

Mechanical Properties of Methyl Methacrylate Copolymers

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Abstract—Methyl methacrylate was used as a main monomer in this paper. Firstly poly(methyl methacrylate) (PMMA) was synthesized by bulk polymerization of methyl methacrylate(MMA) in mold. Subsequently MMA was copolymerized with acrylonitrile (AN) and styrene (St) respectively in mold. The as-prepared products were tested by tensile and impact test. The results of test show that with the increase of the AN content in the copolymer, the tensile strength of the copolymer showed a downward trend for the internal defects after rising first for the forming of intermolecular hydrogen bond. The impact strength of the copolymer showed a rising trend for the formation of hydrogen bonds. Meanwhile, with the increase of the St content, the tensile strength of the copolymer showed a rising trend for the introduce of strong rigidity benzene. The impact strength of the copolymer increased first for the rigidity of benzene pendant group and then decreased for the decline accumulation degree of molecular chain.

Keywords- methyl methacrylate; copolymer; mechanical properties; tensile strength; impact strength

I. INTRODUCTION

It is the features such as high optical transmittance, long service life, high UV resistance, and no color selection limits that make PMMA stand out in the plastic [1]. As time goes on, the fields of its application are more and more widely. In addition, PMMA can be manufactured by any thermoforming method, which making its application extends to aerospace, aviation, agriculture, medicine and optical field, etc [2, 3]. It is a never neglected advantage that PMMA material can be 100% recycled, which make a great contribution to save natural resources. Thermal processing results show that when the temperature reaches 400oC, PMMA will be decomposed to MMA, which makes the disposal of waste products become easier. When MMA was distilled to the concentration of more than 99%, it can be used as a raw material for production, which makes monomer source and

pretreatment become simpler. Although PMMA itself has many merits, but it shows insufficiency in the resistance to chemical reagent, solvent resistance and flame resistance, etc. Obvious hygroscopicity and poor wear resistance also limits its application. In order to make up the deficiency of PMMA itself, people are busy with PMMA modification to improve its wear resistance, flame retardant and heat resistant performance[4-14]. Based on previous work, MMA and copolymerization monomer was polymerized by bulk polymerization, and by adjusting the ratio of polymer to study the change of the polymer mechanics performance, in order to find a formula that the tensile strength of PMMA can be improved.

II. EXPERIMENTAL SECTION

A. Chemicals

MMA and AN were purchased from Tianjin Kermel Chemical Reagent Co.,Ltd. St, DVB and MA were purchased from Tianjin Guangfu Fine Chemical Research Institute.

B. Homopolymerization of MMA

50mL distilled MMA was added into a dry and clean conical flask. After, 1% of the monomer BPO was added into reaction system, the system was heated to 80oC by water bath, when the monomer conversion ratio in the conical flask met the requirement of the prepolymer, immediately taking the flask out from the water bath and cooling to room temperature with cold water. The as-prepared prepolymer was poured into the mold through the clean glass funnel. Then the mold was sealed with cellophane and was carefully placed into the oven. Under 40 oC the monomer was further polymerized over 24h. After the polymer solidified, the temperature was raised to 100 oC for another 1h. Finally, disconnecting the oven power, the polymer is gradually cooled to room

temperature and then washed with cold water to make its volume shrinkage, in order to more easy to open the mold.

C. Copolymerization of MMA

The AN was respectively added to MMA by a ratio of MMA: AN (V) = 5:1 (4:1; 3:1; 2:1). The methods are the same as homopolymerization. Another monomer St was copolymerized with MMA in this study, the step was the same as AN/MMA copolymerization.

D. Characterization

Fourier transform infrared (FT-IR) spectra were recorded from KBr pellets at room temperature using a Nicolet Avatar FT-IR spectrometer. The tensile strength was tested by microcomputer control electronic universal testing machine. The impact strength was tested by izod impact tester.

III. RESULTS AND DISCUSSION

A. FT-IR Analysis

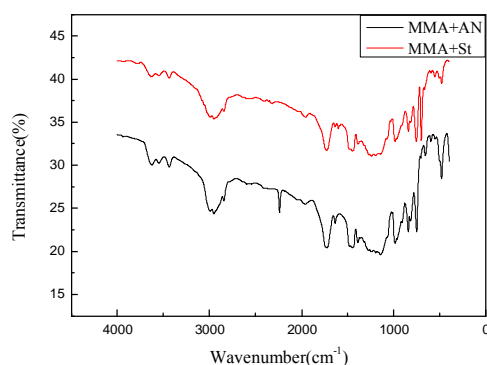


Figure 1. FT-IR spectra of MMA/AN and MMA/St copolymers

Figure 1 shows the Fourier transform infrared (FT-IR) spectra of MMA/AN and MMA/St copolymer. As shown in MMA/AN curve, the peaks of the free and the hydrogen bond association $-OH$ at 3630cm^{-1} should be derived from the moisture that not divided or absorbed in the samples. The $-CH_3$ and $-CH_2$ stretching vibration peaks appear at 2950cm^{-1} and 2845cm^{-1} . The $-C\equiv N$ stretching vibration peak at 2240cm^{-1} , $-C=O$ stretching vibration peak at 1730cm^{-1} , $-CH_2$ bending vibration absorption peak at 1450cm^{-1} and bending vibration peak of methyl in the $-CH_3O-C=O$ at 1390cm^{-1} show that MMA is successfully copolymerized with AN, including stretching vibration peak of $C-O-C$ in ester and skeletal vibration peak of $C-C$ in the copolymer at the vicinity of 1145cm^{-1} .

As shown in MMA/St curve, in addition to containing the characteristic peak of PMMA, the infrared absorption peak at the vicinity of 1630cm^{-1} can be described as the skeletal vibration of benzene in the St or the stretching vibration isolation of $C=C$ in the copolymer, and likely covering for each other. The peaks at 1000 cm^{-1} or less are basically the vibration absorption on the benzene, such as the $C-H$ plane bending vibration peak on the benzene at $900-600\text{cm}^{-1}$. These show that MMA is successfully copolymerized with St.

B. Tensile test analysis

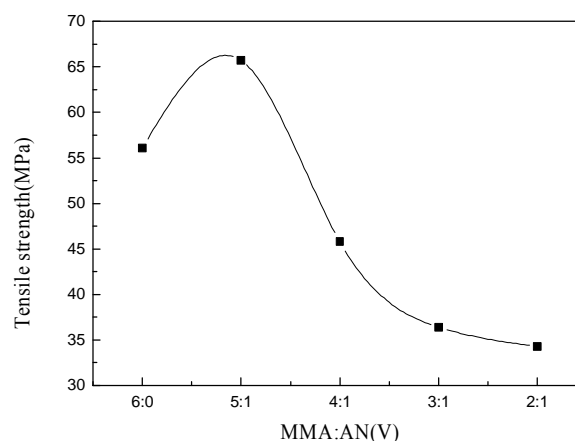


Figure 2. Tensile strength of MMA/ANt copolymer under the different ratio.

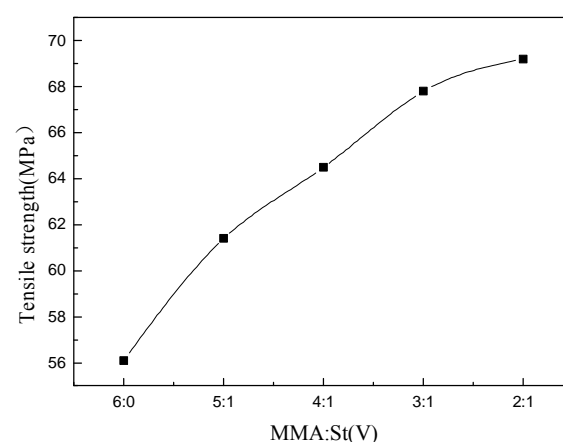


Figure 3. Tensile strength of MMA/St copolymer under the different ratio.

Figure 2 shows the tensile test result of MMA/AN copolymer. As we can see, with the increase of the AN content in the copolymer, the tensile strength of the copolymer showed a downward trend after rising first. When MMA:AN=5:1, the tensile strength is the biggest. The reason is that the tensile strength of PMMA is stronger than PAN, when adding a little AN, the forming of intermolecular hydrogen bond due to the existence of nitrile increases intermolecular forces and eventually leads to the increase of the tensile strength of copolymer. When adding a large number of AN, the tensile strength of copolymer is reduced. The causes of this phenomenon could also be that the copolymer with different molecular weight or the sample with different thickness leads to the different internal defects. Figure 3 shows the tensile test result of MMA/St copolymer. As we can see, with the increase of the St content, the tensile strength of the copolymer shows a rising trend. It can be explained that strong rigidity benzene was introduced into the system.

C. Impact test analysis

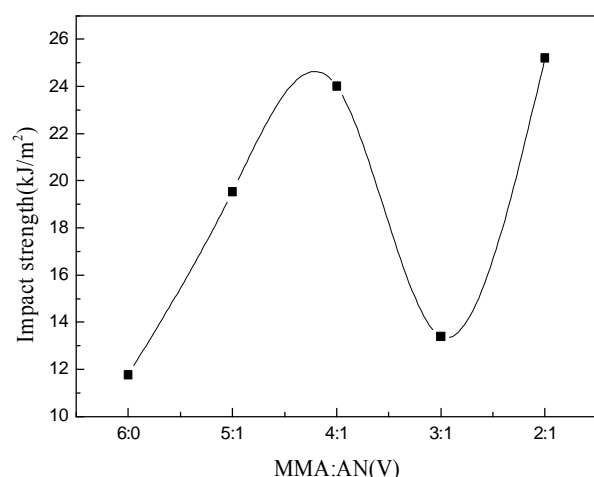


Figure 4. The impact strength of MMA/AN copolymer under the different ratio.

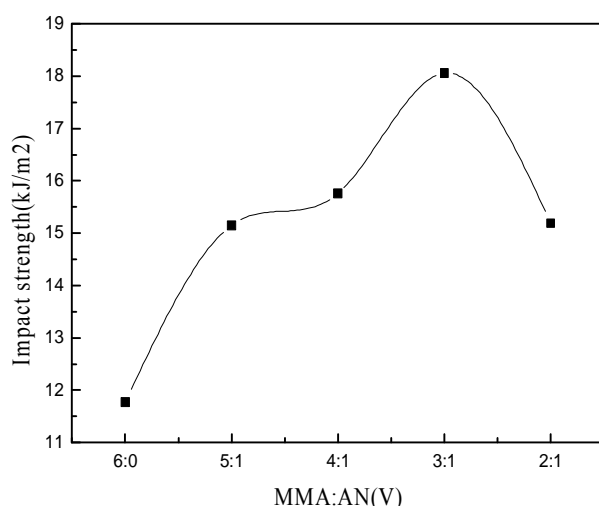


Figure 5. The impact strength of MMA/St copolymer under the different ratio.

Figure 4 shows the impact test result of MMA/AN copolymer. The results of impact test show that with the increase of the AN content in the copolymer, the impact strength of the copolymer showed a rising trend. This is because that on one hand the flexibility of AN structural part is higher than that of MMA structure, on the other hand, $-C\equiv N$ is a strong polar group. It can form hydrogen bonds between the macromolecular chain, strengthening the interact of macromolecular chain. Therefore, the participation of AN is helpful to improve the impact strength of the copolymer.

Figure 5 shows the impact test result of MMA/St copolymer. The results of impact test show that with the increase of the St content, the impact strength of the copolymer increased first and then decreased. The possible reason is that when adding a little St, the rigidity of benzene pendant group is the main influence factor. When adding a large number of St, the accumulation degree of molecular chain is decline, increasing the free volume and the chain activity, leading to the decline of the impact strength.

IV. CONCLUSION

In this work, Methyl methacrylate was used as a main monomer copolymerized with acrylonitrile (AN) and styrene (St) respectively in mold. The tensile strength of the copolymer showed a downward trend after rising first. However, with the increase of the St content, the tensile strength of the copolymer showed a rising trend. The results of impact test show that with the increase of the AN content in the copolymer, the impact strength of the copolymer showed a rising trend, but with the increase of the St content, the impact strength of the copolymer increased first and then decreased.

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REFERENCES

- [1] Z. Wang, B. H. Tan and H. Hussain, "pH-responsive Amphiphilic Hybrid Random-type Copolymers of Poly (acrylic acid) and Poly (acrylate-POSS): Synthesis by ATRP and Self-assembly in Aqueous Solution," *Colloid and Polymer Science*, vol. 291, 2013, pp. 1803-1815, doi:10.1126/science.1065467.
- [2] R. Kreis, "Short Curing Times for the Polymer Concrete," *International Journal of Cement Composites and Lightweight Concrete*, vol. 7, 1985, pp. 49-54, doi:10.1126/science.1065467.
- [3] S. Deb, R. Doiron and L. DiSilvio, "PMMA Bone Cement Containing a Quaternary Amine Comonomer with Potential Antibacterial Properties," *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, vol. 85, 2008, pp. 130-139, doi:10.1126/science.1065467.
- [4] B. J. Ash, R. W. Siegel and L. S. Schadler, "Glass-transition Temperature Behavior of Alumina/PMMA Nanocomposites," *Journal of Polymer Science Part B: Polymer Physics*, vol. 42, 2004, pp. 4371- 4383, doi:10.1126/science.1065467.
- [5] Y. S. Choi, M. H. Choi and K. H. Wang, "Synthesis of Exfoliated PMMA/Na-MMT Nanocomposites via Soap-free Emulsion Polymerization," *Macromolecules*, vol.34, 2001, pp. 8978-8985, doi:10.1126/science.1065467.
- [6] Z. Yang, B. Dong and Y. Huang, "A Study on Carbon Nanotubes Reinforced Poly (methyl methacrylate) Nanocomposites," *Materials Letters*, vol.59, 2005, pp. 2128-2132, doi:10.1126/science.1065467.
- [7] S. Sepeur, N. Kunze, and B. Werner, "UV Curable Hard Coatings on Plastics," *Thin Solid Films*, vol. 351, 1999, pp. 216-219, doi:10.1126/science.1065467.
- [8] P. Malcolm Stevens, *Polymer Chemistry*. New York: Oxford univ. press, 1990, pp. 185-192.
- [9] C.Y. Luo, W.X. Chen and Y. Gao, "Feather-like morphology of poly(methyl methacrylate)/poly(ethylene oxide) blends: The effect of cooling rate and poly(methyl methacrylate) content," *Journal of Applied Polymer Science*, vol. 132, 2015 pp, DOI: 10.1002/app.41705.
- [10] Y. P. Jiang, X. G. Li, S. R. Wang and Y. Xiao, "Preparation of titanium dioxide nano-particles modified with poly (methyl methacrylate) and its electrorheological characteristics in Isopar L," *Colloid and polymer Science*, vol. 293, 2015 pp. 473-479, DOI: 10.1007/s00396-014-3434-2.
- [11] C. F.Cao, Coarse-Grained Molecular Dynamics Simulations of Stereoregular Poly(methylmethacrylate)/Poly(vinyl chloride) Blends, *Journal of Polymer Science Part B-Polymer Physics*, vol. 53, 2015, pp. 203-212, DOI: 10.1002/polb.23608.
- [12] Y.X. Zhang, M. Zuo, Y. H. Song, X. P. Yan and Q. Zheng, Dynamic rheology and dielectric relaxation of poly(vinylidene fluoride)/poly(methylmethacrylate) blends. *Composites Science and Technology*, vol.106, 2015, pp.39-46, DOI: 10.1016/j.compscitech.2014.10.024.
- [13] G. E. Zsoldos and M. Kollar, Structural analysis of polyolefin-poly(methyl methacrylate) blends. *Journal of Thermal*

Analysis and Calorimetry, vol. 119, 2015, pp.63-72,
DOI: 10.1007/s10973-014-4155-y.
[14] N. S. TAE, J. S. Kim, J. O. Kweon and J. H. Lee, "Synthesis of High
Molecular Weight Poly(styrene-*b*-methyl methacrylate) Using a

Plug Flow Reactor System by Anionic
Polymerization," Macromolecular Research, Vol. 23, 2015,
pp.100-110, DOI: 10.1007/s13233-015-3008-2