

Synthesis and Characterization of Poly(methyl methacrylate-*co*-vinyl triethoxysilane) Prepared by Free Radical Polymerization

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The copolymerization of methyl methacrylate (MMA) with vinyl triethoxysilane (VTES) was carried out in ethyl cellosolve at 70 °C using azobisisobutyronitrile (AIBN) as a free radical initiator. The prepared copolymer was purified and then analysed by FT-IR, NMR, TGA and SEM analyses. FT-IR along with NMR confirm the successful preparation of the copolymer. The prepared copolymer shows better thermal stability than poly(methyl methacrylate). A morphological study was also carried out by SEM analysis. SEM micrographs show that the copolymer surface gets roughened and becomes porous on copolymerization.

Introduction

The free radical polymerization (FRP) is a very prominent polymerization method used to polymerize almost all the vinyl monomers. It is also used to tune the properties in a copolymer via systematic copolymerization. [1, 2] This is a versatile method with respect to reaction conditions and functionality present in the polymerization system and also is compatible with a wide range of monomers. [3]

The polyacrylate is a class of important polymers. They have been produced in industry on a large scale due to their extensive use in adhesives, latex paints, floor tiles, paper

coatings, and textiles. Most of the acrylic polymers are stable at room temperature but become slightly sticky at elevated temperatures due to their linear structure. Perhaps, they have poor water resistivity too. To overcome these poor properties, acrylic monomers are frequently copolymerized with other monomers. The copolymerization of vinyl silane with acrylic monomer is anticipated to improve such properties.

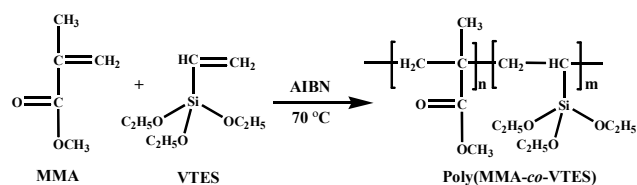
The radical copolymerization of various organofunctional silane monomers has attracted considerable interest based on the improvement of properties and economic advantages [4].

Silane units in a copolymer may play an important role in the preparation of polymer/silica composite. Moreover, silicon-containing polymers and copolymers show high hydrophobicity. They are versatile for chemical modifications and have extremely low glass transition temperature, high chain flexibility, UV stability, biocompatibility, surface activity, and high oxygen permeability [5-7]. Because of these properties, copolymers of organofunctional silane with vinyl monomers find a wide application in areas like gas separation, surface modification, enzyme immobilization, biomedical applications, etc. Organofunctional silane has been used as a coupling agent to enhance the performance, adhesive strength, weather resistance, and stain resistance of polymeric materials. [5, 6, 8] Vinyl triethoxysilane (VTES) is one such organofunctional silane, which has three hydrolysable ethoxy groups attached to silicon. Because of these groups, VTES gives additional flexibility to the polymer and also enhances the adhesive strength of the polymer against substrates containing Si such as glass, stone etc. The position of the silicon atom in the vinyl silane also affects its reactivity in copolymerization with other vinyl monomers. [9] Moreover, vinyl silane has been used in copolymerization with acrylate to enhance the miscibility of the two phases. [10-14]

There have been several reports on the copolymerization of MMA with different monomers. Yusuf et al. prepared a photodegradable copolymer of MMA with methyl α -chloroacrylate (MCA) via radical addition-fragmentation chain transfer (RAFT) polymerization technique using 2-cyano-2-propyl dodecyl trithiocarbonate (CPDTC) as RAFT agent and AIBN as an initiator. [15] The thermal property of this copolymer was found to be similar to that of PMMA while the thermal resistivity was lower and showed good photodegradability in the presence of $Mn_2(CO)_{10}$ due to the reactivity of chlorine groups in the main chain of the copolymer. It was also found that as the ratio of MCA increases, the degradability of the copolymer increases. Nashir et al., prepared a copolymer of dimethylamino ethyl methacrylate (DAEMA) with MMA via solution polymerisation using AIBN as an initiator. This copolymer showed good antimicrobial properties against *E. coli* and *S. aureus*, and the antimicrobial properties increased with the concentration of DAEMA. [16] Leiza et al. prepared copolymers of vinyl acetate with three different vinyl silane monomers (vinyl trimethoxysilane, vinyl triethoxysilane and vinyl silanetriol) via emulsion polymerization. They found that the rate of copolymerization was comparatively slow. [17] Similarly, Chuang Ma et al. prepared a copolymer of MMA with butyl acrylate (BA) and then modified it with VTES via solution

polymerisation using AIBN as an initiator under the N₂ atmosphere. [18] It has been found that the increasing amount of VTES enhanced the anti-ageing property as well as the hydrophobicity of the copolymer. Due to this, it may be used in the protective coating.

The main objective of this present investigation is to prepare a copolymer of methyl methacrylate (MMA) with vinyl triethoxysilane (VTES) via free radical copolymerization (Scheme 1) and its subsequent characterizations.



Scheme 1. Preparation of Poly(MMA-co-VTES)

Experimental

Materials

MMA (Aldrich; 99%, India) was purified by passing through a basic alumina-packed column and stored at 0 °C. VTES (Sigma-Aldrich), AIBN (Sigma-Aldrich), ethyl cellosolve (99%; Emplura, India), precipitated silica and Tetrahydrofuran were used as received.

Synthesis of copolymer of methyl methacrylate with vinyl triethoxysilane via free radical polymerization

In a typical free radical polymerization reaction, ethyl cellosolve (20g), the monomers MMA (5g) and VTES (1g) were taken in a dry Schlenk tube equipped with a stirrer, a magnetic bar and a rubber septum. The mixture was stirred

for 15 minutes, and then the initiator azobisisobutyronitrile (0.06g) was added to the solution. The polymerization was started by placing the Schlenk tube in a preheated oil bath at 70 °C. The polymerization was carried out for 3 hrs. The aliquot was taken out to determine the monomer conversion gravimetrically. The half volume of residual polymer was then dissolved in THF, re-precipitated from water, filtered and dried in an oven at 60 °C to get the pure polymer. The pure polymer was characterized by FTIR, NMR and SEM analyses.

To half the volume of residual polymer, THF (5g) and silica (0.05g) were added and stirred for 3 hrs. The mixture was then re-precipitated from water to obtain the copolymer/silica composite. A thermal study of this composite was also carried out by TGA analysis.

Characterization

Nuclear magnetic resonance (NMR) spectra were recorded on Jeol 9.4 Tesla/400 MHz Bruker NMR spectrometer and also in 400 MHz Bruker NMR spectrometer using CDCl₃ as solvent. Fourier Transform Infrared (FTIR) spectra were recorded for the samples by model spectrum/KBr pressed pellets on an Omnic Avatar 360. Thermogravimetric Analysis (TGA) was performed in STA 449 F1 Jupiter thermogravimetric analyser at a heating rate of 10 °C min⁻¹ and was heated from 50 to 600 °C under nitrogen atmosphere. Scanning electron

microscopy (SEM) images of the copolymer coated with gold were recorded in a Zeiss EVO LS10 SEM machine.

Result and discussion

Scheme 1 shows a single-step free radical copolymerization of MMA with VTES at 70 °C. The structural elucidation of the copolymer was carried out by FT-IR, ¹H NMR and ¹³C NMR analyses to confirm the successful preparation of the copolymer.

FT-IR analysis

Figure 1 shows the FT-IR spectrum of the copolymer. The broad band at 2957 cm⁻¹ is due to C–H stretching vibration of methyl and methylene groups whereas, bands at 1236 cm⁻¹ and 1448 cm⁻¹ are assigned to symmetric CH₃ and asymmetric CH₃/CH₂ vibrations respectively. The strongest absorption peak at 1730 cm⁻¹ is assigned to C=O stretching of the ester moiety of MMA while the characteristic band at 977 cm⁻¹ is assigned to the Si-O-C group of VTES. The absence of the absorption band at 1642 cm⁻¹ in the copolymer indicates that the vinyl group of both the monomers have taken part in the copolymerization.

¹H NMR and ¹³C NMR analysis

The synthesis of copolymer was further confirmed by ¹H NMR and ¹³C NMR analyses. The ¹H-NMR spectrum of poly(MMA-co-VTES) is consistent with the chemical structure shown in **Figure 2**. The signal belonging to the

vinyl protons of the monomer disappeared from the region close to 6.0 ppm in the ¹H-NMR spectrum of the copolymer. Moreover, for the copolymer, methyl protons in MMA resonate at 0.8-1.0 ppm and -OCH₃ protons resonate at 3.6 ppm, while CH₂ protons of the main chain backbone of monomers resonate at 1.7-1.9 ppm. ¹H NMR signal for Si-O-CH₂- appears at 3.84 ppm and ¹H NMR signal for -CH₃ in -Si-O-CH₂CH₃ appears at 1.0–1.2 ppm. This confirms the presence of VTES unit in the copolymer. The CH protons of the two monomers resonate at 4.7 ppm.

The ¹³C NMR spectrum of the copolymer is shown in **Figure 3**. The ¹³C NMR spectrum has the characteristic peaks of the monomeric units. The ester carbonyl carbon of the MMA unit shows a peak at 178 ppm. The signal at 66.6 ppm is assigned for -OCH₃ of the MMA unit, while at 54.6 ppm for -OCH₂ group of VTES unit. The backbone methylene carbons of both the comonomers are observed at 44.7 ppm. The signal at 18.9 ppm corresponds to the methyl carbons. The NMR analysis shows the presence of MMA as well as VTES units in the copolymer and hence confirms their successful copolymerization.

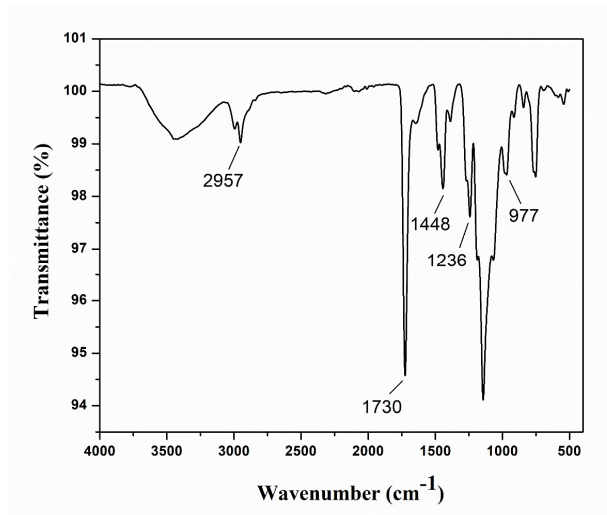


Figure 1. FT-IR spectrum of the copolymer

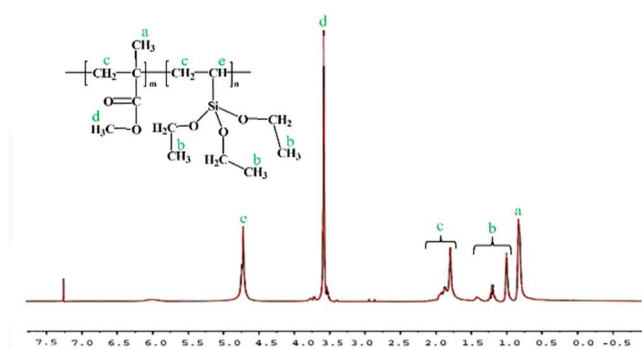


Figure 2. ¹H NMR spectrum of the copolymer

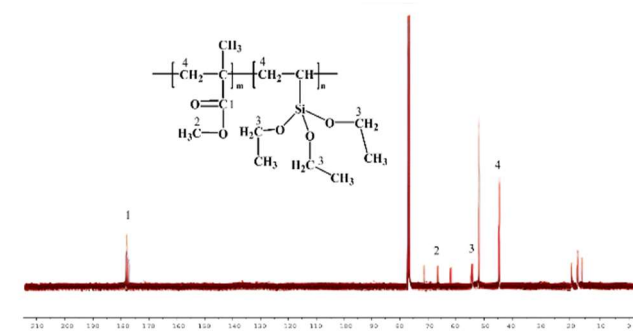


Figure 3. ¹³C NMR spectrum of the copolymer

Thermal study

Typical weight loss (TG) and derivative of weight loss (DTG) curves of the homopolymer of methyl methacrylate (PMMA), copolymer poly(MMA-co-VTES) and the poly(MMA-co-

VTES)/Silica composite are shown in **Figures 4** and **5** respectively. The initial and final decomposition temperatures are determined from the TG curves, while the maximum degradation temperature is determined from the DTG curves.

PMMA prepared by free radical polymerization starts to degrade at approximately 175 °C. The degradation occurs at the sterically hindered linkages which are formed due to head-to-head coupling during polymerization. [15-17] Unsaturated end groups start to degrade at 225 °C which are formed by disproportionation during polymerization, while the other possible saturated end groups are thermally stable in an N₂ atmosphere up to 300 °C. [18, 19] Random chain fractionation occurs above 300 °C leading to rapid depolymerization of PMMA to form volatile MMA monomer. [20]

The TG/DTG curves of PMMA also show a single-stage degradation. The maximum degradation temperature (under nitrogen atmosphere) for PMMA is 343.6 °C (**Figure 4**), whereas the maximum degradation temperature for poly(MMA-co-VTES) copolymer is found to be 373 °C (under N₂ atmosphere). This indicates that the copolymerization with VTES enhances the thermal stability of poly(MMA-co-VTES) copolymer. The TG and DTG curves of the copolymer are found to be similar to those of the copolymer/silica composite (**Figures 4** and **5**) curves. Both copolymer and copolymer/silica composite also exhibit a single-stage degradation.

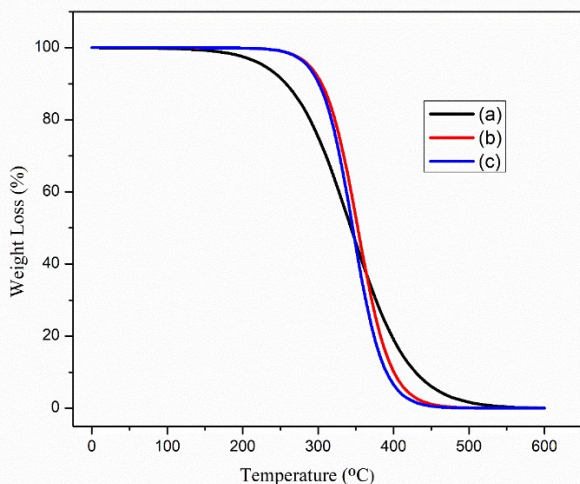


Figure 4. TG thermograms of (a) PMMA, (b) poly(MMA-co-VTES) and (c) poly(MMA-co-VTES)/silica composite

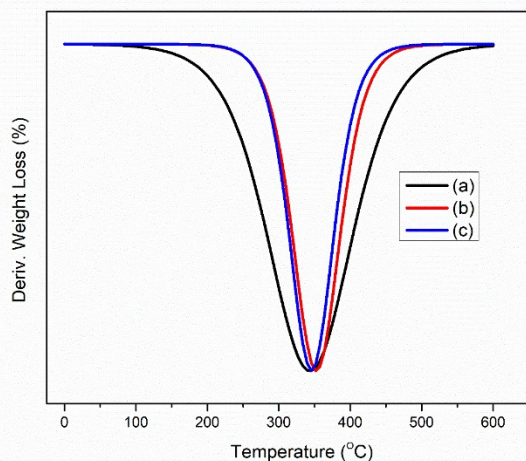


Figure 5. DTG thermograms of (a) PMMA, (b) poly(MMA-co-VTES) and (c) poly(MMA-co-VTES)/silica composite

Surface morphology

Scanning electron microscopy was used to study the surface morphology of the copolymer. **Figure 6** shows the SEM micrographs of poly(MMA-co-VTES) copolymer. Non-uniformly distributed porous morphology is seen in the SEM micrographs of the copolymer where the size of the pores varies from 0.5 to 4.6 μm with a depth of less than 1

μm . This indicates that the prepared copolymer surface has good air permeability.

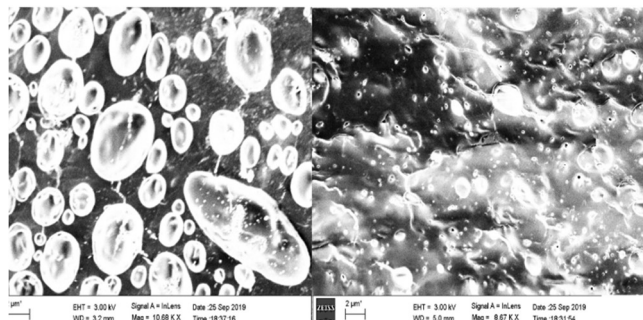


Figure 6. SEM micrographs of the copolymer Poly(MMA-co-VTES)

Conclusion

Poly(MMA-co-VTES) was prepared via free radical copolymerization of MMA with VTES at 70 °C. The successful copolymerization was confirmed by the FT-IR, ^1H NMR and ^{13}C NMR analysis. The absence of an absorption band at 1650 cm^{-1} in the FT-IR spectrum of the copolymer and the absence of ^1H NMR signal at 6.0 ppm in the NMR spectrum of the copolymer indicates the formation of the copolymer. The copolymer has higher thermal stability as compared to the PMMA. SEM analysis prevails the porous structure of the copolymer. The information generated through this investigation has given us insight into the potential applications of a silane-modified thermoplastic elastomer.

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