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Synthesis of Polycarbonate-Poly(methyl methacrylate) Copolymer via Sonochemical Polymerization of Methyl Methacrylate in Polycarbonate Solution

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Summary: Methyl methacrylate (MMA) was polymerized in the presence of polycarbonate (PC) by ultrasonic irradiation-initiated polymerization. The resulting products consisted of mixtures of homopolymers of poly(methyl methacrylate) (PMMA), PC and PC-PMMA copolymer because of the homopolymerization of MMA itself and copolymerization with macroradicals of PC. Formation of the PC-PMMA copolymer was confirmed by FTIR analysis of the reaction products after a proper extraction of free PMMA from the mixture. In order to verify the effectiveness of the PC-PMMA copolymer as a compatibilizer for PC/styrene-co-acrylonitrile (SAN) blend, 5 phr of PC-PMMA was added during melt mixing of PC/SAN in a batch mixer. It was found from the investigation of morphology and rheological properties that interphase of SAN and PC was fortified by numerous ligaments of PC-PMMA copolymer, which resulted in increase of melt viscosity and storage modulus of the blend.

Keywords: copolymerization; poly(methyl methacrylate); polycarbonate; sonochemical polymerization

Introduction

Along with the synthesis of low molecular mass compounds, applications of the sonochemical effects in polymer system have yielded a variety of useful consequences. For example, ultrasound was used as an initiator in radical polymerization of vinyl monomers. The majority of studies have concerned with the homopolymerization in bulk or solution system. Another area of the applications involves degradation of polymer molecules in solution.[1] When macromolecules are under sonication in liquid phase, they are subject to shock waves emanated from the collapse of the cavities. On the molecular level, this implies a rapid motion of solvent molecules to which the macromolecules embedded in the solvent cannot follow. At such condition, friction is generated, which causes strain and eventually bond rupture in the macromolecules. Thus, the primary product of the sonochemical cleavage of polymer chains is a macromolecular radical(or macroradical). Besides the effect of controlled degradation, one important aspect of this process is the possibility that macroradicals can act as active sites for further reaction with other monomers or polymers. By this means, it becomes possible to build block or graft type copolymers in a relatively simple manner compared to conventional polymerization techniques such as anionic polymerization, as demonstrated by a number of workers. [2,3]

In this study, an attempt has been made to produce Polycarbonate (PC)-Poly(methyl

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methacrylate) (PMMA) copolymer via ultrasonic irradiation in the mixture of PC and methyl methacrylate (MMA) monomer. The copolymer of PC and PMMA may be industrially useful for the compatibilization of the PC/PMMA blend or PC/styrene-co-acrylonitrile (SAN) blend mainly because of the complete miscibility between SAN and PMMA for AN contents in the range of 9–33 % by weight.[4] In particular, blend of PC/SAN constitutes a major element of PC/acrylonitrile-butadiene-styrene (ABS) which is an important engineering plastic. Based on its excellent toughness, heat resistance and processability, it has been widely used in various parts for automobiles and appliances. However, due to the incomplete miscibility between PC and SAN, the blend often experiences significant changes in its phase morphology during compounding and injection molding, which results in phase coalescence and deterioration of mechanical properties.[5,6] In order to overcome such drawbacks, attempts have been made by reactive functionalization of SAN or introduction of PC-PMMA block copolymer synthesized from vinyl terminated PC.[7–9] Compared to other studies, the present work was performed in a relatively simple manner without any chemical initiators or reactive functionalizations.

Experimental Part

PC used in this study was a low viscosity grade (Panlite L-1225Y, Mn = 9,200) made by Teijin (Japan). SAN copolymer was provided by Cheil Industries, Inc. of Korea under the trade name of Starex. The AN content of SAN was 25 wt. % and number average molecular weight (Mn) of SAN was about 42,000 with a polydispersity of 1.64. MMA monomer (Junsei Chemicals, Japan) was purified using an inhibitor removal column (Aldrich) and stored in a refrigerator. Poly(vinyl alcohol) (PVA) with weight average molecular weight (Mw) in the range of 85000–125,000 and degree of saponification of 89% (Aldrich) was used as a dispersant.

The reactions were carried out in a probe batch reactor (Suslick), where a horn type ultrasonic homogenizer (Sonics & Materials, Inc., VCX 750) was used. The reactor was surrounded by a thermostatted water bath to set the starting temperature of the reaction. The equipment is capable of automatic tuning and the horn consists of a titanium tip with 1/2″ in diameter. The frequency of ultrasound was 20 kHz and the ultrasonic intensity was fixed as 70% in the instrument. The sonication intensity was determined by calorimetrically for the 150 ml of deionized water.[10] The temperature rise of the medium was measured with a thermocouple and the calculated sonication intensity was 27 W/cm^2.

Several suspension systems were polymerized under different conditions to study the nature of the ultrasonically initiated polymerization. Various sonication intervals were used by changing the irradiation and rest periods. For example, one cycle of a protocol included 15 min irradiation followed by 10 min rest. The reaction temperatures investigated were 5, 20, 35 °C. Prior to make a suspension system, 6 g of PC and 20 ml of THF were stirred for 2 hrs and 6 ml of MMA monomer was added to the solution. Then, a suspension was made by pouring the solution into the 130 ml of aqueous solution containing 1 g of PVA. Before sonication, the reactor was deoxygenated by bubbling with nitrogen gas for 3 min. During the ultrasonically initiated polymerization, argon was bubbled continuously through the solution at a flow rate of 45 ml/min to attain a condition of stable cavitation.[11] After polymerization, samples were coagulated with acetone and filtered, followed by several water washings. Before subsequent experiments, all the polymerized samples were dried in a vacuum oven at 80 °C overnight. Conversion of MMA was calculated by measuring the weight of the polymerized product.

In order to assure the formation of the PC-PMMA copolymer, the reaction products were put into a Soxhlet extraction procedure by using acetone for 48 hrs, by which only PMMA homopolymer (free

PMMA) was removed from the mixture.[9] The existence of PMMA units in the undissolved remnants after the Soxhlet extraction was investigated by Fourier transform infrared spectroscopy (FTIR, Perkin Elmer). Information on the molecular weight of PC-PMMA copolymer was also gained from GPC (Waters 410) analysis with the isolated PC-PMMA copolymer which was obtained by dissolving the sonicated product without free PMMA overnight in m-cresol for the removal of free PC. Scanning electron microscopy (SEM, Jeol, JSM 5800) was used to observe the phase size in various blends considered in this study.

Melt mixing of blends based on PC, SAN and the reaction product made in this study were performed in an intensive mixer (Haake Rheomix 600). Each blend was prepared on a fixed volume basis of 70% and loaded at 230 °C. The rotor speed was set as 60 rpm and the mixing time was 5 min. The samples obtained from the intensive mixer were compression-molded at 230 °C for 5 min. Disk-shaped specimens with a thickness of 2 mm and a diameter of 25 mm were prepared. An ARES rotational rheometer (Rheometric Scientific) was used to measure the complex viscosity and complex modulus. The measurements of the dynamic viscosities were performed in a parallel-plate fixture (diameter = 25 mm) with a gap distance of 1.2 mm. The strain was kept at 10% to ensure linear viscoelasticity. The frequency range was 0.1–500 rad/s, and the temperature was 230 °C. The work was conducted under a nitrogen atmosphere to prevent degradation.

Results and Discussion

The effect of sonication protocol on the outcome of ultrasonically initiated suspension polymerization of MMA in the presence of PC at a starting temperature of 5 °C was summarized in Table 1. It was found that the conversion of MMA was sensitive to the sonication protocol; when we applied a protocol of 5 min of irradiation followed by 3 min of rest or a protocol of 7 sec of irradiation followed by 3 sec of rest, no appreciable amount of polymer was yielded, while other cases gave conversions more than 50%. For a proper protocol (PC/PMMA (15/10)* in Table 1), a prolonged sonication resulted in the increase of conversion up to 87%. The results listed in Table 1 indicate that a frequent switch of irradiation and rest periods is detrimental to the desired copolymerization of MMA with PC. In other words, sufficient irradiation period is essential for the generation of critical number of both MMA radials and PC macroradicals, so that the effective copolymerization can proceed.

As previously described, collapse of bubble in monomer and solvent phase induces flow fields of high velocity gradient, i.e. inhomogeneous flow of the molecules. If a PC chain is located in a region of a high

Table 1.
Effect of sonication protocol on the polymerization.

Sonication protocol	Designation	Conversion (MMA Wt.%)	Wt.% of free PMMA in PMMA[b)]	Wt. % of free PC in PC[b)]	Mn of copolymer
15 min-irradiation/10 min rest 2 cycles	PC-PMMA (15/10)	55	19.8	52.0	9,700
15 min-irradiation/10 min rest 3 cycles	PC-PMMA (15/10)*	87	22.0	48.1	9,800
10 min-irradiation/8 min rest 3 cycles	PC-PMMA (10/8)	57	20.7	43.6	9,800
5 min-irradiation/3 min rest 6 cycles	PC-PMMA (5/3)	No polymerization	–	–	–
7 sec-irradiation/3 sec rest[a)]	PC-PMMA (7s/3s)	No polymerization	–	–	–

[a)] Total sonication time was 60 min;
[b)] Based on the amount of soluble portion after extraction.

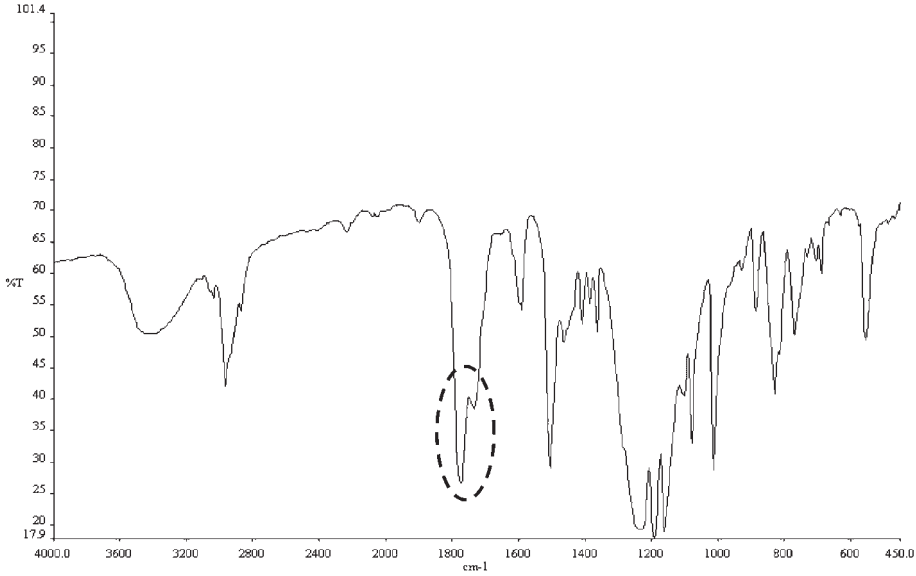

Figure 1.
FTIR spectrum of a PC-PMMA copolymer.

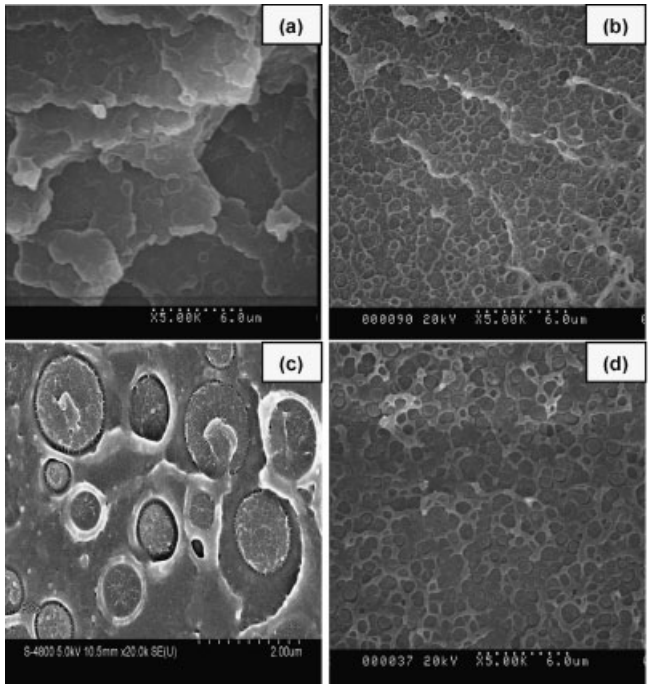

Figure 2.
SEM micrpgraphs for (a) PC/SAN, (b) PC/SAN with PC-PMMA (15/10), (c) PC/SAN with PC-PMMA (15/10) (high magnification), (d) PC/SAN with PC-PMMA (15/10) (after annealing).

velocity gradient and if it is sufficiently strained, chain scission become feasible and thus macroradicals of PC having the active site in the chain end are formed. In the event of chain scission by ultrasound, it should be noted that the nature of the fracture is non-random and occurs close to the center of the polymer chain, as proposed and verified by Kuijpers et al..[12] In case of a PC molecule, it is presumed that the chain scission process predominantly takes place at C–O bond of the carbonate linkage; simply because its bond energy is lowest (330 kJ/mol) along the main chain axis.[13] Within this context, we can expect the formation of PC-PMMA block copolymers by the propagation of MMA at the ends of the PC macroradicals or by interpolymer radical coupling reactions of PC and PMMA. Although a rigorous analysis on the copolymer structure was not made, an evidence for the copolymer formation was found in the FTIR analysis of samples prepared by removing free PMMA

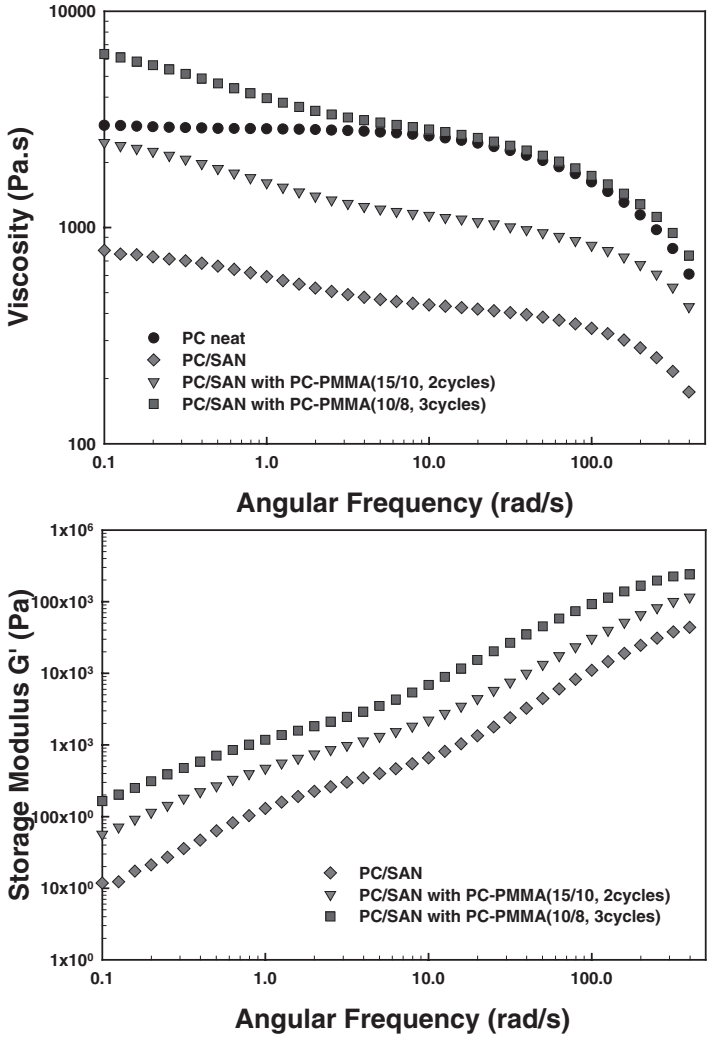

Figure 3.
Effect of PC-PMMA copolymer on the rheological properties of PC/SAN blend: (a) viscosity vs. angular frequency (b) storage modulus vs. angular frequency.

from the reaction products. As presented in Figure 1, the FTIR spectrum showed two carbonyl peaks at 1776 cm^{-1} and 1731 cm^{-1}, which correspond to the stretching vibration peak of carbonyl group of PC and PMMA, respectively. Additional evidences for the copolymer formation were available from the observation of phase size in SEM and measurement of rheological properties of the PC/SAN blends with the reaction product. When 5 wt % of the PC-PMMA(15/10, 2 cycles) was incorporated into the blend of PC/SAN(8:2), domain size of SAN was remarkably reduced by adding PC-PMMA as shown in Figures 2(a) and 2(b).

Especially, it is important to note in Figure 2(c) that numerous ligaments are observed in the interfacial region of domain and matrix. We believe that those ligaments are PC-PMMA copolymers which were preferentially located at the interface during the melt mixing. According to the interfacial activity of the copolymers, entanglements between the component polymers were enhanced to suppress the coalescence during annealing treatment (10 min, 200 °C), as demonstrated in Figure 2(d).

From the investigation of the rheological properties of the blends, it was found that both melt viscosities and storage moduli of PC/SAN were enhanced by the addition of PC-PMMA copolymer (Figure 3), which was caused by the improvement of interfacial adhesion between PC and SAN.

In Figure 3, it is worthy to note that addition of PC-PMMA obtained from 10/8 protocol led to higher viscosities and strorage moduli of PC/SAN, compared to the case of the 15/10 protocol for the same sonication time of 30 min. In particular, viscosities are even higher than those of neat PC at low frequency region, reflecting robust coupling at the interface promoted by PC-PMMA copolymers. For the clear explanation of the trend shown in Figure 3, detail information on the structure of copolymers would be necessary. Nevertheless, one possible reason can be found from the Table 1 by comparing the data for two protocols. It appears that conversion, amount of free PMMA, and even molecular weight of the isolated copolymer are comparable; however, the amount of free PC is about 8% less in 10/8 ptotocol. This implies that more molecules of PC were involved in copolymerization with PMMA, which is associated with the higher concentration of the effective copolymers. In addition to the sonication interval, reaction temperature turned out to be an important variable to influence the quality of the reaction

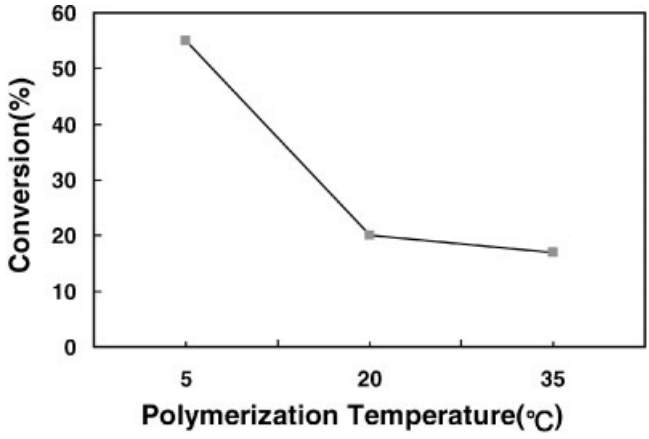

Figure 4.
Effect of polymerization temperature on conversion of monomer.

products. As shown in Figure 4, when the temperature increased from 5 °C to 35 °C, monomer conversion decreased from 55% to 17% for a protocol of 15/10. This result indicates the importance of PC macroradicals in the polymerization of MMA.

As the temperature is elevated, radical concentration is reduced; since polymer molecules are more easily relaxed upon the cavitation and ultrasonic degradation of polymer molecules is retarded.[1] Beside the negative impact on the monomer conversion, it was also found that the increase of reaction temperature deteriorated the effectiveness of the reaction product as a compatibilzer; the stablity of morphology in PC/SAN blend was not assured during annealing process.

Conclusions

Polymerization of MMA monomer was conducted in the presence of PC by using ultrasonic irradiation. The expected roles of the ultrasonic wave were to generate radical species of MMA and to induce chain scission of PC molecules, by which both homopolymerization of PMMA and copolymerization with PC were accompanied. For the effective generation of PC-PMMA copolymers, it was of critical importance to apply proper sonication protol and polymerization temperature. Within the limited range of experimental conditions, it is suggested that a useful copolymer can be made at the lowest possible temperature when the initial sonication time is sufficient to overcome the induction period of the polymerization. The compatibility of PC/SAN blend was successfully improved by PC-PMMA copolymer produced by sonochemical means applied in this study.

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