Synthesis, Characterization and Photoinduced Cross-linking of Functionalized Poly(cyclohexyl methacrylate) Copolymer/Clay Nanocomposite as Negative Image Patterning Material

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A novel strategy to prepare network structured polymer/clay nanocomposites, namely poly(cyclohexyl methacrylate-co-2-hydroxyethyl methacrylate)/montmorillonite (PCHMA-co-PHEMA/MMT) nanocomposites by combination atom transfer radical polymerization (ATRP) and photoinduced cross-linking processes is described. In the first step, ATRP initiator modified clay (MMT–Br) was prepared by treating the organo-modified clay, Cloisite 30B (MMT–OH) with 2-bromoisobutyryl. Subsequent copolymerization of cyclohexyl methacrylate and 2-hydroxyethyl methacrylate via ATRP using MMT–Br as initiator resulted in the formation of PCHMA-co-PHEMA/MMT nanocomposites. Then, methacrylate groups were introduced to the nanocomposite structure by reacting 2-isocyanatoethyl methacrylate isocyanate with the hydroxyl groups on of PCHMA-co-PHEMA chains. Finally, upon irradiation of the functional nanocomposite in the presence of the long wavelength absorbing photoinitiator, bis(2,4,6-trimethylbenzoyl) phenylphosphine oxide yielded network structured nanocomposites. The structures, thermal and morphological properties of the nanocomposites were investigated by spectral, thermal and microscopic analyses.

Keywords: Polymer/clay nanocomposite, cross-linking, negative image, poly(cyclohexyl methacrylate)

1. Introduction

Design and fabrication of new photopolymers capable of undergoing photoinduced degradation or cross-linking result in positive and negative image patterning, respectively has been academic and industrial challenge [1]. For both processes, various photopolymers possessing photosensitive groups creating solubility differences by exposing light have been developed and their photochemistry has been studied in detail [2]. Recently, we have introduced poly(cyclohexyl methacrylate) (PCHMA) based copolymers with photo cross-linkable double bonds as side chains as negative image patterning materials [3]. The rigid cylohexyl groups prevented intra-molecular interaction of the double bonds and thus facilitated more efficient photo cross-linking through inter-molecular free radical process. Prolonged irradiation and thermal treatment during the baking processes may lead to failure in the image patterning process. To prevent these shortcomings, development of novel photopolymer materials with high thermal stability and good mechanical properties is one of the long-term goals in photopaterning applications.

In the present materials research, polymer/clay nanocomposites occupy an important place due to the advantages offered by their natural abundance, cost and environmental benign [4]. Moreover, compare to the neat polymer analogous,
polymer/clay nanocomposites exhibit remarkable property improvements such as high moduli, increased strength and heat resistance, decreased gas permeability, and flammability [5]. Recently, it was also shown such these materials can also be used for selective cell adhesion when the polymer component is biocompatible and nanocomposite is modified with folic acid [6].

Several synthetic approaches, namely solution mixing, melt mixing, and in-situ polymerization have been proposed and successfully applied to prepare polymer nanocomposites [7]. Among them, in-situ polymerization method appears to be the most widely applied strategy since it is modular process applicable to wide range of polymerization processes through appropriate functional groups and homogenous dispersion of the clay layers in the polymer matrix can be achieved [8]. The monomer, initiator, or catalyst functionalities are incorporated to the organoclay which is then dispersed in the monomer. The accordingly designed in-situ polymerization or molecular interactions in the clay galleries yield nanocomposites with exfoliated structures. A wide range of conventional thermal [9] and photochemical [10], and controlled/living polymerizations [8] have been successfully used to activate the in-situ polymerizations resulting in the formation of polymer/clay nanocomposites with linear [11], branched [12], star [13], block [14] and graft copolymer [15] structures.

Quite recently, we reported conceptually different approaches based on “click” reactions [16] or supramolecular association such as hydrogen bonding [17] to prepare the polymer/clay nanocomposites. In both cases, exfoliation is rooted in the functional units of the intercalant that readily interact with the antagonist groups of the preformed polymers.

In continuation of our investigations into the development of photopolymers for image patterning application, herein we report synthesis and characterization of PCHMA copolymer/clay nanocomposites as novel negative resist material. Two-step synthesis of nanocomposite was carried out by first incorporation of initiator followed copolymerization of cyclohexyl methacrylate (CHMA) using atom transfer radical polymerization (ATRP) protocol. The obtained nanocomposite is endowed with photo cross-linking property by esterification process. As it will be shown below, due to the presence of the rigid cyclohexyl groups, the clay nanocomposite underwent efficient photoinduced cross-linking of the methacrylate groups that were also incorporated. The material exhibited better thermal properties than those having the same structure prepared without the clay component under identical experimental conditions (Scheme 1).

2. Experimental

2.1. Materials

Organo-modified clay, Cloisite 30B (MMT-OH) was purchased from Southern Clay Products (Gonzales, TX). The organic content of the organo-modified MMT, determined by thermogravimetric analysis (TGA), was 21 wt %. Before use, the clay was dried under vacuum at 110 °C for 1 h. 2-Hydroxyethyl methacrylate (HEMA, 95%, Aldrich) was passed through a neutral alumina column to remove the inhibitor. N,N,N′,N″,N‴-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich), as a ligand, was distilled before use. 2-isocyanatoethyl methacrylate (MOI, 98%, Aldrich), cyclohexyl methacrylate (CHMA, 98%, Kanto Chemical), bis(2,4,6-trimethylbenzoyl) phenylphosphine oxide (BAPO, BASF), lithium bromide (LiBr, 95%, Kanto Chemical), dibutyltin dilaurate (DBTDL, 95%, Tokyo Chemical Industry), copper(I) bromide (CuBr, 97%, Aldrich), ethyl 2-bromopropionate (EtBP, 98%; Aldrich), and 2-bromoisobutyryl bromide (98%, Aldrich) were used as received.

Scheme 1. Strategy for photoinduced cross-linkable polymer/clay nano-composite.
2.2. Modification of MMT-OH with 2-bromoisobutyryl bromide

MMT-OH (0.500 g, -OH content determined theoretically = 6.10 × 10^{-4} mol) was dispersed in 50 mL of pyridine at 100°C for 30 minutes. Then, 2-bromoisobutyryl bromide (0.450 mL, 3.66 × 10^{-3} mol) was added and the mixture was stirred for 21 h at 100°C. After cooling to room temperature and removing the solvent by filtration, modified MMT (MMT-Br) was washed with THF and water three times and finally dried under reduced pressure. (0.434 g; yield: 64%).

2.3. Synthesis of poly(cyclohexylmethacrylate-co-2-hydroxyethylmethacrylate)/montmorillonite (PCHMA-co-PHEMA/MMT) Nanocomposites via ATRP

MMT-Br (273 mg, 2.44 × 10^{-4} mol), CHMA (5 mL, 2.87 × 10^{-2} mol), HEMA (872 μL, 7.17 × 10^{-3} mol), CuBr (35 mg, 2.44 × 10^{-4} mol) and PMDETA (51 μL, 2.44 × 10^{-4} mol) were put into a Schlenk tube equipped with a magnetic stirring bar then the reaction mixture was degassed by two freeze–pump–thaw cycles and left in a vacuum. The mixture was placed in a thermostated oil bath at 100°C for 22 h. At the end of the polymerization, the mixture was precipitated into excess diethyl ether, filtered and dried under reduced pressure (1.22 g).

2.4. Synthesis of acrylate (Ac) functional PCHMA-co-PHEMA/MMT Nanocomposites (PCHMA-co-PHEMA/MMT-Ac)

PCHMA-co-PHEMA/MMT (0.600 g, 7.47 × 10^{-4} mol, polymer content) and DBTDL (27 μL, 4.47 × 10^{-5} mol) were dissolved in THF (10 mL) in a three necked round bottom flask under dry nitrogen. The mixture was stirred to create a homogeneous solution then, cooled to 0°C and MOI (931 μL, 6.54 × 10^{-3} mol) in CHCl₃ (5 mL) was added dropwise. The reaction mixture was heated to 40°C, and kept stirring for 24 h. After cooling down to ambient temperature, the mixture was precipitated in excess methanol and dried under reduced pressure.

2.5. Synthesis of PCHMA-co-PHEMA via ATRP

CHMA (5 mL, 2.9 × 10^{-2} mol), HEMA (872 μL, 7.2 × 10^{-3} mol), PMDETA (75.0 μL, 3.59 × 10^{-4} mol), CuBr (51.5 mg, 3.59 × 10^{-4} mol) and EtBP (46.6 μL, 3.59 × 10^{-4} mol) were put into a Schlenk tube equipped with a magnetic stirring bar, and the reaction mixture was degassed by two freeze–pump–thaw cycles and left in a vacuum. Then, the mixture was stirred for 1 h at 100°C. After cooling down to ambient temperature, the resulting polymers were precipitated in excess methanol and dried under reduced pressure (3.56 g; yield: 62%).

2.6. Synthesis of acrylate functional PCHMA-co-PHEMA (PCHMA-co-PHEMA-Ac)

PCHMA-co-PHEMA (3.50 g, 4.36 × 10^{-3} mol) and DBTDL (118 μL, 1.18 × 10^{-4} mol) were dissolved in chloroform (10 mL) in a three necked round bottom flask under dry nitrogen. The mixture was stirred to create a homogeneous solution then, cooled to 0°C and MOI (931 μL, 6.54 × 10^{-3} mol) in CHCl₃ (5 mL) was added dropwise. The reaction mixture was heated to 40°C, and kept stirring for 24 h. After cooling down to ambient temperature, the mixture was precipitated in excess methanol and dried under reduced pressure.

2.7. Photo-crosslinking reactions

PCHMA-co-PHEMA/MMT-Ac or PCHMA-co-PHEMA-Ac (50 mg), BAPO (5 mg) and 1 mL of DMF were put in a Pyrex tube and filled with dry nitrogen prior to irradiation by a Ker-Vis blue photoreactor equipped with six lamps (Philips TL-D 18 W) emitting light nominally at 400–500 nm at room temperature. After given time the gel was immersed in a large excess of DMF to wash out unreacted initiator and any soluble polymer for 24 h. The swollen gel was removed from DMF, immersed in acetone, and eventually dried under vacuum.

2.8. Characterization

Molecular weights were determined by gel permeation chromatography (GPC) composed of a HITACHI L-6000 pump, HITACHI L-4200 UV detector, or JASCO RI-2031 RI detector, and GL Science Inc. DG660 degasser with columns of TOSOH TSK gel GMHHR-M. 1H NMR spectra were recorded on a Bruker DPX300 at room temperature in CDCl₃ with TMS as an internal standard. Before the GPC and 1H NMR measurements, the polymers were cleaved from clay by LiBr refluxing in THF for about 24 h, followed by centrifugation and filtration through a filter. Thermogravimetric analysis (TGA) was carried out by means of a Rigaku Thermo plus EVO II Series, TG-DTA TG8120 with a heating
rate of 10 °C min⁻¹ under nitrogen flow (250 mL min⁻¹). Photo differential scanning calorimetry (photo-DSC) measurements were performed on a modified PerkinElmer Diamond DSC equipped with a Polilight PL400 Forensic Plus light source between 350 and 500 nm. A uniform UV light intensity was delivered across the DSC cell to the sample and reference pans. The measurements were carried out in an isothermal mode at 25 °C. FT-IR analyses were performed on a PerkinElmer FT-IR SpectrumOne B spectrometer.

3. Results and Discussion

The first step of the synthetic strategy was to incorporate the initiator functionality to the organo-modified clay, Cloisite 30B (MMT–OH) through esterification in the presence of pyridine (Scheme 2).

The followed conventional ATRP of CHMA and 2-hydroxyethyl methacrylate (HEMA) resulted in the formation of clay/polymer nanocomposite as presented in Scheme 3. In the resulting composite, PHEMA repeating units provided hydroxyl functionalities for further modification, while PCHMA introduced rigidity.

The hydroxyl groups PHEMA was partially converted to photo cross-linkable methacrylate functionalities through urethane formation by using the corresponding isocyanate compound, 2-isocyanatoethyl methacrylate (MOI) and catalyst, dibutyltin dilaurate (Scheme 4).

The starting organoclay, intermediates and final nanocomposite were characterized by FT-IR spectral analysis. As can be seen from Figure 1, the pristine MMT–OH showed typically O–H stretching bands at 3683 cm⁻¹. After modification with 2-bromoisobutyryl bromide a new peak around 1700 cm⁻¹ corresponding to the C=O moiety was clearly detachable. By the formation of (poly(cyclohexyl methacrylate-co-2-hydroxyethylmethacrylate)/montmorillonite) PCHMA-co-PHEMA/MMT nanocomposites, O-H and C=O bands increased due to the additional groups from PHEMA and PCHMA chains. After conjugation of the acrylate groups appearance of new bands corresponding to the C=C-H and C=C moieties clearly indicates the presence of acrylate groups. IR studies clearly evidences that the all steps of the process were successfully achieved and the final composite possessed the desired cyclohexyl and methacrylate side groups.

![Scheme 2. Synthesis of MMT–Br.](image)

![Scheme 3. Synthesis of PCHMA-co-PHEMA/MMT nanocomposites.](image)

![Figure 1. FT-IR spectra of MMT-OH, MMT-Br, PCHMA-co-PHEMA/MMT and PCHMA-co-PHEMA/MMT-Ac.](image)
The structures of the polymers were further confirmed by ¹H-NMR analysis of the cleaved products. As can be seen from Figure 2, the appearance of the new signals corresponding to the acrylate moiety in addition to the characteristic bands of the PCHMA-co-PHEMA main chain, clearly indicates the successful modification.

Figure 2. ¹H NMR spectra of PCHMA-co-PHEMA and PCHMA-co-PHEMA-Ac cleaved from clay.

In order to demonstrate the capability and kinetic profile of the photocross-linking of the nanocomposite photo-DSC measurements were performed. As can be seen from Figure 3 demonstrates that the during the irradiation course an exothermic peak indicating the polymerization was observed.

The thermogravimetric analysis (TGA) curves of clay, nanocomposites and related pure polymer recorded in inert atmosphere are shown in Figure 4. The weight loss of PCHMA-co-PHEMA/MMT and PCHMA-co-PHEMA/MMT-Ac was higher

Figure 3. Kinetics profile of the photopolymerization of PCHMA-co-PHEMA/ MMT-Ac with BAPO by means of photoDSC with the light intensity of 40 mW cm⁻².

Figure 4. TGA thermograms of MMT-Br, PCHMA-co-PHEMA/MMT, PCHMA-co-PHEMA/ MMT-Ac, PCHMA-co-PHEMA/MMT-Ac (cross-linked) and PCHMA-co-PHEMA-Ac (cross-linked).
than that of MMT–Br as a result of degradation of the additional organic content. Furthermore, it is quite obvious that the degradation temperatures of the cross-linked PCHMA-co-PHEMA/ MMT-Ac nanocomposites shifted significantly toward higher temperatures compared with those of the neat PCHMA-co-PHEMA. This beneficial effect can be explained by the addition of clay as an inorganic material with high thermal stability and great barrier properties that can prevent the heat from transmitting quickly and can limit the continuous decomposition.

4. Conclusion
In conclusion, we herein present the design and synthesis of a photoreactive polymer/clay nanocomposite that can be cross-linked for rapid and efficient free radical reactions by using long wavelength photoinitiator (>350 nm). An initiator moiety incorporated in the clay layers is activated to initiate atom transfer radical copolymerization of CHMA and HEMA to give the desired nanocomposite which can be easily functionalized with methacrylate groups over hydroxyl groups by urethane formation. Photoinitiated radical polymerization chemistry is indisputably proved to be very promising in building robust networked polymer-based materials for negative image patterning purpose. Moreover, the advanced demands of thermal stability for the resist materials were satisfied with the current system, as the obtained nanocomposite exhibited comparable thermal properties to that of the structurally the same polymer without clay content.

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References