

Porous nanocomposites prepared from layered clay and PMMA [poly(methyl methacrylate)]

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Abstract

The aim of the present work is the preparation of PMMA based porous nanocomposites that contain clay (montmorillonite, MMT) platelets as reinforcements within the cell walls of the porous structure. To render the clay layers organophilic, MMT was surface treated by an ion exchange reaction between interlayer cations of the clay and ammonium ions of a surfactant. Clay/PMMA based porous nanocomposites were prepared by polymerization of water-in-oil emulsions with and without clay addition. The microstructure and compressive mechanical behavior of the nanocomposites were investigated. The results of mechanical tests showed that the porous systems with the addition of 1 wt.% of organoclay (OMMT) exhibited a 90% and 50% increase of collapse stress and elastic modulus values, respectively, as compared to neat porous PMMA.

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1. Introduction

Poly(methyl methacrylate) (PMMA) is an attractive engineering polymer due to its some unique properties; such as high strength, special optical properties, environmental durability, in comparison with other polymers. Therefore, it has been commonly employed in automotive, transportation, construction, biomaterials, and other applications. In addition, these materials have been recently used as molding material in the fabrication of ceramic whiteware and sanitaryware articles with slip casting technique that has been traditionally performed using plaster molds [1,2]. Due to the long casting periods (1–2 h), long drying time and limited service life of the plaster of Paris, the trend in the ceramic industry is the utilization of the high pressure casting process that provides automation. In this technique, a porous mold material that allows the drainage of water from the slip under high pressures of typ-

ically 13–15 bars is needed [1,2]. The materials with an open cell structure need to provide high water permeability, high mechanical strength and fatigue performance. The desired materials are also expected to keep the integrity of the structure without deformation and allow the usage of high pressures to provide a tight seal around the mold without cracking along about 20,000 cycles during expected service life. Polymeric materials, especially PMMA-based porous materials, became the most suitable ones for this purpose [1,3]. However, further improvements on the mechanical properties of those materials are needed for the expected service life and performance during the application due to their high costs. Therefore, modification of the microstructure in these materials is essential to obtain optimized performance. Incorporation of layered silicates (i.e., clay minerals) into the polymer microstructures to improve the mechanical, thermal and barrier properties has been an attractive approach developed recently [4,5]. Nanocomposites with different morphology, i.e., agglomerated, intercalated and exfoliated structures are accessible based on the processing conditions and

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interactions between the layered clays and polymer systems. A number of studies revealed the enhanced properties of clay/polymer nanocomposite systems [4–6].

Also, a number of studies were reported on the preparation of porous PMMA polymers and clay/PMMA nanocomposites by suspension and emulsion polymerization [7–11]. Jimenez-Pique et al. [11] performed fracture tests on a PMMA based open-pore materials prepared by polymerization of a water-in-oil emulsion. The fracture tests were performed at dry room temperature and in water at 45 °C. A fictitious crack model was used to obtain experimental fracture data and an excellent result was obtained for all the tests performed. In our previous study [3], we produced PMMA-based open-cell porous materials using various concentrations of water-in-oil emulsion constituents and PMMA bead sizes. It was revealed that the porous network is mainly formed by the water droplets surrounded with surfactants and the cell walls are formed by the polymerized monomer molecules with the contribution of PMMA beads. It was found that constituent concentrations significantly affect the porosity, pore morphology, water permeability, collapse stress and elastic modulus of the porous plastics. It was found that the collapse stress, elastic modulus and fracture toughness (K_{IC}) values decrease as the concentration of water-surfactant increases, that is mainly related to the increase of porosity and formation of thin cell walls.

However, to our knowledge there is very limited work reported in the literature about the preparation of porous polymer nanocomposites. In only a recent study, Dortmans et al. [12] prepared porous nanocomposites by incorporation of the clay sheets into the PMMA porous matrix during polymerisation using a PEO–PMMA block copolymer. A significant improvement in mechanical properties and in lifetime was obtained. The optimum load of modified clay was determined to be about 3–4 wt.%.

Based upon the findings from our previous work [3], we aimed to enhance the mechanical properties of the porous structure by exfoliation of clay platelets within the cell walls to reinforce them. For this purpose, in the present study, clay/PMMA based porous nanocomposites were prepared by polymerization of water-in-oil emulsions with

and without clay additions. The clay particles were also surface treated through an ion exchange reaction to effect the dispersion of the platelets within the cells. The pore morphologies were investigated by SEM techniques. Compressive mechanical testing was performed to obtain the stress–strain behavior, elastic modulus and collapse stresses and to investigate the deformation mechanisms of the materials.

2. Experimental

2.1. Materials

The layered clay/PMMA based porous nanocomposites were prepared by the polymerization of water-in-oil emulsion from hardenable composition containing methyl methacrylate (MMA-C₅H₈O₂, Degussa, Germany), polymethyl methacrylate beads (PMMA, Keramische Laufen, Germany), dibenzoyl peroxide (BPO-C₁₄H₁₀O₄) as initiator of the polymerization reaction (Peroxid-Chemie GmbH), emulsifier (Keramische Laufen, Germany) and water. Two different sizes of PMMA beads with average bead sizes of 157 and 35 µm were used as filler material (Fig. 1 (a) and (b)). To provide the homogeneity and the stability of the emulsion, water-soluble nonionic surfactant of ethylene oxide–propylene oxide (EO–PO) block-copolymer was used. Clay (Na⁺-montmorillonite (Na⁺-MMT), Aldrich) particles were used to prepare nanocomposites. Hexadecyltrimethylammonium chloride (CTAC, (CH₂)₁₅N(CH₃)₃⁺Cl⁻, Aldrich – 0.047 mol) and hydrochloric acid (HCl, 0.048 N) was used for clay surface treatment.

2.2. Surface treatment of clay

Montmorillonite (MMT) is needed to be organophilic in order to disperse it in a polymer system. To render the clay layers organophilic, MMT was surface treated prior to its incorporation into emulsion systems. Na⁺-MMT was first dispersed in deionized water. A solution of CTAC and HCl in deionized water was prepared, separately. These two solutions were mixed and stirred for 1.5 h at 75 °C. Organophilic MMT was formed by replacing the charge

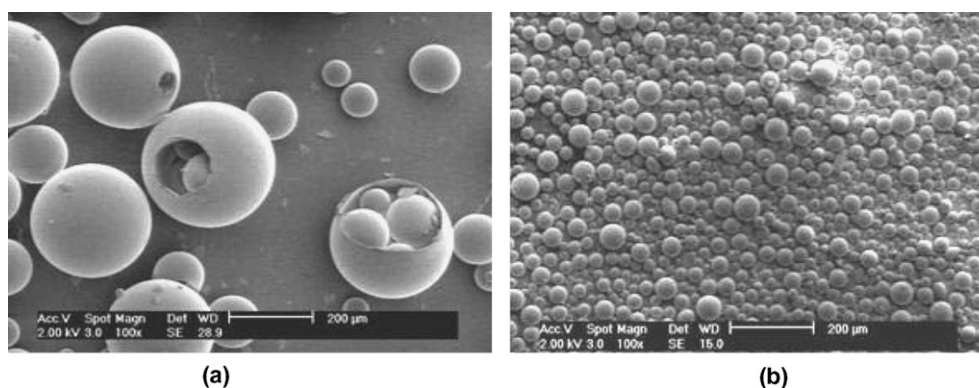


Fig. 1. SEM micrographs of PMMA beads with average particle diameter of (a) 157 µm and (b) 35 µm.

balancing interlayer cations of MMT with CTAC in the suspension. With the penetration of alkyl ammonium ion into the galleries, the spacing within the galleries also increases. The suspension was then filtered and the solid residue was washed with deionized water until no residual chloride was detected in the wash, using the silver nitrate test. Finally, the organoclay product (OMMT) was dried in an air oven at 70 °C for 24 h and sieved before usage.

2.3. Preparation of Clay/PMMA based porous nanocomposites

Clay/PMMA-based porous nanocomposites were produced by water-in-oil emulsion polymerization from a hardenable composition that contains water and oil phases with the following concentrations. The water phase contained finer PMMA beads (25 wt.%) suspended in the mixture of water and the surfactant. During the preparation of emulsions, water/surfactant ratio was kept constant (1/3) while their total concentration was 35 wt.%. The oil phase contained the coarser PMMA beads (19.5 wt.%), dibenzoyl peroxide (0.5 wt.%) and methyl methacrylate monomer (20 wt.%). For the systems containing clay additions, prior to the formation of the oil phase, the MMA was mixed with the clay (MMT or OMMT) and stirred for 2 h using a magnetic stirrer. Oil phase was then prepared by stirring shortly the MMA system and coarser PMMA beads. Finally, water and oil solutions were mixed together for very short period of time until the homogeneous emulsion was obtained. The emulsion was cast on an epoxy mold. Final emulsion consisted of an immiscible water phase dispersed in monomer phase and additionally PMMA beads suspended in the emulsion. Once the polymerization is completed, the cast material is demolded and washed with tap water. The described procedure results with randomly distributed open cell porous structure with an irregular pore morphology. In addition, PMMA based porous polymers (called as PMMA) without clay addition was also prepared for comparison purposes using the same procedure described above excluding the clay addition stages.

2.4. Characterization

To investigate the microstructural properties a field emission scanning electron microscope (SEM) was used. XRD technique was used for phase identifications and measurements of the clay basal distances. Compressive mechanical tests were performed on the porous materials to investigate the effects of the clay particle addition on the mechanical behavior of the porous materials. Specimens with 15 mm diameter and 20 mm length were sectioned from larger slabs and all the specimens were dried at 35 °C for 24 h prior to testing. At least five specimens from each set were tested at room temperature and under a constant crosshead speed of 1.3 mm/min (strain rate of 0.001 s⁻¹), using a ShimadzuTM universal testing machine.

The strain values were calculated based on the initial length of the cylindrical specimens and the cross head displacements. The displacement values were corrected for any machine compliances. Compressive stress–strain values were obtained after the tests. Elastic modulus values were calculated from the initial linear part of the compressive stress–strain graph. Stress values at transition point from elastic to plastic deformation region was taken as the collapse stress of the materials.

3. Results and discussion

Fig. 2 shows the XRD analysis results of MMT and OMMT. As seen from the figure, the structure of the montmorillonite is significantly affected from the modification process. It was found that the distance between the (001) basal planes increased from 14.8 Å to 19 Å. This indicates that the spaces among galleries within the layered silicate structure were expanded by the diffusion of the CTAC and also MMA molecules into the gallery spaces and also by the replacement of interlayer cations with ammonium ions. This intercalated structure is expected to form nanocomposites with a better dispersion of clay plaques (exfoliation) within the polymer system.

Clay/PMMA based porous nanocomposites were produced from water-in-oil emulsions with and without clay particulate additions. Fig. 3 shows the SEM micrograph of a porous specimen.

It was revealed that the porous network is mainly formed by the water droplets surrounded with surfactants. The cell walls are formed by the polymerized MMA molecules surrounding the PMMA beads. Clay particles were blended with MMA and PMMA beads during the preparation of the oil phase. So, clay plaques are expected to disperse in the polymerized MMA forming the cell walls together with the PMMA beads. On the other hand, a fraction of hydrophilic MMT particles may separate from the oil phase and accumulate in the water phase while the rest

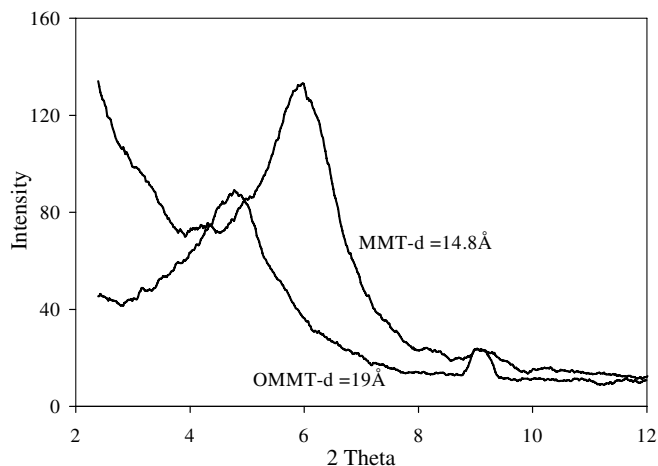


Fig. 2. X-Ray diffraction (XRD) analysis results of MMT and OMMT.

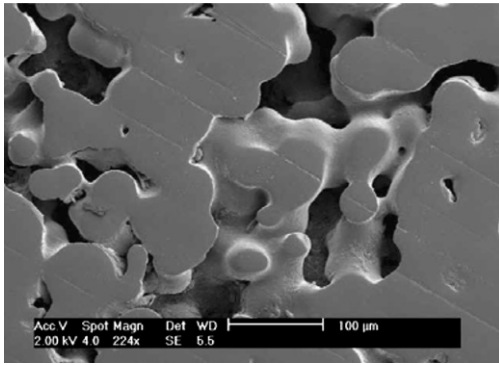


Fig. 3. SEM micrograph showing the cross section of the PMMA based porous polymer.

is located within the polymerizing MMA. To produce an optimized open-cell porous structure, it is essential to obtain homogeneous distribution of the water droplets with high connection and the stabilization of the emulsion throughout the polymerization reaction. It is known that the pore fraction, morphology and cell connectivity are significantly affected by the total concentrations of water and surfactant. The amount of water in the emulsion is directly related to the pore fraction and connectivity.

The typical compressive stress–strain test results of the porous materials are given in Fig. 4. For comparison, the results for the porous materials without clay addition (samples called as PMMA) are also given in the same figure. Porous PMMA system exhibited a collapse stress and elastic modulus values of 12 ± 0.5 MPa and 520 ± 20 MPa, respectively. Incorporation of organoclay (OMMT) into the porous polymer system significantly affects the mechanical behavior of porous PMMA system. Materials with 1 wt.% of OMMT addition exhibited about 90% and 50% increase in collapse stress and elastic modulus, respectively, as compared to those without clay addition. This result

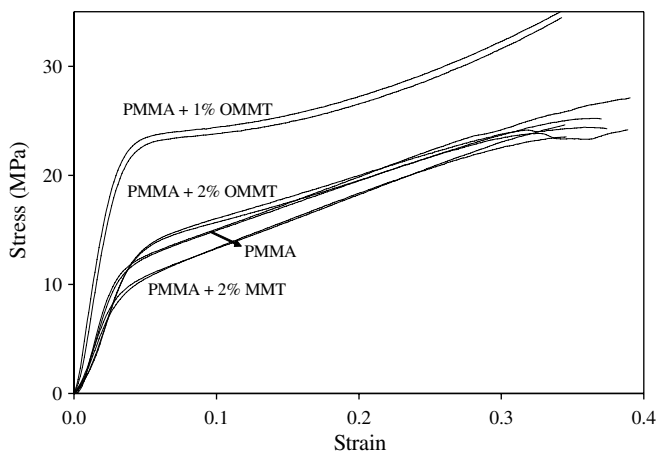


Fig. 4. Compression stress–strain behaviors of PMMA based nanocomposites produced with (MMT and OMMT) and without clay particles (PMMA).

may be associated with the formation of expected exfoliated microstructure. However, the further addition of OMMT (2 wt.%) resulted with negligible improvement on the mechanical properties of the structures as compared to those without clay addition. The reduction may be related to the agglomeration tendency of the clay platelets at higher concentrations within the polymer. So, the percolation of the OMMT platelets is expected at 1 wt.%. It was also found that the materials with MMT particles (2 wt.%) have lower collapse stress values as compared to the material without clay addition (PMMA). Unmodified clay particles are expected to form agglomerated morphology due to lower wetting by the oil phase and the lack of the organophilic surfaces and intercalated layers.

On the compressive stress–strain graphs, the initial part is a linear elastic region that is controlled by stretching and partial bending of cell walls. The second region is a long deformation plateau with lower rate increasing stress values as compared to first region. Deformation in this region involves microcracking and brittle crushing of the cells, progressive collapse of the pore network. With the collapse of the cells, opposing cell walls touch each other and further stress begins to compress the solid itself, and creates the final region of densification with a rapidly increasing stress [13]. The material with 1 wt.% OMMT has relatively longer deformation plateau, such that densification begins at much higher strain values. This may be due to higher fraction of pores with open-cell structure that involves less progressive collapse of the pore network for higher densities. A better exfoliation of the clay platelets allows higher fraction of open cells while clay agglomerations may reduce cell connectivities.

4. Conclusions

Clay/PMMA-based porous nanocomposites were produced by water-in-oil emulsion polymerization with and without montmorillonite additions. Surface treatment of the clay was successfully performed by replacing the interlayer cations of the clay with ammonium ions to obtain organoclay. It was found that the porous PMMA network is mainly formed by the water droplets surrounded with surfactants and the cell walls are formed by the polymerized MMA molecules with the contribution of PMMA beads. Mechanical tests showed that the prepared materials exhibit the compressive mechanical behavior similar to elastic brittle foams. A linear elastic region that is controlled by cell wall bending and cell face stretching is followed by a deformation plateau with lower rate increasing stress values and the final region of densification with a rapidly increasing stress. The porous system with the addition of 1 wt.% of organoclay (OMMT) exhibited a 90 and 50% increase of collapse stress and elastic modulus values, respectively, as compared to porous PMMA without clay addition. Incorporation of organoclay (OMMT) into the porous PMMA system has a high potential to improve the mechanical behavior.

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References

- [1] Mazzanti V. *Process Eng DKG* 2002;79(1–2):E11–2.
- [2] Dortmans A, Fischer H, Nelissen RG. *Process Eng DKG* 2002; 79(1–2):E45–8.
- [3] Ergün Y, Dirier C, Tanoğlu M. *Mater Sci Eng A* 2004; 385(1–2):279–85.
- [4] Giannelis EP. *Appl Organometal Chem* 1998;12:675–80.
- [5] Fischer H. *Mater Sci Eng* 2003;C23:763–72.
- [6] Schmidt D, Shah D, Giannelis EP. *Curr Opin Solid State Mater Sci* 2002;6:205–12.
- [7] Okaamoto M, Morita S, Taguchi H, Kim YH, Kotaka T, Tateyama H, et al. *Polymer* 2000;42:3887–90.
- [8] Salahuddin N, Shehata M. *Polymer* 2001;42:8379–85.
- [9] Park JH, Jana SC. *Polymer* 2003;44:2091–100.
- [10] Huang X, Brittain WJ. *Macromolecules* 2001;34:3255–60.
- [11] Pique EJ, Dortmans LJMG, de With G. *Mater Sci Eng A* 2002;335:217–27.
- [12] Dortmans A, Batenburg LF, Koster TPM, Nelissen RG, Fischer H. *e-polymers* 2002;10:1–10. <http://www.e-polymers.org>.
- [13] Gibson LJ, Ashby MF. *Cellular solids*. 2nd ed. Cambridge, UK: Cambridge University Press; 1997.