A Survey about Grafting Density of Oleic Acid on Alumina Nano Particles Preparing for PMMA/Al₂O₃ Nanocomposite

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Abstract- In this paper, PMMA/Al₂O₃ nanocomposite was prepared by emulsion polymerization after alumina surface modification with oleic acid as coupling agent. Grafting density calculations were carried out to reach the best coupling agent content by means of elemental analysis CHN. FTIR analysis confirmed the presence of chemical bond between alumina and oleic acid in nanocomposite. The results of XRD showed the presence of cubic gamma alumina in nanocomposite in comparison with the amorphous nature of PMMA. Agglomeration occurred by using 25% mass alumina in nanocomposite compare with 15% which was verified by TEM images. The results from TGA exhibited thermal improvement of PMMA with alumina incorporation.

Kyewords— PMMA, Alumina, Emulsion polymerization, Grafting density.

I. INTRODUCTION

Ceramic materials are common candidates to improve some physical and mechanical properties of polymers such as hardness, young modulus, creep resistance and thermal stability[1]. Polymethyl methacrylate (PMMA) is one of the most important acrylates due to exceptional optical clarity[2] and mechanical features[3] but suffers from weak thermal stability which restricted its application to low temperature usages. Thermal stability can be improved by using different fillers such as halogenated compounds, clay and ceramic additives[4]. Aluminum oxide, alumina, is one of the valuable ceramic materials due to prominent features such as mechanical, thermal and chemical properties that provides the opening of new opportunities for applications both as bulk and filler [5-8]. By using alumina as a filler thermal stability of PMMA will be improved[9, 10] but first its surface must be modified[9] to be able to bond properly to the polymer chains. Having sufficient information about the amount of coupling agent required for the sustainable surface modification is mandatory to reach the best grafting of coupling agent to the surface of alumina nano particles. In this paper, after surface modification of nano alumina particles, the emulsion polymerization of MMA would be conducted in the presence of surface modified alumina and samples are tested by means of FTIR, XRD, TEM and TGA. Grafting density and grafting yield will be calculated by using CHN analysis, as well.

II. EXPERIMENTAL PROCEDURE

A. MATERIALS

In this work the following materials were used as received without further purification. Methyl methacrylate $(100.12 \text{ g} \cdot \text{mol}^{-1})$, Oleic acid (282.46 g.mol⁻¹), ammonium per sulfate (APS 228.2 g/mol), sodium dodecyl sulfate (SDS 288.372 g/mol), and ammonia solution (25%) all from Merck and alumina nanoparticles from Scharlo were used.

B. CHARACTERIZATION

FTIR characterization of nanocomposite materials was performed using Shimadzu (8400S) Fourier Transform infrared spectrophotometer. FTIR spectra were measured in the range of 400-4000cm⁻¹ with KBr. TEM analysis was conducted with a PHILIPS microscope (accelerating voltage of 80kV). In order to investigate the thermal properties of nanocomposites, thermogravimetric analysis (TGA) was performed with a TGA STA503 using alumina crucible and rate of 10°C per minute at ambient condition. XRD experiment was carried out by using XRD PHILIPS model PW1800. CHN elemental analysis was carried out by means of Costech ECS 4010.

C. NANOCOMPOSITE PREPARATION

In a typical process, alumina nanoparticles were vacuum dried at 100°C to remove water. Then by using proper OA/Al₂O₃ ratio, alumina particles were surface modified under exposing vigorous stirring of OA/toluene solution at 50°C for 12h. After surface modification of Al₂O₃ particles, they were dried again at 80°C for 5h. The surface modified alumina particles (SMA) then were dispersed in methyl methacrylate (MMA) by means of ultrasonic instrument. Emulsification of monomer-SMA mixture was carried out by solution of sodium dodecyl sulfate in water. Finally emulsion polymerization was conducted at 80°C by ammonium per sulfate as initiator under nitrogen stream for 3h. The process was done for PMMA/15Al₂O₃ (P15A) and PMMA/25Al₂O₃ (P25A). The flowchart of preparing nanocomposites are shown in figure.1.



Fig.1. Overall flowchart of nanocomposite synthesis.

III. Results and discussion A. Grafting density

Different OA/Al₂O₃ ratios were made to choose the highest grafting yield as a main composition. Based on the results of CHN analysis, the carbon content difference of alumina and oleic acid grafted alumina after surface modification can be obtained. The presence of carbon on alumina particles after modification is because of surface modification with oleic acid. Additionally, grafting density (GD) can be calculated from the following equation[11]:

Grafting density
$$\left(\frac{\mu mol}{m^2}\right) = \frac{10^6 \Delta C}{\left[\left(1200Nc - \Delta C(M-1)\right)s\right]}$$
 (1)

Where ΔC is the carbon difference between alumina after and before modification, *Nc* and M are the number of carbon atoms and molar mass of oleic acid, and S is the surface area of nano alumina particles (m²/g). The grafting yield, which corresponds to the fraction of OA grafted onto alumina, can be calculated using following equation:

Grafting yield (%) =
$$\frac{grafting \ density}{[Oleic \ acid]} \times 100$$
 (2)

Where [Oleic acid] $(\mu mol.m^{-2})$ is the initial concentration of OA. The results of grafting density and grafting yield are shown in Table.1.

TABLE 1. Grafting density and grafting yield of different OA/alumina weight ratios.

OA/Al ₂ O ₃	$[OA] \left(\frac{\mu mol}{n}\right)$	Carbon	Grafting	Grafting
ratio	- 'm²'	difference	density($\frac{\mu mol}{2}$)	yield (%)
(mass)			• m²	
0.5	25.288	0.5813	0.387392	1.53192
1.0	50.576	1.4274	0.96194	1.901968
1.5	75.864	2.2471	1.531007	2.018094
2.0	101.152	2.3104	1.575473	1.55753

As can be seen, the maximum grafting yield obtained for $OA/Al_2O_3=1.5$ which is 2.018094. Therefore, this ratio was used for preparing nanocomposites. The variations of GD and GY with OA/Al_2O_3 weight ratio are shown in figure.2. There is an increasing trend in GD and GY with increasing OA/Al_2O_3 ratio up to 1.5 which reaches its maximum value for GY and after that GY decreases sharply while GD increases slightly with increasing OA/Al_2O_3 ratio to 2.



Fig. 2. Variations of GD and GY vs OA/Al₂O₃ weight ratio.

B.FTIR analysis

Infrared spectroscopy is used for investigation of structural configuration of materials specially containing organic compounds because of proper sensitivity of these groups to infrared energy.



Fig.3. FTIR of pure PMMA, P15A and P25A.

Figure 3 shows FT-IR spectra for both pristine PMMA and polymer covered aluminum oxide[12]. Disappearance of peak at 1636cm⁻¹ which is related to C=C bond, can be the result of monomer conversion to polymer. There is a sharp peak at 1716cm⁻¹ that is related to carbonyl group (C=O) which is present in all samples because this bond is not changed during polymerization. Stretch vibrations of methyl groups are identified with the frequency of 2958cm⁻¹ which is sharp in the first sample (PMMA), while for the other samples is broadened because of the formation of aluminum oleat. The existence of bond between aluminum ions and carboxylate groups of oleic acid is confirmed with 1610cm⁻¹band that cannot be seen in pristine polymer. Since the oleic acid contains a lot of CH2 groups, it seems in P15A and P25A there must be intensive peak associated with them. The peak at 2854cm⁻¹in PMMA is weaker than P15A and P25A which is a deal for existing oleic acid in the system. Peaks below 1000 cm⁻¹ correspond to Al-O

stretching absorption such as vibrations at 585cm⁻¹ and 470cm⁻¹ that are attributed into the vibrational stretch of Al-O octahedral groups[13, 14].In general, the absorption peaks of PMMA in organic groups are stronger than nanocomposite which is due to incorporation of inorganic components.

C. XRD investigation

Powder X-ray diffraction (XRD) patterns of pure PMMA and PMMA/Al2O3 nanocomposites (P15A and P25A) are shown in figure.4. In general, the powder X-ray diffraction patterns in amorphous systems present broadened peaks as can be seen for PMMA which is entirely amorphous therefore the diffraction pattern of PMMA shows the most intense peaks at 2theta values of 13°, 27° and 41° according to JCPDS Card no. 13-0835 file. A comparison of the spectra of PMMA and PMMA/Al₂O₃ indicated different behavior between the two materials.



Fig. 4. XRD patterns of PMMA, P15A and P25A.

It was observed that the intensity of the diffraction peaks in pristine PMMA was significantly decreased as a result of the alumina incorporation. In addition, the presence of new peaks were detected by the presence of alumina, as expected.

The peak at 65° reveals the presence of gamma alumina with cubic structure. It is observed an increasing crystallinity for the PMMA/Al₂O₃ with increasing alumina content from15 to 25% in mass. The broadening peaks concerns with nano nature of samples.

D. TEM micrographs

Figure 5 shows the TEM of PMMA, P15A and P25A. The bonding between hydrophilic alumina and hydrophobic PMMA was conducted by means of oleic acid as coupling agent. The surface of nano alumina was modified by oleic acid before polymerization, and after that surface modified particles were mixed with MMA and finally polymerized by emulsion polymerization.



Fig. 5. TEM images of PMMA, P15A and P25A.

According to figure.5 increasing alumina content from 15 to 25% wt in nanocomposite results in appearance of agglomerates of alumina particles because of particles affinity to each other. The size of fillers has been almost remained constant while the polymer shape has been changed from spherical in pure state to a shell like around filler. Before polymerization the surface of particles was modified with oleic acid which introduces C=C on the surface of alumina particles. During polymerization double bond can open and polymerization takes place on the surface of fillers. Therefore, the above (figure.5) morphology for nanocomposites can be achieved. It is possible to create a polymer shell around filler particles provided that grafting sufficient coupling agents on the surface of inorganic constituents occurs.

E. THERMAL GRAVIMETRIC ANALYSIS

The thermal behavior of nanocomposites are shown in figure.6 by means of thermal gravimetric analysis (TGA) which was conducted at ambient conditions between 150 to 550°C with the rate of 10°C/min. According to figure.6 the decomposition of PMMA takes place at higher temperatures by using alumina as filler in the nanocomposite[15].



Fig. 6. TGA curves for PMMA, P15A and P25A at ambient conditions.

The thermal decomposition of PMMA starts at 270°C while for nanocomposites increased to 280°C and 287°C for PA15 and PA25, respectively. It means the starting temperature of polymer decomposition has been increased by using alumina. The mass residues are 0, 15.087 and 25.934 for PMMA, PA15 and PA25, respectively. Based on the results of TGA, the thermal stability of PMMA improves by adding alumina. As alumina particles adhere to polymer chains by chemical bond (provided by OA), the mobility of chains restricts, therefore the thermal stability is altered.

IV. CONCLUSION

PMMA/Al₂O₃ nanocomposites were prepared successfully by emulsion polymerization with different amounts of alumina nanoparticles. The results of FTIR and XRD showed the presence of chemical bond between PMMA and alumina and cubic gamma alumina, respectively. Increasing the filler content from 15% to 25% results in agglomeration of particles which was confirmed by TEM images. Thermal stability of PMMA was improved by using alumina nanoparticles that was illustrated by TGA curves.

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