Sigma J Eng & Nat Sci 38 (3), 2020, 1113-1120

Sigma Journal of Engineering and Natural Sciences
Sigma Mühendislik ve Fen Bilimleri Dergisi

Research Article

POLY(MPAEMA)/CLAY NANOCOMPOSITES: SYNTHESIS, CHARACTERIZATION, STRUCTURAL, AND THERMAL PROPERTIES

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Received: 16.03.2020 Revised: 08.05.2020 Accepted: 10.05.2020

ABSTRACT

In this study, the synthesis, characterization, and thermal properties of poly(2-(4-methoxyphenyl amino)-2-oxoethyl methacrylate) (MPAEMA) polymer/clay based nanocomposites were investigated by in situ polymerization. At the characterizations of nanomaterials FTIR, XRD, SEM, and TGA techniques were used. It was determined from XRD and SEM measurements that the morphology of nanocomposites was exfoliated when the clay content in the polymer matrix was kept at 3% and 5%. From thermal analysis, a positive correlation was observed between the clay ratio and thermal stability of nanomaterials.

Keywords: MPAEMA, polymer/clay nanocomposite, organoclay, thermal stability, in-situ polymerization.

1. INTRODUCTION

Organoclays consist of the replacement of cations in clay minerals with organic substances such as alkylammonium, dialkylammonium, quaternary ammonium cations [1, 2]. When ion exchange takes place in the clay, organoclay is formed, so the surface energy of the clay decreases, the physicochemical properties of the surfaces change, the interaction characteristics with the monomer/polymer structure improve, and as a result, the distance between the layers can be opened up to approximately 1 nm. This expansion facilitates diffusion of polymer chains between the organoclay layers in subsequent steps. In addition to diffusing large molecular weight compounds between layers, this feature also allows cations between layers to be replaced with large molecular weight compounds. Thus, the clay surface can be modified by adding hydrophobic properties. There are two consequences in the reaction of converting clay into organoclay. I: Organic cations settle in the range of clay layers, reducing the surface energy of the clay and widen the layer intervals of the clay. II: By changing the surface properties of the clay, the hydrophilic structure turns into a hydrophobic or organophilic structure [3, 4]. The type, chemical structure, amount and hydrophobic character of the clay-modifying organic agent also change the characteristics and behavior of the organoclay. Thus, these organic agents provide functional groups with which the polymer matrix and reagent can interact [5-7].

Polymer/clay nanocomposites are now an important area of research as opposed to pure polymer because of their improved physical, mechanical, and chemical properties. Clay minerals such as MMT, due to some advantages, are the most widely selected nanofiller for the preparation

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of polymer/clay nanocomposites. In this study, I.28E organoclay MMT derivative, was used. The purpose of present study is the synthesis and characterization of polymer/organoclay nanocomposites containing oxo methacrylate. First of all, MPAEMA (2-(4-methoxyphenyl amino)-2-oxoethyl methacrylate) monomer was synthesized and its nanocomposites were prepared with organoclay by in situ free-radical polymerization. Changes in thermal properties associated with the clay were discussed, and morphology.

2. EXPERIMENTAL

2.1. Materials

Nanomer® I.28E organonanoclay (25–30 wt % trimethyl stearyl ammonium) was purchased from Sigma-Aldrich. For the synthesis of MPAEMA monomer, 4-methoxyaniline, triethylamine, chloroacetyl chloride and sodium methacrylate (Aldrich) were used. For nanocomposite synthesis, azobisisobuturonitrile (AIBN) was used as Initiator and 1,4-Dioxane and ethyl alcohol as solvent.

2.2. Instrumental Measurements of Nanocomposite

The FTIR spectra of all samples were performed with a PerkinElmer Spectrum Two (UATR) IR spectrometer in the range of 4000-450 cm^{-1}. XRD patterns were obtained using a Bruker Axs D8 Advance diffractometer with a back monochromator and a Cu target and $K\alpha$ (λ=1.5418 nm) in 2θ=10-45^o (step of 0.01º, at room temperature). Scanning electron microscope observation was recorded with a Zeiss Evo LS 10 at 25 kV. Thermal analyzes were obtained with a Hitachi 7000 TGA/DTA/DTG simultaneous system a heating rate of 10^{o}C min^{-1} in nitrogen atmosphere.

2.3. Preparation of Poly(MPAEMA)/Organoclay Nanocomposites

MPAEMA homopolymer was re-synthesized according to the literature (Fig.1) [8-10]. Poly(MPAEMA)/organoclay nanocomposites were prepared with in-situ method. 3% and 5% amount of I.28E organonanoclay was dispersed in 1,4-dioxane and stirred by magnetic stirrer at 70 °C for 24 h. 1 M MPAEMA monomer was dissolved in 1,4-dioxane at room temperature in another flask. AIBN was added as a free radical initiator to the 3% and 5% organoclay added monomer mixture in separate bottles. In separate magnetic stirrer, polymer/organoclay composites were formed by mixing at 73 °C for 48 hours. The composites were precipitated in excess ethyl alcohol, removed from impurities, dried in the oven, and sifted through a 20micron sieve.

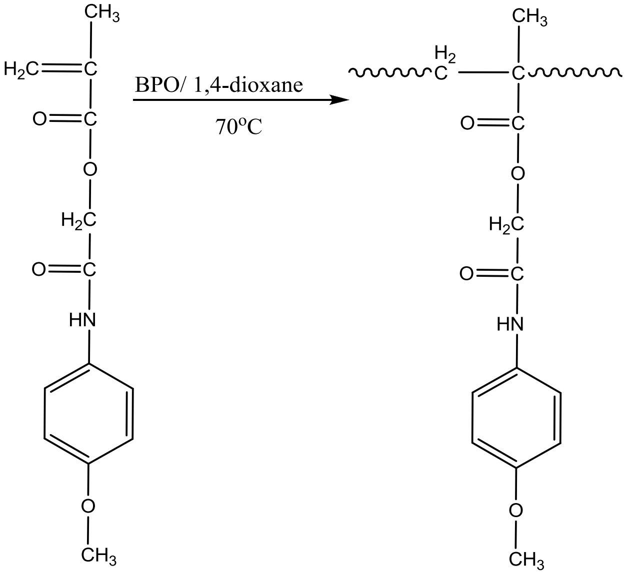

Figure 1. Synthesis of poly(MPAEMA) homopolymer [8]

3. RESULTS AND D ISCUSSIONS

3.1. FTIR Spectroscopy

Figure 2 shows FTIR spectra of poly(MPAEMA)/3%clay and poly(MPAEMA)/5%clay nanocomposites. The spectrum of I.28E organoclay show the characteristic bands at 3620 cm^{-1} OH stretching, 1001 cm^{-1} Si–O stretching, 913 cm^{-1} Al–OH deformation, 797 cm^{-1} silica Si–O stretching, 621 cm^{-1} out of plane Al–O and Si–O stretching, 520 cm^{-1} Al–O–Si deformation. Also, organoclay includes trimethyl stearyl ammonium structures used in the modification. The following are the peaks from the chemical modifier; aliphatic C–H stretching at 2922–2850 cm^{-1}, aliphatic C–H shear vibration at 1469 cm^{-1} [11, 12]. The most characteristic bands observed for poly(MPAEMA) units are seen in (cm^{-1}) 3300 (N-H), 3400 (C Ar-H), 2900 (aliphatic C-H), 1739 (C=O ester stretch), 1679 (C=O amide stretch), 1602 (C=C stretch on aromatic ring), 1250 and 1500 (symmetrical and asymmetrical C-O-C) [8]. The peaks observed in the homopolymer are also seen in nanocomposites. On the other hand, in nanocomposites, the absorption band characteristic for clay and attributed to Al–O–Si stretching shifts 517 cm^{-1} frequency. From these results, it can be said that the organomodified clay presents in polymer matrix as is reported by other articles [11-17].

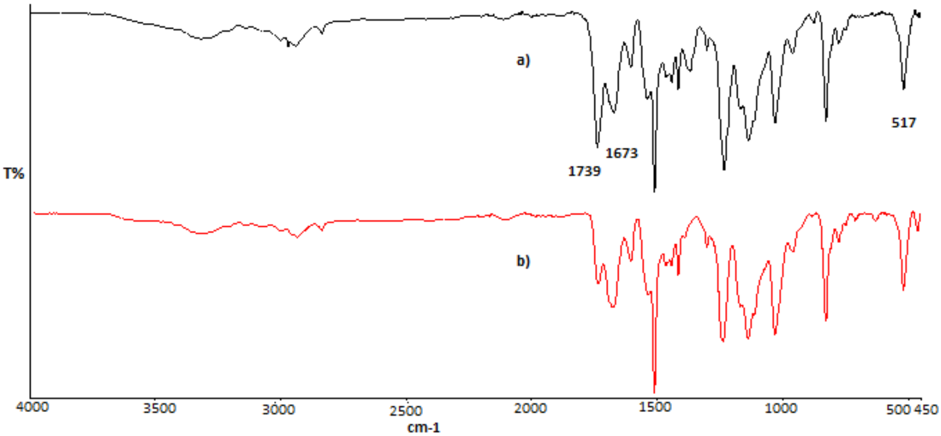

Figure 2. FTIR spectra of a) poly(MPAEMA)/3%clay b) poly(MPAEMA)/5%clay nanocomposites

3.2. XRD Measurements

X-ray diffraction is the preliminary technique to verify whether the layered structure has altered or not. In the literature, the characteristic crystalline peaks of I.28E organoclay is 3.9° (d=2.27 nm) [12], and 3.6° (7.91 A˚) [18-20], The distribution of the polymer between the layers of the clay causes that a clear XRD peak in the nanocomposites to be unreadable. The absence of component-specific peaks in nanocomposite materials can be explained by the fact that the polymer is intercalated between clay layers and clay layers become so irregular that they cannot give an XRD signal [12-20], therefore it can be considered as an exfoliated structure. Also, all peaks present in the XRD curve of the clays are not observed in the nanocomposites. The XRD patterns of the poly(MPAEMA)/organoclay nanocomposites are shown in Fig.3.a-b.

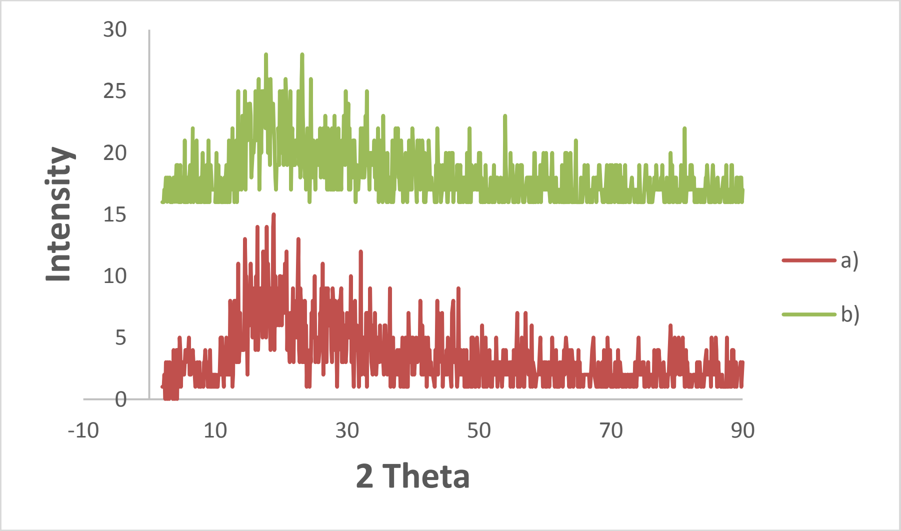

Figure 3. XRD patterns of a) poly(MPAEMA)/3%clay b) poly(MPAEMA)/5%clay

3.3. Morphological Study using SEM

SEM micrographs were used for further characterization of nanocomposites. The homogeneous distribution of nanoparticles from SEM photographs is presented in Figure 4.a-b. As seen in the SEM micrographs, the clay was dispersed in the polymer matrix. The increase in the amount of clay resulted in particle size. This exfoliated structure was observed in the XRD results and confirmed with the help of SEM effects [12-14].

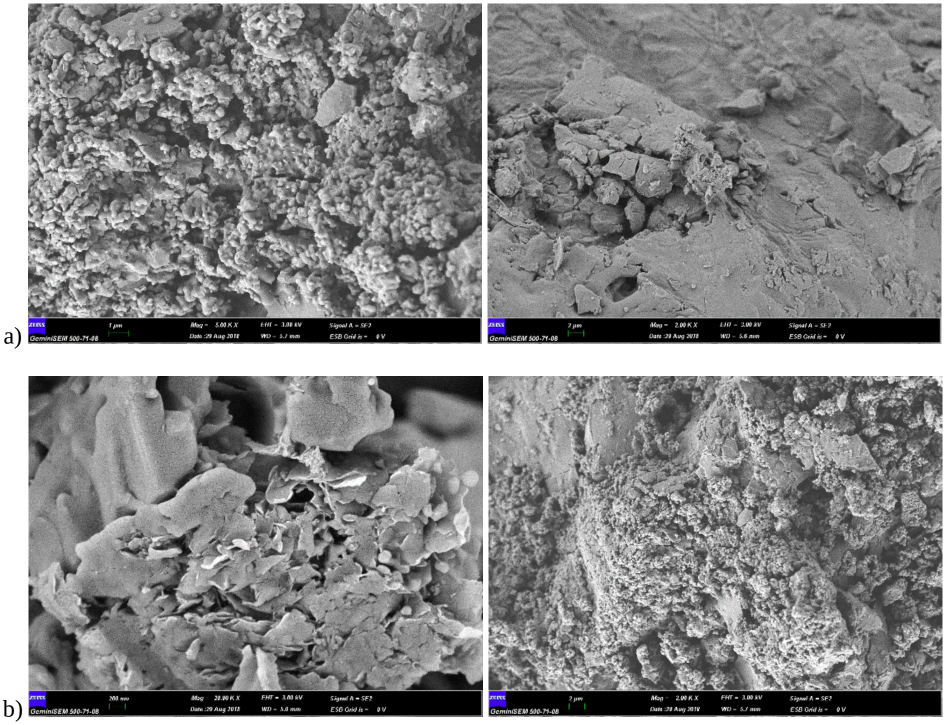

Figure 4. SEM micrographs of a) poly(MPAEMA)/3%clay b) poly(MPAEMA)/5%clay

3.4. Thermal Characterization

In the literature, it is known that the thermal data of composites synthesized with low amount of clay fillers give similar results to each other [12-17]. When polymers' thermal behaviors are compared, nanocomposites have been observed to have better thermal stability than homopolymer. These thermal changes prove that polymer chains break into the clay galleries and form nanocomposites. The nanodispersion of polymer molecules in silicate layers limits thermal movement, which increases thermal stability. It was observed that thermal stability of nanocomposites formed with clay increased with the increasing amount of clay in the composite, resulting in a clay thermal barrier [12-17]. Thermogram obtained for nanocomposites are presented in Figure 3, while some thermal data are given in Table 1.

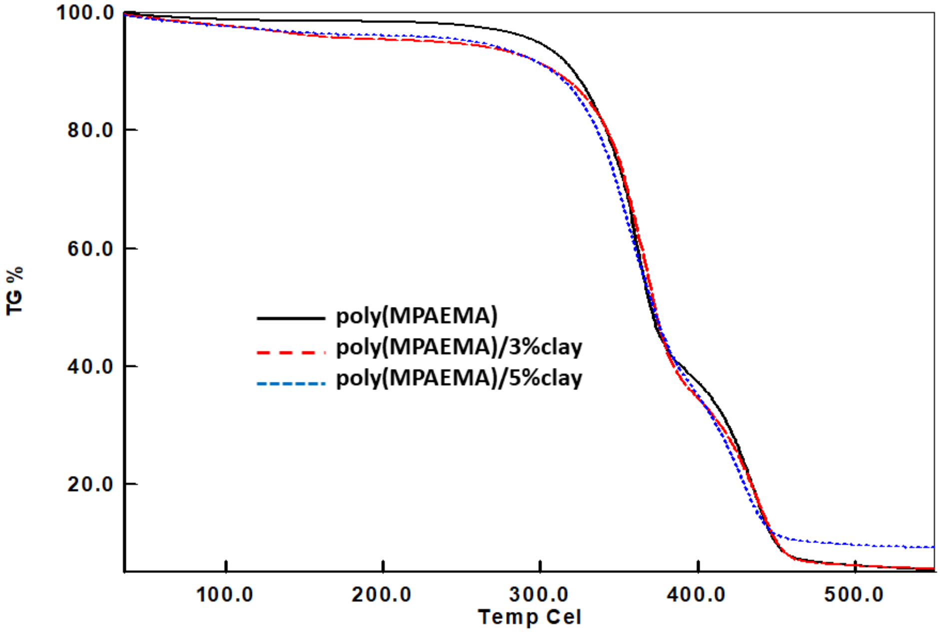

Figure 5. Comparative TGA curves for MPAEMA homopolymer and its nanocomposites

Table 1. Some thermal data of MPAEMA homopolymer and its nanocomposites

Sample	**Initial Decomp. Temp.**	**Max. Decomp. Temp. (°C)**	**Temp. of 50% weight loss at (°C)**	**%Weight loss at (300°C)**	**%Weight loss at (400°C)**	**%Weight loss at (450°C)**	**%Weight loss at (500°C)**	**% Residue at (550°C)**
poly(MPAEMA)	~300	360	370	95	63	90	94	5
poly(MPAEMA) /3%clay	~310	~372	372	91	35	89	94	6
poly(MPAEMA) /5%clay	~311	~362	372	91	35	88	90	9

4. CONCLUSION

In this research, polymer/clay based nanocomposites synthesis, characterization, and thermal properties of poly(2-(4-methoxyphenyl amino)-2-oxoethyl methacrylate) (MPAEMA) were investigated by in situ polymerization. FTIR, XRD, SEM, and TGA techniques were used at characterizations of nanomaterials. From XRD and SEM images, it was observed that the morphology of nanocomposites was exfoliated when the clay content in the polymer matrix was kept at 3% and 5%. It was observed that the thermal stability of nanomaterials increased as the clay rate increased from thermal analysis.

Acknowledgement

The authors would like to thank to Uşak University Research Fund for financial support of this work (2016/TP001).

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