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Preparation of Macroporous Aluminium Oxide using Template of Poly(methacrylic acid-co-glycidylmethacrylate) Crosslinked with Methylenebisacrylamide

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Poly(methacrylic acid-co-glycidylmethacrylate), poly(MA-co-GMA) samples were prepared by exposure to γ -irradiation, at fixed concentration of methylenebisacrylamide MBA, 0.5% wt/wt as crosslinker while the MA/GMA ratio was varied. FTIR spectra showed bands refer to MA, as well as GMA, indicating the involvement of both in the copolymerization. $Al(NO_3)_3 \cdot 9H_2O$ as a precursor for the preparation of aluminium oxide was templated as a guest into the crosslinked gels by soaking the gels in a methanol solution. The perturbation of the bands at 3439, 2926, 1635, 1476, 1394, and 1166 cm^{-1} after the templation of the guest, provides evidence for the loading of the guest species into the gel. The swelling behavior of the prepared samples found to be dependent on the composition of the gel and the pH. The templation of the aluminium nitrate into the gel was further proved by thermal gravimetric analysis (TGA). Scanning electron microscopy (SEM) was used for investigating the produced oxide particles, which revealed macropores with maximum diameter at MA/GMA, 40:60 wt/wt (H3) and complete disappearance at 80wt% of methacrylic acid (H5). X-ray diffraction (XRD) showed an amorphous structure of the aluminium oxide. Increasing the hydrophilicity of the template leads to an increase in the Lewis acidic sites on the surface of the produced aluminium oxide up to 60wt% of methacrylic acid (H4) while a further increase was met by a rededcrease in the surface acidity (H5).

Keywords aluminium oxide, macroporous, poly(methacrylic acid-co-glycidylmethacrylate), template

Introduction

Porous materials are very important because of their applications and uses as filtraters, separation materials, catalyst supports, and cell immobilizers and advanced biomaterials. Therefore, technologies have been, and continue to develop porous materials with a variety of prescribed pore sizes and open up new engineering possibilities. The classical templating methods depended on using surfactant micellar systems, colloidal crystals, emulsions and even bacteria as templates. This traditional approaches were

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reviewed in many contributions (1, 2). However, poor control over the pore size was the main drawback of using such techniques so new technique based on the use of polymers, especially block copolymers, as templates has been actively studied (3–6). Generally, copolymer templates are always dissolved into certain solvent and form micelles whose shape and size are controlled by varying the polymerization conditions. Some reports on the use of crosslinked gel based on poly hydroxyl ethylmethacrylate (HEMA) and ethyleneglycol dimethacrylate (EGDMA) as template appeared recently (7, 8). The advantage of using crosslinked polymeric systems as templates is the ease of variation of the architecture, chain length and composition (8).

Futhermore, the polymer template can easily be removed by calcinations. Crosslinked polymers with high content of hydrophilic centers are able to expand their volumes due to their swelling in water and other diluents which facilitate the incorporation of the solids that are soluble in water into these crosslinked gels by the spontaneous swelling in water. In their studies, Jiu et al. (7, 8) focused their work on the variation of HEMA/EGDMA ratio and according to their model, polymeric gels with high swelling % may lead to oxides with large or small pores according to the chemical structure, architecture, chain length and composition. For this reason, we synthesized crosslinked copolymer of methacrylic acid (MA) with a hydrophobic monomer, glycidylmethacrylate (GMA) at different MA/GMA ratios while keeping the ratio of the crosslinker, methylenebisacrylamide, MBA, constant. The insertion of the hydrophobic component can invoke more controllable swelling and as a result the loading of the metal oxide precursor, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, will be differently distributed over a high number of mesh units which we aim to lead to porous Al_2O_3 . The direct preparation of metal oxide from their nitrates has been developed before (9, 10). The gel and the inorganic moieties are mutually interactive in the molecular scale. Hydrogen bondings are expected to form and it is thought to be the driving force for the inorganic moieties migrating from solution into the gel network (11–13).

Experimental

Materials

Methacrylic acid (MA) and methylenebisacrylamide (MBA) were supplied by Merck (Germany). Glycidylmethacrylate (GMA) was purchased from Fluka. $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ extra pure was provided from Loba Chemie PVT Ltd., Mumbai-India. Pyridine with 98% minimum assay was obtained from El-nasr Pharmaceutical Company, Egypt. Methanol (pure) was obtained from El-ghomhoria Company, Kalag, Egypt.

Preparation of Poly(methacrylic acid-co-glycidylmethacrylate) Gel

Methacrylic acid and glycidylmethacrylate were used as received for the polymerization process. Poly(MA-co-GMA) samples were prepared with the same concentration of the crosslinker, MBA (0.5%) and varying the MA:GMA ratio, by subjecting them to γ -irradiation from a ^{60}Co source to a total dose 10 kGy.

The formed gels were crushed into smaller granules and immersed in distilled water for 24 h to eliminate any water soluble components that may be present. The samples composition is shown in Table 1 and the expected chemical structure of the resultant cross-linked gel is represented in Figure 1.

Table 1
Compositions of the prepared crosslinked gels

Sample	MA : GMA, wt/wt	MBA, wt%
H1	0 : 100	0.5
H2	20 : 80	0.5
H3	40 : 60	0.5
H4	60 : 40	0.5
H5	80 : 20	0.5

Swelling Behavior of (Methacrylic acid-co-glycidylmethacrylate) Gel

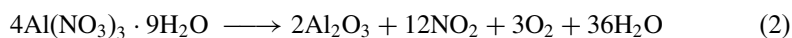
The swelling behavior of the prepared samples was investigated at different pH values by soaking in distilled water until reaching equilibrium. The pH values were adjusted using HCl and NaOH. Finally, the equilibrium water content (EWC) was determined by accurately weighing the sample, both in the hydrated and dried states, and applying Equation (1):

$$\text{EWC} = (m_s - m_d)/m_s \times 100 \quad (1)$$

where m_s and m_d are the weights of the sample in the hydrated and dried states, respectively.

Preparation of Porous Aluminium Oxide

Following the crushing of the crosslinked gels to granules, 3 gm from each was subsequently soaked in methanol (10 ml) containing 10 gm of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ for 24 h, thereafter, separated from the solution and dried at 40°C for 2 days, and finally calcined at 500°C for 6 h to eliminate the copolymer template and obtain Al_2O_3 according to Equation (2)



Pyridine Adsorption

The Al_2O_3 samples were immersed in pyridine at 40°C for 24 h under shaking in order to estimate the presence of Lewis acidic sites on the surface quantitatively using TGA in the range $50\text{--}500^\circ\text{C}$.

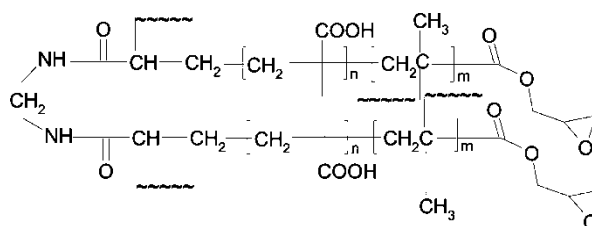


Figure 1. The expected chemical structure of Poly(MA-co-GMA).

Characterizations

Fourier transform infrared spectra of the poly(MA-co-GMA) were collected from KBr pressed disks of the grinded gels using FTIR spectrophotometer, Nicolet, Nexus 821, Medison, USA, in the range $400\text{--}4000\text{ cm}^{-1}$. The thermal stability was measured on a thermal gravimetric analyzer (TGA), Perkin-Elmer using about 20 mg of the samples at a heating rate of $10^\circ\text{C}/\text{min}$ in nitrogen atmosphere. The microstructure of the samples was examined using JEOL-JXA-840A scanning electron microscope (SEM) with 30 KV operating voltage. The samples were gold plated prior to observation. X-ray diffraction patterns (XRD) of the aluminium oxide particles were recorded on a Diano X-ray diffractometer using $\text{CoK}\alpha$ radiation source energized at 45 KV.

Results and Discussion

The FTIR spectra of samples H1 and H5 before and after templating the $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ are shown in Figure 2a–c. The spectra of poly(GMA-co-MA), Figure 2b, is compared with that of the pure poly(GMA), Figure 2a, where the profile comprises bands from both GMA and MA blocks. In addition, two kinds of carbonyl absorption appeared overlapped after the copolymerization, the first at 1600 cm^{-1} , related to GMA and the second at 1680 cm^{-1} related to MA. Among the GMA bands present in the spectra of the copolymer is the band

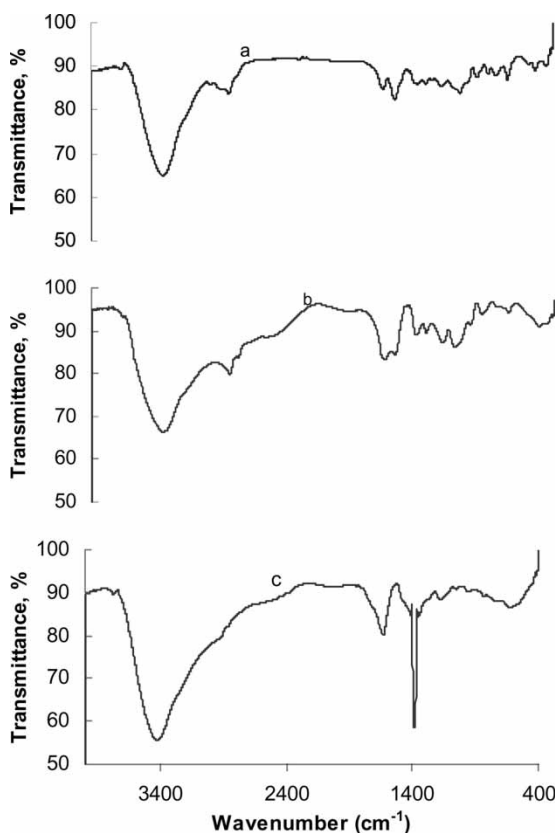


Figure 2. FTIR spectra of a) H1, b) H5, c) H5– $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ hybrid.

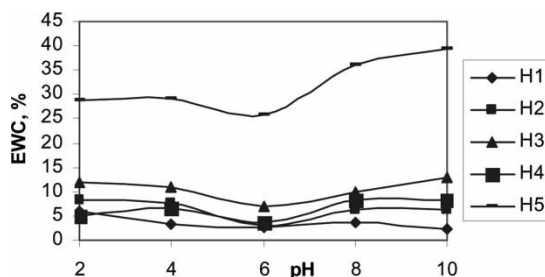


Figure 3. The equilibrium water content of the prepared samples in dependence of pH.

at 835 cm^{-1} , which refers to the oxirane ring of the GMA so it can be concluded that the crosslinked copolymer consisting of GMA and MA formed. The bands at 3439 (-COOH) , $2926\text{ (-CH stretching)}$, $1476\text{ (-CH bending)}$, $1394\text{ (-CH}_3\text{)}$, and $1166\text{ (-CO) cm}^{-1}$, Figure 2b, are perturbed after the templating of the guest species (Figure 2c) and interaction between inorganic moieties and organic functional groups (11) derived from the hydrogen bonding has also been reported

The composition of the prepared gels was expected to have an influence on the swelling behavior in dependence of the pH. Figure 3 displays the EWC, %-pH relationship in the pH range 2–10 for the samples. It is obvious that the samples showed a very similar swelling trend over the investigated pH range and for a given sample, the lowest EWC value was always acquired at pH 6, while this value can be enhanced slightly with respect to H1, H2, H3, H4 and appreciably with respect to H5, on increasing or decreasing this pH. Also, the EWC of the crosslinked poly(glycidylmethacrylate) without any copolymerization with methacrylic acid (H1) did not exceed 6% along the entire pH range. Increasing the copolymerization share with methacrylic acid to 20, 40, 60 wt% did not stimulate EWC over 13% (H2, H3, H4) whereas a substantial improvement in the EWC was noticed upon rising the methacrylic acid constitution in the gel to 80 wt% (H5) and the EWC reached 39% at pH 10.

The TG scans of H5 before and after hybridization with the nitrate species is shown in Figure 4. It is clear that hybridized gel started to degrade earlier than H5 in the range $150\text{--}350^\circ$, which corresponds to the decomposition starting of the $\text{Al(NO}_3)_3 \cdot 9\text{H}_2\text{O}$. At 500°C (calcination conditions), the organic layer was almost removed. The interaction between the formed metal oxide and the gel after hybridization is assumed to be the cause of the slight retardation of the weight loss upon further heating.

Figure 5 shows the SEM of the Al_2O_3 templated from H2, H3, H4, and H5, respectively, since H1 was excluded due to its very poor swelling. A macroporous structure

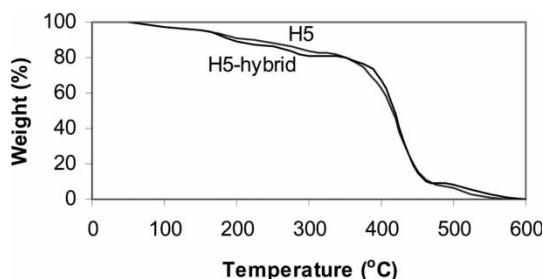


Figure 4. TG scans of, a) H5, b) $\text{H5-Al(NO}_3)_3 \cdot 9\text{H}_2\text{O}$ hybrid.

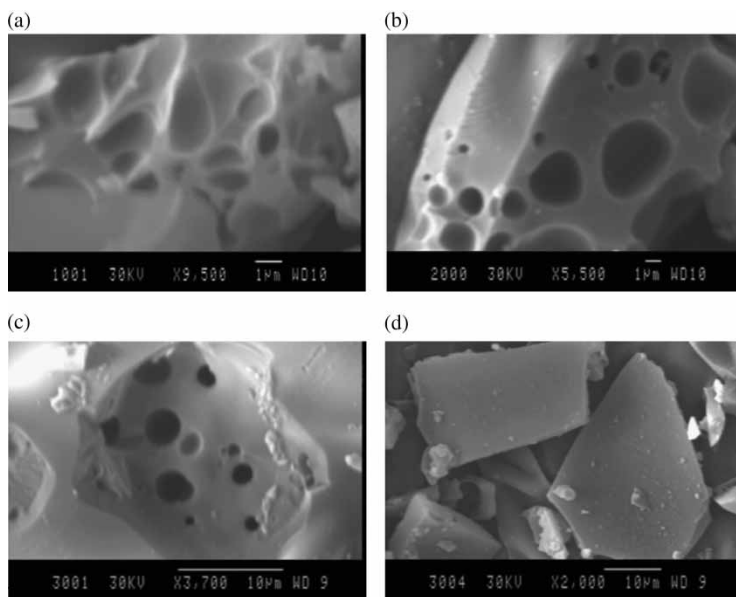


Figure 5. SEM of Al₂O₃ templated by a) H2, b) H3, c) H4, d) H5.

with pore diameter of 0.5 μm in average is observed (H2) which broadened to about 1–4 μm with increasing the MA/GMA ratio (H3) afterwards started to collapse (H4) and finally vanished at 80% MA (H5), where a well-defined platelets produced. The changes in the gel polarity with increasing the hydrophobe ratio and the associated changes in the swelling results out decrease in yield of the nitrate species that can diffuse to the gel network (14) and accordingly, became faraway enough from each other at the calcination conditions, consequently, a porous structure is obtained which disappears when the penetrating species accumulate in the gel network at high MA/GMA ratio. In other words, the tendency for pore formation decreases with increasing the MA/GMA ratio beyond 40:60 wt/wt (H4, H5) and this can be explained out by the high super saturation and low interfacial tension in the regions at which MA predominates, since the gel prepared under these conditions is expected to have inhomogenities in some regions so concentration of the formed colloid in these regions where MA exists, is probable and as a result more packed structure with no pores was obtained (H5). Also, from the pH sensitivity of the gel, it is obvious that the low pH of the nitrate solution

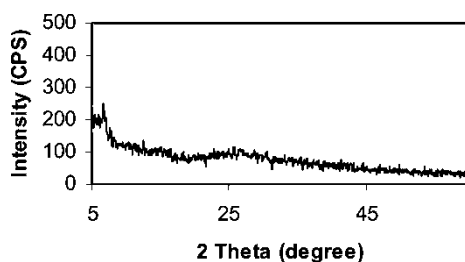


Figure 6. XRD of Al₂O₃ particles templated by H4.

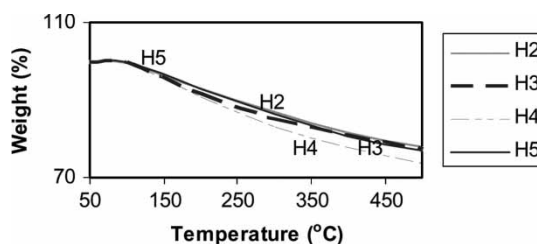


Figure 7. TG scans of pyridine treated Al_2O_3 (originally templated by H2, H3, H4, H5).

greatly influences the swelling in methanol and hinder its penetration into the gel network which is at a highly shrunk state at low pH values (Figure 3) so tailoring polymer gels that can functionalize under these templating conditions to give high mass output will be a challenging point in this laboratory. XRD of a representative sample of aluminium oxide, templated by H4 is shown in Figure 6, which revealed that the produced particles are amorphous as expected.

The prepared aluminium oxide originally templated by H2, H3, H4, and H5 were treated with pyridine for 24 h at 40°C . This would help to investigate the sites of activity on the surface (Lewis acid sites). The adsorbed amount of pyridine was estimated quantitatively for every sample by running a thermal gravimetric analysis in the range $50\text{--}500^\circ\text{C}$ as demonstrated in Figure 7. At 500°C , the remaining is aluminium oxide only and the difference is attributable to the thermally decomposed pyridine. This difference was calculated and collected in Table 2.

It is clear, the acidic sites increase significantly with increasing the hydrophilicity in the initial hosting template (methacrylic acid units) and reached a maximum value with H4 as indicated in Table 2 and is considered to be a strong indication of an increase in the surface area, however, more increase in the hydrophilicity of the template (H5) was associated with a decrease in the surface acidic sites and became of equivalent acidity to H2.

Conclusions

Crosslinked Poly(MA-co-GMA) gels can be used as hosts for the templation of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as a precursor for the production of macroporous Al_2O_3 . The templation

Table 2

The relation between the template hydrophilicity and adsorbed amount of pyridine on the surface of the produced aluminium oxide

Template	Adsorbed amount of pyridine, wt%
H2	24
H3	25.1
H4	26.5
H5	24

process can be confirmed using FTIR spectroscopy as well as TGA. The swelling behavior of the gels is dependent on the chemical composition of the samples as well as the pH of the solution. The crosslinked copolymer gels can provide more controllable pore sizes in comparison with the conventional approaches based on soluble block copolymers. The produced aluminium oxide particles under these conditions are amorphous. The acidic sites on the surface of the produced aluminium oxide increase significantly with increasing the hydrophilicity in the initial hosting template (methacrylic acid units) and reaches a maximum at 60 wt%, more increase in the hydrophilicity of the template to 80 wt% (H5) led to a redecree in the surface acidity.

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