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Free Radical Initiation Copolymerization of Glucose-with MMA and analysis of its thermal stability

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Abstract. D-glucose was used to react with methyl methacrylate (MMA) (and methyl acrylate(MA) as comparison) to generate new biomass-based materials in presence of free radical initiator. Potassium peroxydisulfate was used as free-radical initiator in the reaction. The final chemical structure and thermal stability were analyzed by FT-IR and TGA. The results showed that the Glucose-co-MMA (G-MMA) and Glucose-co-MA (G-MA) copolymers had better thermal performance than PMMA and PMA.

Introduction

Methyl methacrylate and methyl acrylate are commonly used in organic synthesis as intermediates, they are also important monomer for synthetic polymers. MMA was one of the most important industrial products of methacrylic acid esters. Polymethyl methacrylate(PMMA) was highly transparent amorphous thermoplastic polymer. PMMA has the advantage that good light transmission (the rate of visible light transmittance was 90% to 92%, the rate of infrared light transmission was 85% to 90%), high mechanical strength and toughness[1-2]. PMMA was widely used in the field of artificial decorative materials, construction of industrial parts, the materials of optical information and electrical components package[3]. Because of the poor thermal stability, the application of PMMA was limited in many fields although PMMA was a performance transparent material that has the strongpoint of apparent gloss and excellent weathering performance. Improving the toughness and heat resistance of the acrylic copolymer was an important part of research interests[4-8]. In this paper, the abundant and inexpensive natural glucose was used to react with acrylic monomers and the thermal property of the products was explored.

Materials and experiment

Materials. The following chemicals including methyl methacrylate (MMA), methyl acrylate(MA), chloroform,D-glucose and potassium peroxydisulfate were all of analytical grade and obtained from Chendu Kelong Chemicals Company). The chemicals were used without further purification.

Experimental. 1.Synthesis of PMMA and PMA: 1g potassium peroxydisulfate as initiator was dissolved in 10ml distilled water (not all dissolved). 30ml methyl methacrylate or methyl acrylate was added while stirring. The mixture was sealed in a beaker. After 4h of reaction at approximately 60–65 ^{o}C under stirring conditions, the product was cooled to room temperature. The final product was cut into small piece then dried to constant weight under the condition of 30 ^{o}C

2. Synthesis of G-MMA and G-MA copolymers: 2g D-glucose was dissolved in 10ml distilled water, then 1g potassium peroxydisulfate as initiator was added into the solution (the potassium peroxydisulfate was not all dissolved). Subsequently, 30ml methyl methacrylate or methyl acrylate was added while stirring. The mixture was sealed in a beaker. After 4h of reaction at approximately

60–65 °C under stirring conditions, the product was cooled to room temperature naturally and then dissolved in chloroform. Chloroform solution was dropped in distilled water with stirring. After stirred for 2h, the organic layers obtained from centrifuging was dried in an oven for 2 days under the condition of 45 °C。

Characterization 1.FT-IR spectroscopy.

Infrared spectra were obtained using a Fourier transform infrared spectrometer (Nicolet 6700, USA). PMMA and G-MMA copolymers were prepared by the KBr disc method and the spectra were recorded in the 400–4000 cm $^{-1}$ range with 32 scans at a resolution of 4 cm$^{-1.}$ PMA and G-MA copolymer were cut into thin slices and measured by attenuated total reflection. The spectra were recorded in the 700–4000 cm $^{-1}$ range with 32 scans at a resolution of 4 cm^{-1}. **2. Thermal analysis (TGA):** TGA of the samples were carried out by using Q500 (TA Instruments, USA). 3-5 mg each samples were heated from 20 to 620 °C under N_2 stream (10 ml/min) at a heating rate of 10 °C/min.

Results and discussion

From IR spectrum of G-MA copolymer and PMA (Fig1), it can be seen that the characteristic band of hydroxyl was at 3378.8cm^{-1} which did not appear in the spectrum of PMA. D-glucose was proven to react with MA and formed a G-MA copolymer. The peak at 2954cm^{-1} corresponds to C-H stretching vibration of methylene groups and the peak at 1437cm^{-1} was asymmetric vibration of methylene groups. The absorption band of carbonyl of acetyl groups was at 1732 cm^{-1} and the band at 1163 cm^{-1} was assigned to C-O-C vibration of G-MA copolymer and MA.

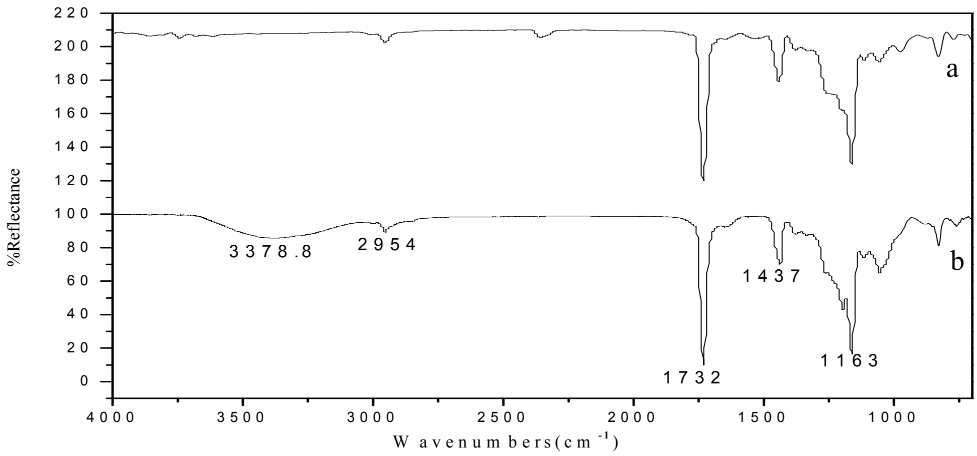


Fig.1. FT-IR spectra of (a) PMA and (b) G-MA copolymer.

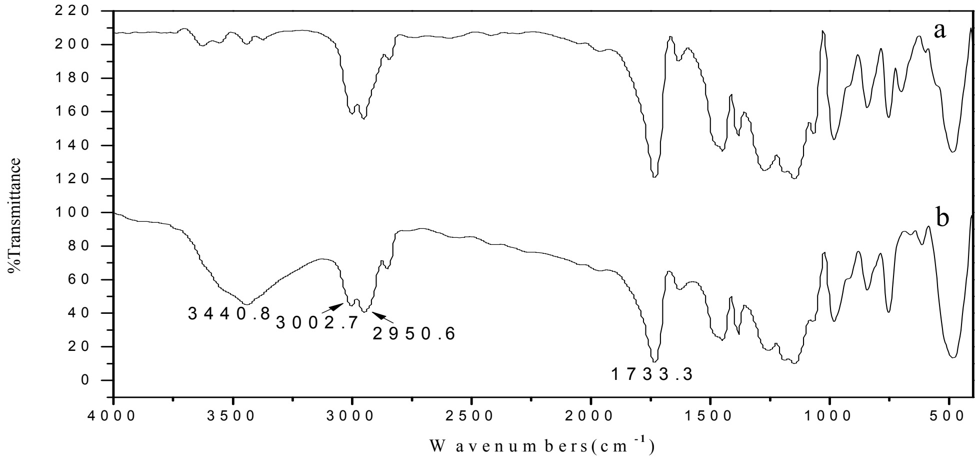
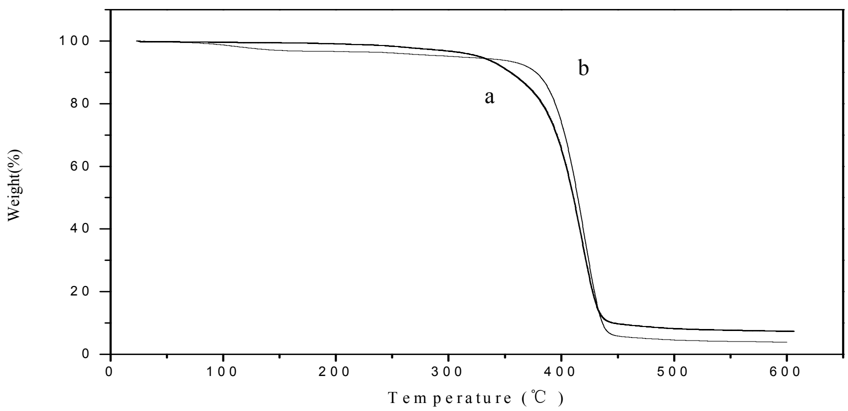


Fig.2. FT-IR spectra of (a) PMMA and (b) G-MMA copolymer.

As seen in the IR spectrum of G-MMA copolymer and PMMA (Fig2), the absorption band of hydroxyl was at 3440.8cm^{-1} which did not appear in the spectrum of PMMA. It has proven that the D-glucose reacted with MMA and new –OH groups from glucose were present in G-MMA copolymer. The peaks at 3002.7cm^{-1} and 2950.5cm^{-1}correspond to, respectively, C-H stretching vibration of methyl and methylene groups, and the peak at 1449.8cm^{-1} was asymmetric vibration of methylene groups. The absorption band of carbonyl of acetyl groups was at 1733.3 cm^{-1}.

Thermogravimetric data（Fig.3）show the weight loss in association with temperature increased in a N_2 atmosphere. It can be seen from Fig.3(Top) that PMA and G-MA copolymer exhibit one degradation step in N_2 atmosphere during 300-450℃. G-MA copolymer has a better thermal stability than PMA because the decomposing temperature of G-MA copolymer was 330 ^{o}C that is 30 ^{o}C higher than that of PMA. The G-MA copolymer started to decompose at 330 ^{o}C and the maximum weight loss rate occurred at 420.8 ^{o}C. PMA started to decompose at 299 ^{o}C and the maximum weight loss rate occurred at 418 ^{o}C. There was about 4% weight loss of the G-MA copolymer between 100 ^{o}C and 300 ^{o}C due to the water and chloroform contained in the samples. As showed in Fig.3(Down), PMMA exhibited four degradation steps in N_2 atmosphere during 100-450 ^{o}C and G-MMA copolymer exhibited three degradation steps in N_2 atmosphere during100-450 ^{o}C. The decomposing temperature of PMMA was about 140 ^{o}C higher than 108 ^{o}C of G-MMA copolymer. PMMA started-to decompose at 140 ^{o}C and the maximum weight loss rate occurred at 398 ^{o}C. The G-MMA copolymer starteds to decompose at 108 ^{o}C and the maximum weight loss rate occurred at 386 ^{o}C .



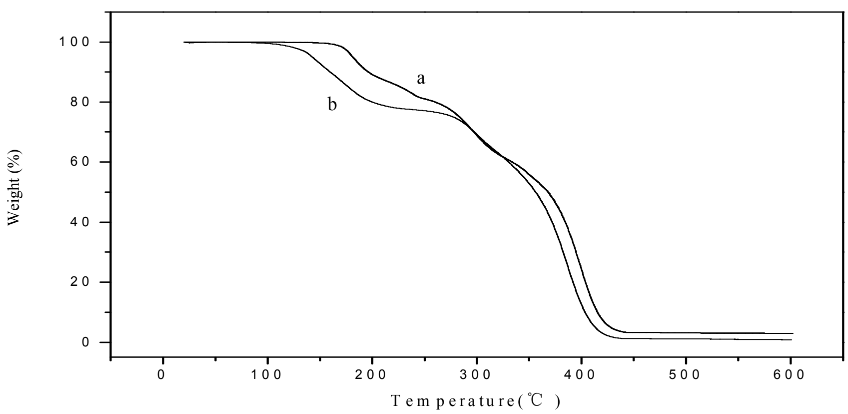


Fig.3. (TOP) TGA curves of (a) PMA and (b) G-MA copolymer; (Down) TGA curves of (a)PMMA and (b) G-MMA copolymer

Conclusion.

The results of FT-IR indicated that D-glucose was successfully reacted with MMA and MA through free radical polymerization reaction and the copolymers have shown different thermal stability than PMMA and PMA. The decomposing temperature of G-MA copolymer was improved 30 ^{o}C based on PMA. The thermal ability of G-MMA copolymer was not significantly improved and further studies were needed in the future.

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