

Xue Feng, Fu Weiwen, Cheng Rongshi

Characterization of Acetone-Solution Casting Film of PMMA

© Higher Education Press and Springer-Verlag 2006

Abstract Acetone solution-casting films of poly(methylmethacrylate) were analyzed by differential scanning calorimetry and pyrolysis gas chromatography-mass spectroscopy under natural evaporation and ultrasonic vibration, respectively. Analytical results indicate that both the condensed structure of the polymer and the residue solvent in the films vary in different film-forming conditions and that the residue-solvated acetone in films prepared under natural evaporation is 12 times greater than that under ultrasonic vibration.

Keywords solution casting, poly(methylmethacrylate), ultrasonic, condensed structure, characterization

1 Introduction

Extrusion of the thermoplastic polymer melts by providing electromechanical vibration led Qu to invent the electromagnetic dynamic extruder and injector. These novel polymer processing machines have significant advantages, such as low energy consumption, lower processing temperature, and diminished die swelling. Hence, it is possible to get final products with superior physical properties when compared with those of conventional single-screw extruder or injector [1–7]. Previous research mainly focused on the rheological behaviors of the polymer during dynamic processing and on the mechanical properties of the final products [8–14]. Relatively, little attention had been paid to the structural changes of polymers when placed in other physical fields such as mechanical vibration. The influences of the extra field on the structure and properties of polymers come under the category of the effects of the metastable state

of polymer. Some researches on this subject have been done [15,16] recently. Since the alternative vibration field seriously affects the polymer melt, we can expect that a similar effect may also occur in the film formation when casting a polymer solution as an external field [17,18]. The aim of the present work is to study the effect of the externally applied ultrasonic field on the nascent films obtained by casting a poly(methylmethacrylate) (PMMA) solution.

2 Experimental

2.1 Materials

Poly(methylmethacrylate) was prepared by free-radical polymerization, with acetone and ethanol as analytical-grade reagents.

2.2 Sample preparation and characterization

The prepared PMMA was dissolved in acetone, filtered, precipitated by the addition of ethanol, and then dried. A 1% acetone solution of the purified PMMA sample was prepared and divided into two equal parts, A and B, and placed in two glass dishes of the same dimensions. Solution A was evaporated under natural conditions, while solution B was evaporated using ultrasonic vibration. Both were put in the same ventilated case. After the solvents in the tubes were almost volatilized, the condensed film was placed in a dryer for 30 min at 70°C, and place the sample on standby in a desiccator.

The samples were studied by differential scanning calorimetry (DSC; MDSC 2910, TA Instruments, USA) using the following procedure. They were scanned from 30 to 200°C at a heating rate of 20°C/min, kept isothermally at 200°C for 5 min, cooled to 30°C at the same cooling rate, and then kept at 30°C for 1 min. Scanning was continued at the same temperature programming for five cycles.

The samples were also studied by pyrolysis gas chromatography-mass spectroscopy (PyGC-MS; JHP-3S Courier Pyrolysis Analyzer, Japan Analysis Industry; HP GC 5973-MS 6890, Agilent Instrument Co., USA) and pyrolyzed at 590°C for 10 s.

Translated from *Journal of South China University of Technology (Natural Science Edition)*, 2005, 33(3) (in Chinese)

Xue Feng (✉), Fu Weiwen, Cheng Rongshi (✉)
College of Materials, South China University of Technology,
Guangzhou 510640, China
E-mail: psfxue@scut.edu.cn

Cheng Rongshi
College of Chemistry and Chemical Engineering,
Nanjing University,
Nanjing 210093, China
E-mail: rscheng@nju.edu.cn

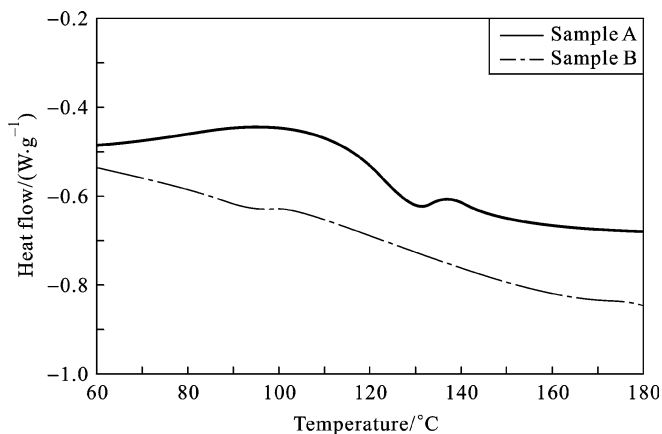


Fig. 1 DSC curve of PMMA film (first heating)

3 Results and discussion

The initial DSC heating curves represent the behavior of the nascent films. Samples A and B display distinct differences, as shown in Fig. 1. A wide exothermic peak at about 100°C is seen in sample A, which appears like a glass transition or as a pair of adjacent endothermic and exothermic peaks. In sample B, neither an endothermic nor an exothermic peak is observed, nor is glass transition.

As the nascent film via first scan is heated to the melting state and then cooled down to low temperatures, the condensed structure of the polymer is spontaneously reassembled. The reassembling course may be followed by successive DSC scan curves. The second to fifth DSC heating curves are shown in Fig. 2. Both samples A and B showed similar behavior, with a distinct glass transition region at around 120°C. This fact indicates that after heat treatment by the first scan, differences in the structural characteristics of the nascent films are almost eliminated. However, if we study the enlarged portion of the glass transition region, as shown in Fig. 3, a nonnegligible difference still exists between the samples. We recorded the temperatures at both the onset and inflection points of various scan curves as the glass transition temperatures (T_g) of the polymer. A plot of T_g vs the order of scan number is

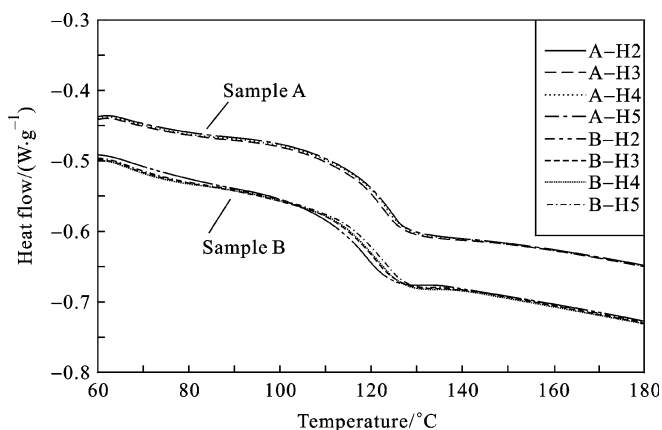


Fig. 2 DSC curve of PMMA film (second to fifth heating)

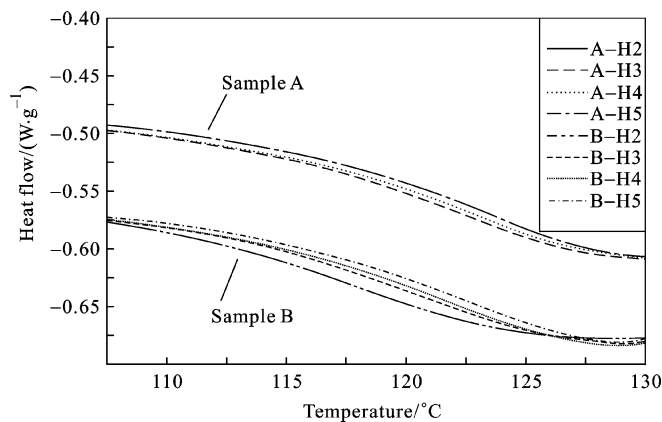


Fig. 3 Enlarged DSC curve of PMMA film (second to fifth heating)

shown in Fig. 4. This figure illustrates that the T_g of the cast film under natural conditions (sample A) is higher than that of the ultrasonic cast film (sample B). The T_g of both samples increases with the order of scan number, but the extent of variation in sample B is greater than that in sample A; it approaches that of sample A only after the fifth cycle of scanning. This implies that the structural difference of the nascent films prepared under different conditions may gradually vanish in the course of cyclic heat treatment in DSC measurements.

There are two possible reasons why the nascent films of the samples have such a great difference when the first DSC scan is performed. The first is that the structure of the condensed state of the polymers under ultrasonic vibration changes. The second is that the residue solvent present in the nascent films formed under varied conditions may be different. In the course of film formation by casting a polymer solution under externally applied ultrasonic vibration, the polymer chain may be rearranged because of the force field to form a more uniform structure similar to the structure of the melt. Hence, in the first DSC scanning of the nascent film, no glass transition region could be observed. However, for successive scans, the cohesive entanglements rebuild spontaneously in the glass state as the temperature is lowered in the melt. Therefore, we may infer that the main

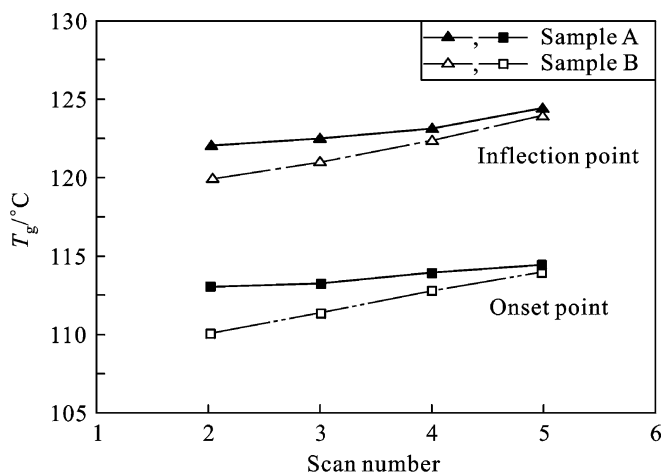


Fig. 4 Relationship between scan number and T_g

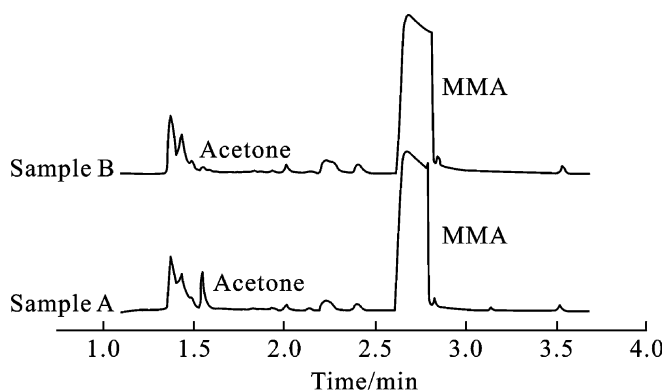


Fig. 5 Total ion chromatogram of samples A and B at a pyrolysis temperature of 590°C

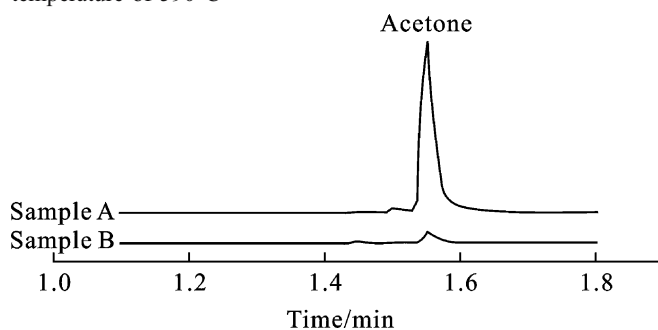


Fig. 6 Extraction ion chromatograms of samples A and B at a pyrolysis temperature of 590°C

action of ultrasonic vibration is to retard cohesive entanglement formation.

To check the premise of the second reason, we performed PyGC-MS on the two samples. Figure 5 shows the total ion PyGC chromatogram of samples A and B pyrolyzed at 590°C. The fragment peak of acetone at a retention time of 1.55 min is determined by MS analysis. This should be the residue solvent remaining in the sample. Figure 6 displays the extraction ion chromatograms of samples A and B. The difference between the peak areas of acetone in the two samples is obvious. After normalization by mass, the amount of acetone in sample A is 12 times more than that in sample B. This demonstrates that the solvated solvent could be more easily removed under externally applied ultrasonic energy. The DSC first scan curve on heating the nascent film of sample A could be attributed to the existence of more residue-solvated solvent.

4 Conclusions

The first DSC scan curve obtained by heating the nascent film of PMMA under ultrasonic vibration is quite different from that by conventional evaporation. The main action of ultrasonic vibration is to retard cohesive entanglement formation in the glass state and to enhance the removal of the residue-solvated solvent in the polymer matrix. The amount of solvent residue in the films prepared by natural

evaporation is 12 times greater than that in films prepared under ultrasonic vibration.

References

- Shangguan Y. G., Tong L. F., Li L. W. et al., Progress in the effect of external field on polymeric material, *Funct. Mater.*, 2003, 34(5): 485–487 (in Chinese)
- Peng X. F. and Qu J. P., Research development of the vibromolding technology of polymers, *Polym. Mater. Sci. Eng.*, 1999, 15(5): 8–12 (in Chinese)
- Ibar J. P., Control of polymer properties by melt vibration technology: a review, *Polym. Eng. Sci.*, 1998, 38(1): 1–20
- Cao Y. R. and Li H. L., Influence of ultrasound on the processing and structure of polypropylene during extrusion, *Polym. Eng. Sci.*, 2002, 42(7): 1534–1540
- Qu J. P., Study on the pulsating extrusion characteristics of polymer melt through round-sectioned die, *Polym. Plast. Technol. Eng.*, 2002, 41(1): 115–132
- Qu J. P., Xu B. P., Jin G., He H. Z. and Peng X. F., Performance of filled polymer systems under novel dynamic extrusion processing conditions, *Plast. Rubber Compos.*, 2002, 31(10): 432–435
- Kalay G. and Kalay C. R. I., Interlocking shish-kebab morphology in polybutene-1, *J. Polym. Sci. Polym. Phys.*, 2002, 40(17): 1828–1834
- Qu J. P., Peng X. F. and Zhou N. Q., Research on elastic behaviors of LDPE melt during capillary dynamic extrusion, *J. South China Univ. Technol. (Natural Science Edition)*, 1998, 26(11): 1–7
- Wang X., Peng Y., Chen Q. et al., Application of oscillation technology in injection molding, *China Plast.*, 1999, 13(4): 49–54 (in Chinese)
- Chen L. M. and Shen K. Z., Biaxial self-reinforcement of isotactic polypropylene prepared in uniaxial oscillating stress by injection molding, I Processing conditions and mechanical properties, *J. Appl. Polym. Sci.*, 2000, 78(11): 1906–1910
- Chen L. M. and Shen K. Z., Biaxial self-reinforcement of isotactic polypropylene prepared in uniaxial oscillating stress by injection molding, II Morphology, *J. Appl. Polym. Sci.*, 2000, 78(11): 1911–1971
- Qu J. P., He G. J., He H. Z., Yu G. H. and Liu G. Q., Effect of the vibration shear flow field in capillary dynamic rheometer on the crystallization behavior of polypropylene, *Eur. Polym. J.*, 2004, 40: 1849–1855
- Zheng Q., Shangguan Y., Tong L. and Peng M., Effect of vibration on crystal morphology and structure of isotactic polypropylene in nonisothermal crystallization, *J. Appl. Polym. Sci.*, 2004, 94(5): 2187–2195
- Fukushima H., Ogino Y., Matsuba G., Nishida K. and Kanaya T., Crystallization of polyethylene under shear flow as studied by time resolved depolarized light scattering, effects of shear rate and shear strain, *Polymer*, 2005, 46: 1878–1885
- Cheng S. Z. D., Zhu L. and Li C. Y., Size effect of metastable states on semicrystalline polymer structures and morphologies, *Polym. Bull.*, 1999(9): 28–33 (in Chinese)
- Zhang J. and Qu J., Effect on the entanglement density of polymer melt in oscillatory in shear force field, *J. South China Univ. Technol. (Natural Science Edition)*, 2003, 31(4): 1–5 (in Chinese)
- Kjøiksen A.-L., Hiorth M. and Nyström B., Association under shear flow in aqueous solutions of pectin, *Eur. Polym. J.*, 2005, 41: 761–770
- Cheng R. S., Yang H., Yan X. H., Wang Z. L. and Li L., The solvation and desolvation process in the course of coil-globule transition of aqueous poly(*N*-isopropylacrylamide) solution, *Chem. J. Chin. Univ.*, 2001, 22(7): 1262–1264 (in Chinese)