. This could be explained by the limited freedom caused by important steric hindrances or the configuration of polymer in the solution.

Grafting Reaction of the Ozonized PC in Styrene

The reaction products were treated with cyclohexane in a Soxhlet apparatus to dissolve homopolystyrene. A time of 24 h was enough to extract most of the homopolystyrene.

IR spectra (Figure 4) confirmed that the reaction products were copolymers of PC-PS. Spectra A and B are for the ozonized PC and the PC after the reaction with styrene, respectively. Spectrum B shows the presence of the peaks that were characterized for both PS and PC. Compared with spectrum A, spectrum B had new peaks at 3100, 3080, 3060, and 3000 cm^{-1}, which are characteristic of PS, and peaks at 700 and 760 cm^{-1}, which are characteristic of monosubstituted phenyl rings.
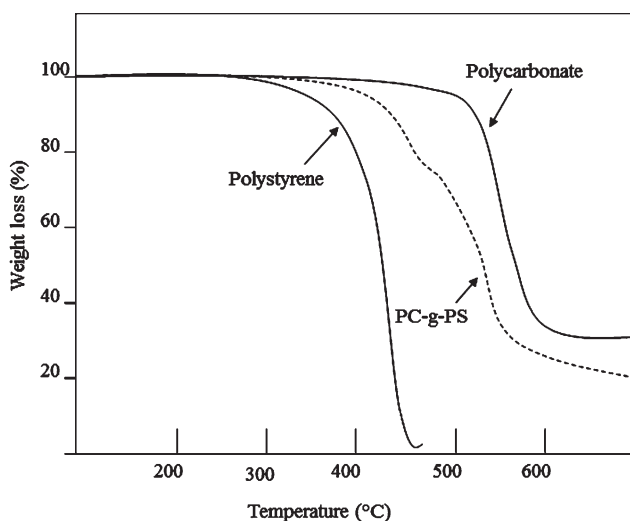

Figure 5. TGA of PS, PC, and PC-*g*-PS copolymer graft.

Table V. Molecular Weight of PS Graft in PC-*g*-PS by GPC

Number-average molecular weight ($\times 10^4$)	Weight-average molecular weight ($\times 10^4$)
8.31	73.19

Thermal Properties and Molecular Weight Determination of the Graft Copolymers

Figure 5 shows the TGA results for PS, PC-*g*-PS, and PC. Both spectra B and C had two incidences of degradation temperatures near 430 and 515°C, respectively. These two temperatures were higher than that of PS (389°C) and lower than that of PC (528°C). The molecular weights of the grafts were determined by GPC. The results are shown in Table V.

Mechanical Properties and TEM Observations

The beneficial effect of the graft copolymer on the dispersion and interfacial adhesion of PC/PS blends was examined by the observance of the tensile properties of the blends. Table VI shows the effect of the graft copolymer on the tensile strength, which had a low value for the uncompatibilized blend and increased appreciably as the amount of copolymer increased. We found similar results for the yield strength. As the amount of copolymer increased, the elongation increased continuously, as shown in Table VI. This result occurred because the copolymer enhanced the interfacial adhesion of the PC and PS phases in the PC/PS blend.

As shown in Figure 6, the domain size of the dispersed PS phase in the PC/PS/graft copolymer blends was reduced with the addition of PC-*g*-PS compared with that of the 75% PC/25% PS blend. This behavior has been frequently observed when immiscible blends were compatibilized with block or graft copolymers.

CONCLUSIONS

Ozonized polymers can initiate radical polymerization and give graft copolymers. The assay by colorimetric techniques of DPPH seems to be the most reliable method for ozonized polymers to determine the quantity of initiators. This study showed that ozonized PC had the ability to initiate styrene radical polymerization to determine the decomposition rate. The activation energy of the decomposition reaction was weak, but it could be explained by induced decomposition. The A value could be particularly attributed to steric hindrances, which disturbed the mobility of the released radicals. Then, the copolymer was introduced as a compatibilizer in the PC/PS blends. The compatibilization of the PC/PS blend with the graft polymer was achieved. The morphologies of the PC/PS/graft copolymer blends were considerably finer compared to that of an

Table VI. Effects of the Copolymer Graft on the Relative Tensile Elongation and Tensile Strength in the PC/PS Blend

Amount of the graft copolymer (%)	Tensile strength (kg/cm^2)	Yield strength (%)
0	405	8.3
5	467	12.8
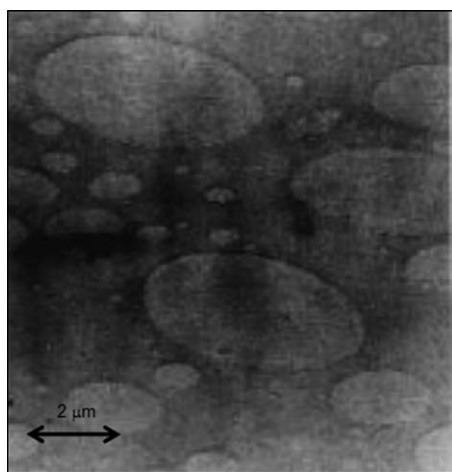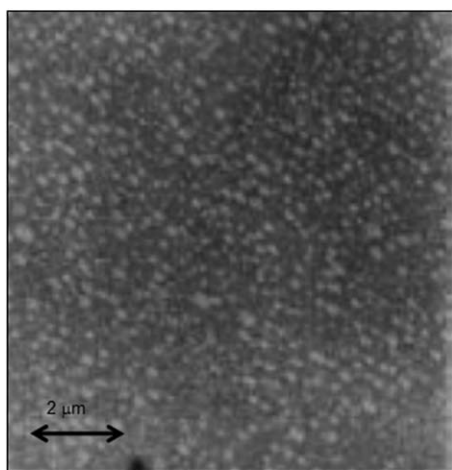
Figure 6. TEM photographs of the 75% PC/25% PS blend with 5% copolymer graft by ionized PC.

uncompatibilized blend. The tensile strength and relative elongation increased as the amount of copolymer increased. This also indicated that the copolymer made it possible to successfully compatibilize the PC/PS blends. However, the characterization of the graft copolymer synthesized from ozonized PC showed a similarity compared to the radiation grafting method published by Pu et al.[23] The radiation method is still an inconvenient method but has the advantages of no initiator, no impurities, high efficiency, and ease of control.

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