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The Role of Initiator in the Synthesis of Poly(Methyl Methacrylate)-Layered Silicate Nanocomposites through Bulk Polymerization

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***Abstract*—**The structure-property relationship and initiator effect on bulk polymerized poly(methyl methacrylate) (PMMA)–oragnomodified layered silicate nanocomposites was investigated. In this study, we used 2, 2'-azobis (4-methoxy-2,4-dimethyl valeronitrile and benzoyl peroxide initiators for bulk polymerization. The bulk polymerized nanocomposites' morphology was investigated by X-ray diffraction and transmission electron microscopy. The type of initiator strongly influences the physiochemical properties of the polymer nanocomposite. The thermal degradation of PMMA in the presence of nanofiller was studied. 5 wt% weight loss temperature (T5d) increased as compared to pure PMMA. The peak degradation temperature increased for the nanocomposites. Differential scanning calorimetry and dynamic mechanical analysis were performed to investigate the glass transition temperature and the nature of the constrained region as the reinforcement mechanism respectively. Furthermore, the optical properties such as UV-Vis and Total Luminous Transmission of nanocomposites are examined.

***Keywords*—**Initiator, bulk polymerization, layered silicates, methyl methacrylate.

I. INTRODUCTION

IN recent decades, a great number of scientists interest to develop different kinds of inorganic and organic hybrid polymer nanocomposites. These nanocomposites have extraordinary physical, chemical and extensive potential applications, such as, biomedical field, tissue engineering, construction materials, optics, microelectronic, automotive industries, aerospace and semiconductor [1]-[5]. Polymer/layered inorganic material nanocomposites have been synthesized by several methods with different kinds of nanofillers such as metal alkoxides (SiO_2, TiO_2 or ZrO_2) or colloidal inorganic nanoparticles and synthetic or natural inorganic layered materials [6]-[8]. Also, there are a number of literature reports on nanocomposites synthesis by using different preparation methods like, solution blending [9], [10], in situ polymerization [11], [12] and melt intercalation etc. [12]-[14]. The filler materials help to enhance polymer nanocomposites properties also provide improved mechanical, thermal, optical, and barrier properties [15]-[17].

One of the challenges for preparing polymer nanocomposites is the agglomeration of the nanofiller in the polymer matrix that leads to poor performance of the composite. It is mainly due to poor chemical bonding, optimized interaction between the matrix and filler. There is much attention has been paid to the preparation of exfoliated and intercalated polymer/clay nanocomposites. There are certain papers have been published on using organomodified nanofiller to make them more compatible with PMMA matrix [21], [22]. Certainly, the nature of organomodifier, the monomer and initiator molecules is also critical, a lot is gained, for instance, in using initiators with strong interactions with the inorganic nanofiller. In our previous research work, we developed organomodified nanofiller (clay) which is highly compatible with PMMA matrix [18].

Recently, Smith et al. reported microwave-assisted polymerization by using different initiators. [20] On the basis of these observations, some investigators have taken a further step and suggested that the use of different initiators effect on bulk polymerization [18]. Although there are no reports on dispersion of nanofiller. This paper particularly focuses on free-radical polymerization of monomer by bulk polymerization.

Here, we report synthesis of PMMA nanocomposites by bulk polymerization of MMA, using organomodified CL120 and BPO or V70 initiator. This is of interest because; different initiators have different reaction and polymerization temperatures. The effect of initiator on polymerization of monomer is investigated. The composite was fully characterized using transmission electron microscopy, XRD, TGA, DMA, DSC and UV-visible instruments.

II. EXPERIMENTAL

A. Materials

All chemicals used were of analytical grade or of the highest purity commercially available. PMMA is purchased from Across, methylmethacrylate (MMA) supplied from Kaohsiung

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Monomer Company Limited./ Lucite International Group, (Taiwan). Acetic acid and (K2) ($C_{24}H_{44}N_2O_6Na_2$) cocoamphodipropionate were purchased from SHOWA. 1-methyl-2-pyrrolidinone, benzoyl peroxide, 2-2'-azobis (4-methoxy-2,4-dimethylvaleronitrile) and toluene were purchased from TEDIA. Commercial natural clay (CL120 (CEC 168 meq/100 g) was purchased from China Glaze Co. Ltd, Taiwan. All the above commercial chemicals were analytically pure and used as received without further purification.

B. Preparation of Organo-Modified Clay

Organo-modified clay is prepared by ion exchange method. First, 2 g of CL120 was dispersed in 100 ml of aqueous solution and stirred overnight at room temperature. In this swelled clay, 2 times of CEC of K2 was added. Afterwards, resulting solution pH adjusted to 4-5 by using 1M acetic acid aqueous solution, and stirred overnight. The obtained product was collected by centrifugation followed by freeze drying. The following equation was used to calculate the intercalating agent used for the cation exchange reaction:

$$CEC * (wt\ of CEC) = \frac{X}{((Mw(K2))*2*1000} \qquad (1)$$

X represents the amount of modifying agent [19].

C. Preparation of PMMA Nanocomposites

At first, the modified clay and benzoyl peroxide (4000 ppm) initiator were added into methacrylate monomer, resulting solution is stirred at 70 °C, to reach certain viscosity. For the viscous PMMA poured into glass mold, further mold was placed in an oven at 70 °C overnight for curing. Afterwards, polymer was removed from the glass mold and post cured in an oven at 105 °C for 2 h. Finally, the synthesized materials are represented as Pure PMMA/BPO and PMMA/BPO-CL120-K2-1.0 wt%.

The modified clay and V70 initiator (1000 ppm) were added into methacrylate monomer under magnetic stirring at room and poured into glass mold at room temperature overnight for curing. Afterwards, the polymer is withdrawn from glass mold and is post cured in an oven at 105 °C for 2 h. Finally, the synthesized materials are represented as Pure PMMA/V70 and PMMA/V70-CL120-K2-1.0wt%.

D. Characterization

XRD analysis of the samples was performed using a Panalytical X'Pert3 powder X-ray diffractometer with Cu target (λ=1.54 Å) at a scanning rate of 2° min^{-1}. Fourier transform infrared (FT-IR) spectra were obtained using pressed KBr pellets with a Jasco FT/IR-4200 type A spectrometer. The microstructure of nanocomposites was imaged with a JEM-2010 (JEOL). The samples for TEM analysis were cut into 80 nm-thick sections with a diamond knife. TGA was carried out at temperatures in the range 40-900 °C and at scanning rate of 10 °C min^{-1} with a TG/DTA 6200 (SII Nano Technology Inc.). Dynamic mechanical analysis (DMA) measurements were performed with a TA-Q800 instrument in air at a scanning range of 40-180 °C with a heating rate of 3 °C min^{-1}. The Gel Permeation Chromatography (GPC) measurements were performed with a GPC-150CV.

III. RESULTS AND DISCUSSION

Free radical polymerization is conducted using conventional heating with two different free radical initiators. It is important to understand how the reaction conditions affect the efficiency of each the different initiator mechanistic steps to produce well-defined polymeric materials. Likewise, it will be equally important to identify how each mechanistic stage is being influenced by reaction temperature and polymerization time. In our experiment we choose the reaction temperature according to type of initiator used in polymerization, due to the decomposition of a free-radical initiator to form two free-radical species [18]. This breakdown takes the form of a hemolytic scission of a specific bond in the molecule as shown Fig. 1. Polymerization temperature profile of present study is shown in Fig. 2. In polymerization temperature profile, the first polymerization peak of BPO and V70 initiated reaction appears after ~2 hours and ~14 hours, respectively. This is an indication that V70 initiated polymerization time is higher compared to BPO initiated polymerization. Slowly initiated polymer molecular weight is lower compared to quick initiated polymer. Furthermore, it can be postulated that reaction temperature and type of initiators might affect the synthesized polymer nanocomposites properties.

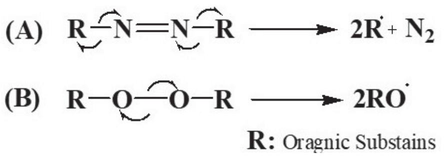

Fig. 1 Mechanism of (A) AZO initiator, (B) Epoxy initiator hemolytic scission

A. Morphology of PMMA/Clay Nanocomposites

The XRD results for the PMMA nanocomposites with 1.0 wt% loaded organomodified clays are shown in Fig. 3. Some lamellar periodicity was maintained on the hydrophilic clays despite of initiator and polymerization process. In XRD in lower angle there is a small clay peak, which indicates the clay particles intercalated or exfoliated morphology within the polymer matrix. Further, the dispersion morphology of nanocomposites was confirmed using TEM, and the TEM images shown in Fig. 4. This indicates that homogenous dispersion and intercalated nano-clay morphology was present in PMMA nanocomposites.

B. Thermo-Mechanical Properties of PMMA Nanocomposites

The thermal stabilities of PMMA nanocomposites were also studied by TGA and DSC analysis. TGA results of PMMA nanocomposites with the organo-clay summarized in Table I. As reported by many researchers, introduction of clay significantly improves the thermal stability of polymers [15]-[17]. The nanocomposites show similar curves; however, the

5% weight loss temperature (T_{5d}) is shifted toward higher temperature by incorporation of clays. T_{5d} of PMMA/V70-CL120- K2-1.0wt% and PMMA/BPO-CL120-K2-1.0wt% nanocomposites increase to 41 °C and 43 °C, respectively as compared to pure PMMA polymer. The T_{5d} increased in a regular manner with the increase of the clay content.

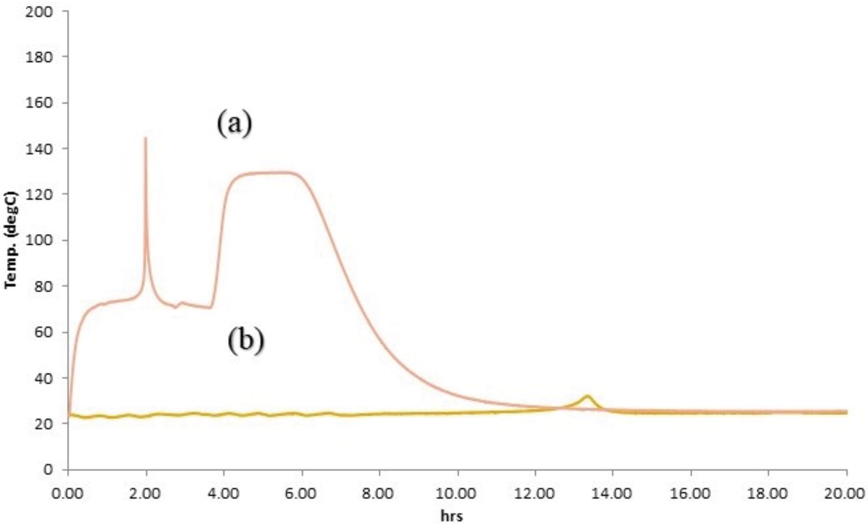

Fig. 2 Temperature curves of (a) BPO, (b) V70 initiated polymerization curves

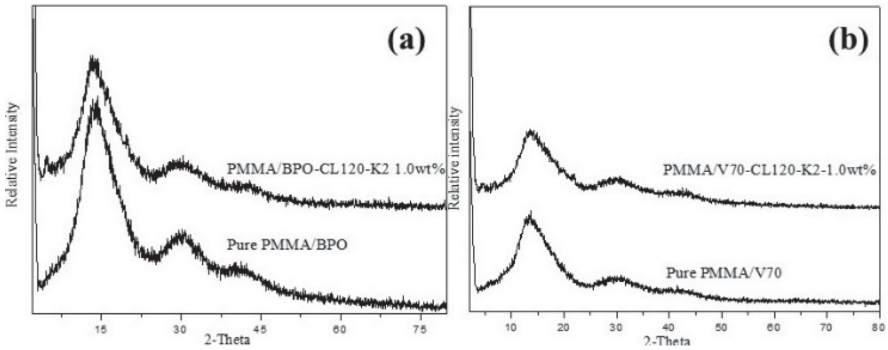

Fig. 3 XRD pattern of PMMA nanocomposites (a) PMMA/BPO and with-CL120-K2-1.0wt% (b) PMMA/V70 and CL120-K2-1.0wt% nanocomposites

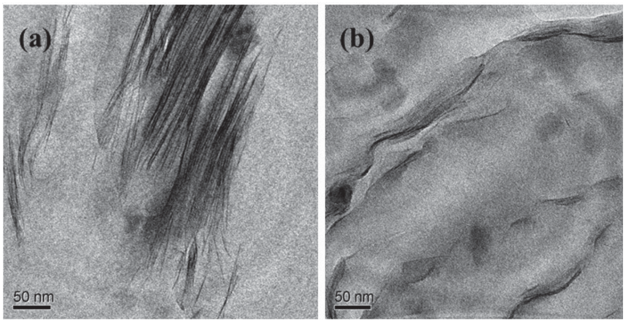

Fig. 4 TEM images of (a) PMMA/BPO-CL120-K2-1.0wt% (b) PMMA/V70-CL120-K2-1.0wt% nanocomposites

The thermal stability increases might be due to homogenous dispersion of clay in the polymer matrix. As shown in Table I, the pure PMMA matrix exhibited a glass transition temperature (Tg) of 110 °C, while the PMMA/V70-CL120-K2-1.0wt% and PMMA/BPO-CL120- K2-1.0wt% nanocomposites exhibited Tg values ranging from 117 to 118 °C as the clay addition. Strong interfacial bonding between the functionalized nanofiller and polymer matrix leads to an increase of the Tg value.

TABLE I
MOLECULAR WEIGHT AND THERMO-MECHANICAL RESULTS OF PMMA NANOCOMPOSITES

Sample	Mw	T_{5d}	Mpa
Pure PMMA/V70	2,601,218	251	2207
PMMA/V70-CL120-K2- 1.0wt%	2,520,504	292	1831
Pure PMMA/BPO	0,510,343	255	1579
PMMA/BPO-CL120-K2-1.0wt%	0,674,086	292	1534

DMA results are summarized in Table I and it is seen that the storage modulus of nanocomposites was in decrease compared to pure PMMA. This indicates that during polymerization, clay polymer might trap free radical resulting in decreasing the polymer nanocomposites' molecular weight.

BPO initiated PMMA nanocomposites are molecularly higher than that of V70 initiated nanocomposites. As shown in Fig. 2 earlier, polymerization reaction temperature and first polymerization time influenced the resulting polymer molecular weight.

It is also noticed that the incorporation of nano-clay into the polymer matrix leads to a considerable decrease in the storage modulus of PMMA nanocomposites over pure PMMA. This decrease storage modulus might be due to reinforcing the effect of nano-clay, initiator, first polymerization time and dispersion morphology of clay affects the interfacial interaction between clay and polymer that restricts modulus of polymer-clay nanocomposites. The heat distortion temperature (HDT) of polymer and polymer nanocomposites' results are summarized in Table II. The HDT temperature of pure PMMA and PMMA nanocomposites are almost same and do not affect temperature, it is might be due to the moderate interaction between polymers.

C. Optical Properties

Table II shows that the PMMA nanocomposites have commendable feature of transparency; however, most PMMA composites are poorly transparent due to the presence of reinforced fillers. Transparency of PMMA/V70-CL120 1.0wt%, PMMA/BPO-CL120-K2-1.0wt% decreases as compared to pure PMMA. Totally luminous transmittance (TLT) similarly deteriorated in the range of 92.8 to 90.6% and from 92.8 to 88.3%, respectively, with loading of CL120. It is important to emphasize here that the transmission of the pure PMMA films for 550 nm light at normal incidence is about 99.8% only as a result of the reflection losses on nanofiller interfaces and not because of absorption and scattering losses. For the films having higher nanofiller contents, for example for the one with 1.0 wt %, the intensity decreases to 81.2 and 76.4 wt% of PMMA/V70-CL120 1.0wt% and PMMA/BPO-CL120-K2-1.0wt%, respectively. In the presence of filler particles, they have higher probability to undergo optical scattering [20].

TABLE II
OPTICAL PROPERTIES OF PMMA NANOCOMPOSITES

				UV-Visible (nm)		
Sample	**TLT**	**Haze**	**HDT**	**500**	**375**	**320**
1	92.8	1.4	108	99	98	91
2	90.6	17.4	108	81	40	13
3	92.8	1.6	108	98	96	79
4	88.3	17.3	108	76	29	8.6

(1) Pure PMMA/V70, (2) PMMA/V70-CL120-K2-1.0wt%, (3) Pure PMMA/BPO, (4) PMMA/BPO-CL120-K2-1.0wt%.

IV. CONCLUSION

Well dispersed PMMA-based composites with nanofiller were produced via bulk polymerization by using BPO and V70 initiator. The effect of initiators on polymerization and physicochemical properties of nanocomposites are investigated. The results demonstrate that the thermal stability of nanocomposites increased with clay loading. Nanocomposites storage modulus was in decrease compared to pure PMMA. This is due to initiator free radical effect termination reactions of the propagating radicals and they were suppressed by the restricted mobility of polymer radicals in the nanofiller to give polymer radical, leading to the molecular weight control of the polymer. Optical properties of nanocomposites decrease with nanofiller loading because nanofillers undergo optical scattering.

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