New Polymerization Using Microwave Radiation

Jae Heung Lee*, Yong Seok Kim, Young Taik Hong, Hyun Min Jung, Hyoung Suk Oh,

Advanced Materials Division, Korea Research Institute of Chemical Technology, Daejeon, 305-600 Korea
*jahlee@krict.re.kr

Introduction

Recently, there has been a growing interest in applying microwave heating to synthetic organic chemistry, waste treatment, polymer technology, drug releasing targeting, ceramics, and alkane decomposition. However, polymerization in the solid-state by microwave irradiation has not yet been reported well. Microwave irradiation produces heat, which is generated in the material itself, instead of using external heating. The dielectric properties, which govern the rate of internal heating, may vary widely in magnitude among the various constituents in the product, and are also functions of temperature. The temperature profile at a given time in a microwave-heated material will depend on the dielectric properties, specific heats and thermal conductivities of the material constituents.[1, 2] There are many reports that reactions of organic and organometallic compounds can be carried out with a reaction rate enhanced up to 1300 times. Another advantage of microwave irradiation is the superior morphological properties due to dielectric heating.[3, 4] Our investigation show that microwave solid-state polymerized polycarbonate (PC) has very high molecular weight of over 40,000 g/mol, within 6 h. This method reduces reaction time exceptionally, compared to conventional solid-state polymerized PC using oil heating. In our study, PC prepolymers were prepared by melt polymerizing bisphenol-A (BPA) with diphenyl carbonate (DPC). The prepolymers intercalated with modified montmorillonite (m-MMT) were further polymerized in a microwave oven to obtain MMT/PC nanocomposites in the solid-state. The microwave assisted polymerization was also effective in polyethersolfone(PES) preparation, thus resulting in good polymer characteristics comparing to conventional methods.

Experimental

Preparation of Polycarbonate using Microwave Assisted Solid State Polymerization. A mixture consisting of bisphenol A and diphenylcarbonate mixed in the molar ratio of 1:1.06 was placed in a vessel and raised temperature to 160 ℃ for 30 min with a nitrogen flowing. Then, the mixture was allowed to react at 240 ℃ for 2 hrs. The reaction was continued under reduced pressure, 200 tor for 1 hr and 0.2 torr for 50 min. The polycarbonate prepolymer prepared in the above step was crushed into small particles of sizes less than 710 μm. The resulting prepolymer particles were added into a beaker filled with acetone and then stirred at 1000 rpm for 1 hr then filtered and dried. The polycarbonate prepolymer was added into a flask wherein a porous plate is attached to its lower part for gas injection. The flask was placed in a microwave oven which generates 2.45 GHz radiation and has 1 kW capacity. The vacuum was applied to maintain the reactor pressure as 60 torr while the prepolymer particles were stirred and nitrogen gas was injected at the rate of 0.2 L/min. The microwave radiation was applied and the solid state polymerization was performed for 2 hrs.

Preparation of Polycarbonate / Montmorillonite Nanocomposite. The pre-intercalated nanocomposites of PC prepolymer and MMT were prepared by internal mixer at 180℃ & 60 rpm during 30 mins. The weight percentage of MMT was 5wt% in each mixture. After pulverization, the pre-intercalated nanocomposites were placed into acetone or chloroform/acetone solvent system bath and stirred with a mechanical stirrer at a rate as high as 1,000 rpm for 1 hour for crystallizing the pre-intercalated nanocomposites. And, the crystallized prepolymers were screened into the sizes from 300 to 700 μm after overnight vacuum drying. The pre-intercalated nanocomposites were polymerized as a solid-state in a microwave oven with various irradiation times at 220℃ for 6 and 12 hours. Same samples were polymerized in silicone-oil bath with same experimental conditions.

Results and discussion

The microwave assisted solid state polymerization for PC was constituted of preparation steps comprising a) preparing polycarbonate prepolymers having a viscosity average molecular weight of 4,000~18,000 g/mole through melt polymerization of BPA and DPC; b) converting polycarbonate prepolymers into crystalline particles having 5-50% of crystallinity; and c) producing polycarbonates by applying microwave radiation for heat generation during solid state polymerization reaction, thus resulting in production of high quality polycarbonates with high molecular weight up to 34,500 g/mol within a short period of time.

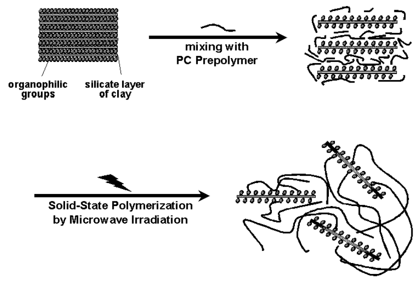

Figure 1. Schematic diagram of microwave solid-state polymerization for PC/MMT nanocomposite.

Polycarbonate/montmorillonite (MMT) nanocomposite was also prepared by microwave solid-state polymerization (Fig. 1). The MMTs were modified with alkyl ammonium salt. Pre-intercalated polycarbonate nanocomposite was prepared using two conventional methods; a melt process and a solution process. Melt processing was accomplished in a Haake internal mixer for 30 mins at 180 ℃. Solution processing was accomplished in a homogenizer using chloroform. Subsequently, microwave solid-state polymerization converted the pre-intercalated nanocomposite into the exfoliated nanocomposite. The wide-angle X-ray diffraction (WAXD) revealed that exfoliation and/or further intercalated structures were obtained when comparing the results from the microwave solid-state polymerization with results from conventional solid-state polymerization using oil heating. This means that microwave solid-state polymerization is more effective than conventional solid-state polymerization using oil heating. It was shown that conventional melt and solution processing of MMT and polycarbonate prepolymer yielded intercalated nanocomposites with interlayer spacing of 2.5 and 2.7 nm respectively. Microwave solid-state polymerized nanocomposite showed the exfoliated and/or intercalated structure, whereas conventional solid-state polymerization using oil heating only increased the gallery size of MMT. The thermal decomposition behavior and morphologies were investigated by thermogravimetric analysis (TGA) and transmission electron microscopy (TEM).

Conclusions

From the novel technology, microwave solid-state polymerization, high molecular weight of PC and PC/MMT nanocomposites was successfully prepared. From the results, it was known that microwave irradiation is more effective than conventional oil-bath heating on achieving the high molecular weight and uniform nanocomposites. Using the polycarbonate prepolymer with low molecular weight made it possible to intercalate the short chains into the galleries of MMT more easily. And it was observed that prepared nanocomposites by microwave solid-state polymerization have more uniform dispersion of silicate of MMT into the polymer matrix than by oil heating.

Support of KRICT and MOCIE program (TS051-19-2) is gratefully acknowledged.

References

[1] Correa, R.; Gonzalez, G.; Dougar, V.; *Polymer* **1998**, *39*, 1471.
[2] Hwu, W. H.; Zurawsky, W. P. *J. Polym. Sci., Part A: Polm. Chem.* **1992**, *30*, 409.
[3] Mallon, F. K.; Ray, W. H. *J. Appl. Polym. Sci.* **1998**, *69*, 1203.
[4] Lu, J.; Zhu, X.; Zhu, J.; Yu, J. *J. Appl. Polym. Sci.* **1997**, *66*, 129.