

## PREPARATION OF OXO METHACRYLATE-CONTAINING POLYMER/CLAY BASED NANOCOMPOSITES

Nevin Cankaya<sup>1\*</sup>

<sup>a</sup> Department of Chemistry, Usak University, Usak, TURKEY.

### ARTICLE INFO

#### Article history:

Received 24 July 2019  
Received in revised form 19  
December 2019  
Accepted 15 January 2020  
Available online 06 February  
2020

#### Keywords:

MPAEMA; Nanofiller;  
Polymer/clay  
nanocomposite;  
Organoclay; Thermal  
stability; In-situ  
polymerization.

### ABSTRACT

In this study, the synthesis, characterization, and thermal properties of poly(2-(4-methoxyphenyl amino)-2-oxoethyl methacrylate) (MPAEMA) polymer/organoclay based nanocomposites were investigated by in situ polymerization. Firstly, OVHAC organoclay that modified with vinylbenzyltrimethylhexadecyl ammonium chloride (VHAC), and MPAEMA monomer were re-synthesized according to the literature. FTIR, XRD, and SEM technique was used in characterization of nanomaterials, and TGA/DTA/DTG simultaneous system was used for thermal characterization of nanomaterials. It was observed from these analyzes that nanocomposite, which was synthesized with the use of high proportion of clay, had an intercalated structure.

**Disciplinary:** Chemistry

2020 INT TRANS J ENG MANAG SCI TECH.

## 1. INTRODUCTION

Polymer/clay composites have been extensively studied in recent years due to the perfect combination of properties they can offer in clay loading. Carbon nanotubes, graphene and (organo)clays are the most frequently used in polymer nanocomposites as nanofiller [1]. Due to its layered structure, clay is suitable for obtaining such hybrid materials. In addition, since clay is a cheap and abundant substance, it is a very economical approach to use as an inorganic matrix and finds a wide application in technical applications [2]. Since clays are hydrophilic inorganic compounds, they are generally not mixed with hydrophobic character polymers. For this reason, clays are usually modified with long chain alkyl salts to ensure both miscibility and to increase the distance between layers. The modification takes place after a simple displacement reaction. After the reaction, the surface of the clay becomes organophilic and dispersed in organic phases [3-5].

Recently, polymer/clay nanocomposites have been of great interest as they exhibit as much thermal and mechanical properties as the polymer itself. Intercalation and exfoliation are perfect compositions of a nano-scale type. In intercalation, when a small amount of polymer is added between the layers of clay, the intermediate layer expands the spacing, thus resulting in a well-organized multi-layer structure. The layers of clay are completely separated in exfoliation, and the layers are dispersed throughout the polymer matrix. Depending on the type and amount of nanoclay used, the status of intercalation or exfoliation also varies [6,7]. Since polymer/clay nanocomposites have improved physical, mechanical and chemical properties compared to pure polymer, it has recently been one of the most studied areas. While preparing polymer/clay nanocomposites, one of the most used clay types among the clay types selected as nanofiller is MMT and has many advantages over other clay types.

In this study, OVHAC organoclay-MMT derivative was used. The purpose of our study is the synthesis and characterization of polymer/organoclay nanocomposites containing oxo methacrylate. MPAEMA (2-(4-methoxyphenyl amino)-2-oxoethyl methacrylate) monomer was first synthesized and its nanocomposite was prepared by free-radical in situ polymerization using organoclay. Then, the morphology and thermal properties of the synthesized composite and organoclay were investigated.

## 2. EXPERIMENTAL

### 2.1 Materials

Na<sup>+</sup>Montmorillonite clay (Na<sup>+</sup>MMT) nanoclay was provided from Esan-Eczacıbaşı. Na<sup>+</sup>MMT, a natural bentonite nanoclay and the particular scale gamut <63 μ [8]. For the synthesis of nanoclay, vinylbenzyl chloride, and dimethylhexadecylamine 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

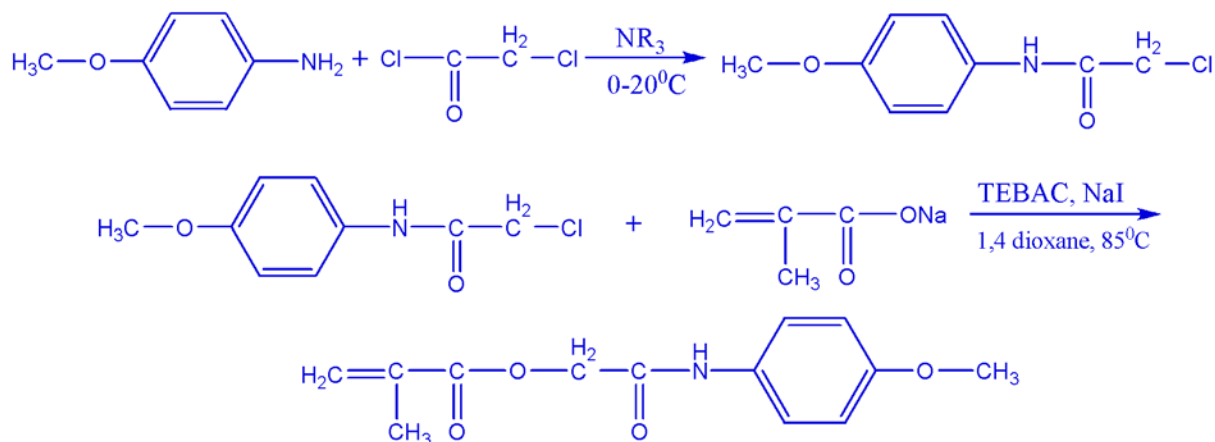
A PerkinElmer Spectrum Two (UATR) IR spectrometer was used to conduct the FTIR spectra of all the materials. XRD patterns were collected using a diffractometer of the Bruker Axs D8 Advance. A Zeiss Evo LS 10 was registered for scanning electron microscope observation. In nitrogen atmosphere, thermal analyzes were conducted using a Hitachi 7000 with a heating rate of 10°C/min.

### 2.3 Synthesis of Organoclay and its Nanocomposites

OVHAC organoclay [9-11], and MPAEMA monomer (Fig. 1) [12-14] were re-synthesized according to the literature. For the synthesis of VHAC, vinylbenzyl chloride was dissolved in diethyl ether solvent, and dimethylhexadecylamine was added dropwise. Later, the precipitate formed was filtered, crystallized and dried. For OVHAC synthesis, 1.5g of Na<sup>+</sup>MMT clay was inflated in pure water, 0.8g of VHAC dissolved in pure water separately and the two solutions were combined, mixed for 1 day, the precipitate formed washed with distilled water.

Poly (MPAEMA)/OVHAC nanocomposite was prepared with in-situ method. 50% amount of organonoclay was dispersed in 1,4-dioxane and stirred at 70 °C for 24 h. 1M MPAEMA monomer was dissolved in 1,4-dioxane at room temperature in another flask. AIBN was added as a free radical

initiator to the 50% organoclay added monomer. Polymer/organoclay composite was formed by mixing at 75 °C for 48 hours. The composite was precipitated in excess ethyl alcohol, removed from impurities, dried in the oven, and sifted through a 20micron sieve.



2-(4-methoxyphenylamino)-2-oxoethyl methacrylate (MPAEMA)

**Figure 1:** The synthesis scheme of MPAEMA.

### 3. RESULT AND DISCUSSION

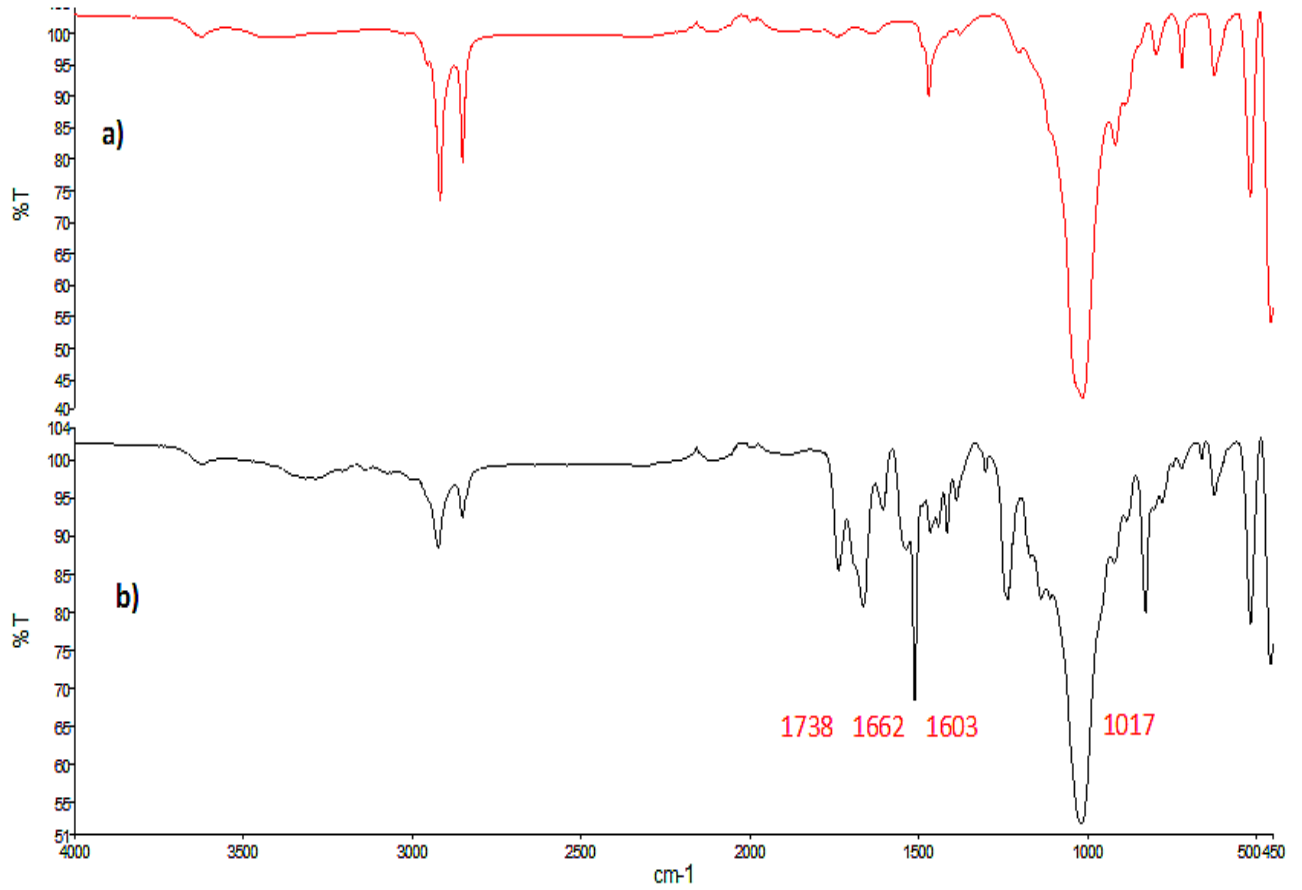
#### 3.1 FTIR SPECTROSCOPY

Figure 2 shows FTIR spectra of OVHAC organoclay, and its nanocomposite. In the FTIR spectrum of the OVHAC organoclay ( $\text{cm}^{-1}$ ), 2920 and 2850 (aliph. C-H), 1630 (aliph. C=C), 1480 (arom. C=C) tensile vibrations are observed from the vinylbenzyl dimethyl methylhexadecyl ammonium chloride (VHAC) that used in the modification. In addition, vibrations from the structure of  $\text{Na}^+$ MMT clay ( $\text{cm}^{-1}$ ) that 3600 (OH), 1020 (Si-O), 510 (Al-O), 460 (Mg-O) tensile vibrations are observed. A similar approach has been proposed by Kurt et al. [9-11].

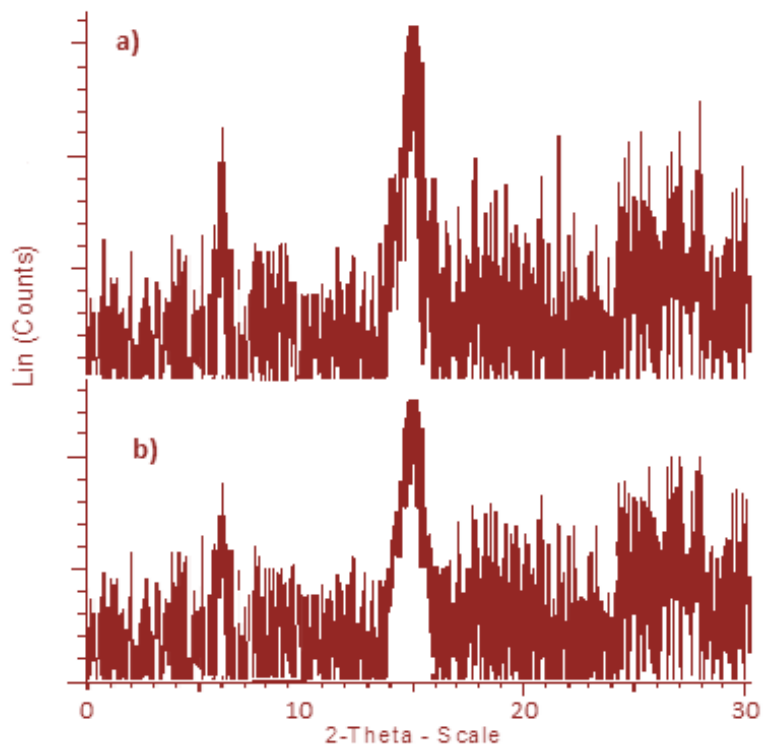
In the FTIR spectrum of the nanocomposite; from the MPAEMA homopolymer, (stretch  $\text{cm}^{-1}$ ) 1738 (C=O ester), 1662 (C=O amide), 1603 (C=C on arom. ring), 1240 and 1509 (symmetrical and asymmetrical C-O-C) are observed and also 2922 and 2623 (aliph. C-H), 1017 (Si-O), 460 (Mg-O) from OVHAC organoclay are observed [15-18].

#### 3.2 XRD Measurements

It was read that the  $\text{Na}^+$ MMT nanoclay was  $2\theta=7^\circ, 20^\circ, 22^\circ$  ( $d=1.26, 0.44, 0.40$  nm) from the XRD curve provided by Esan company [8]. In the literature, the crystalline peaks of OVHAC organoclay is  $8.7^\circ$  and weak  $3.8^\circ$  [9-11]. The shift between the layers of clay indicates that the layers of clay are isolated from each other and that natural clay organomodification has been accomplished. In the XRD patterns in Figure 3, the peaks of the OVHAC organoclay were read as  $15^\circ$ , and weak  $6^\circ$ . The peak values of the nanocomposite are the same as the organoclay. This is an expected result in the use of a high proportion of clay [19-29]. The polymer chains enter between the layers of the clay and slightly widen the distance between the layers of the clay; however, the morphological structure in which the crystal layouts of the clay layers are still intact, is known as intercalated. Therefore, we can say that for the nanocomposite, the polymer chains are in an intercalated structure where the chains are placed between the clay layers and the layers expand [17,19-29].



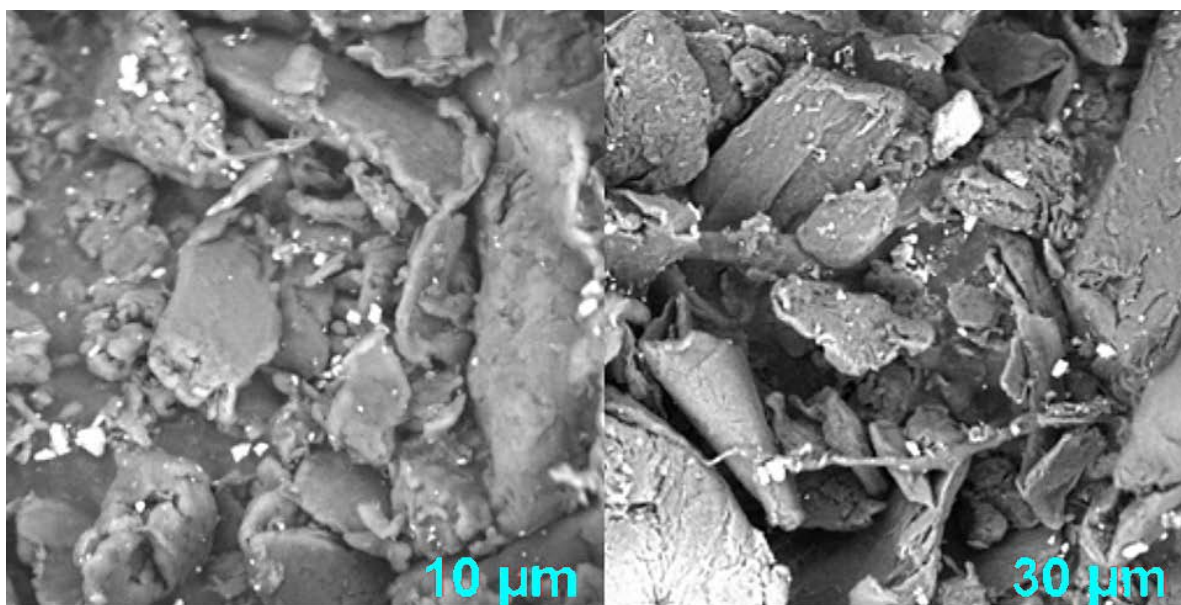
**Figure 2:** FTIR spectra of a) nanocomposite b) OVHAC, respectively.



**Figure 3:** XRD patterns of a) OVHAC b) nanocomposite.

### 3.3 MORPHOLOGICAL REVIEW WITH SEM

The distribution of nanoparticles from SEM photographs is presented in Figure 4. As seen in the micrographs of SEM the clay was dispersed in the matrix of polymers. As with the XRD results, the intercalated structure was confirmed in SEM photographs [11,18, 20-22].



**Figure 4:** SEM micrographs of nanocomposite.

### 3.4 THERMAL CHARACTERIZATION

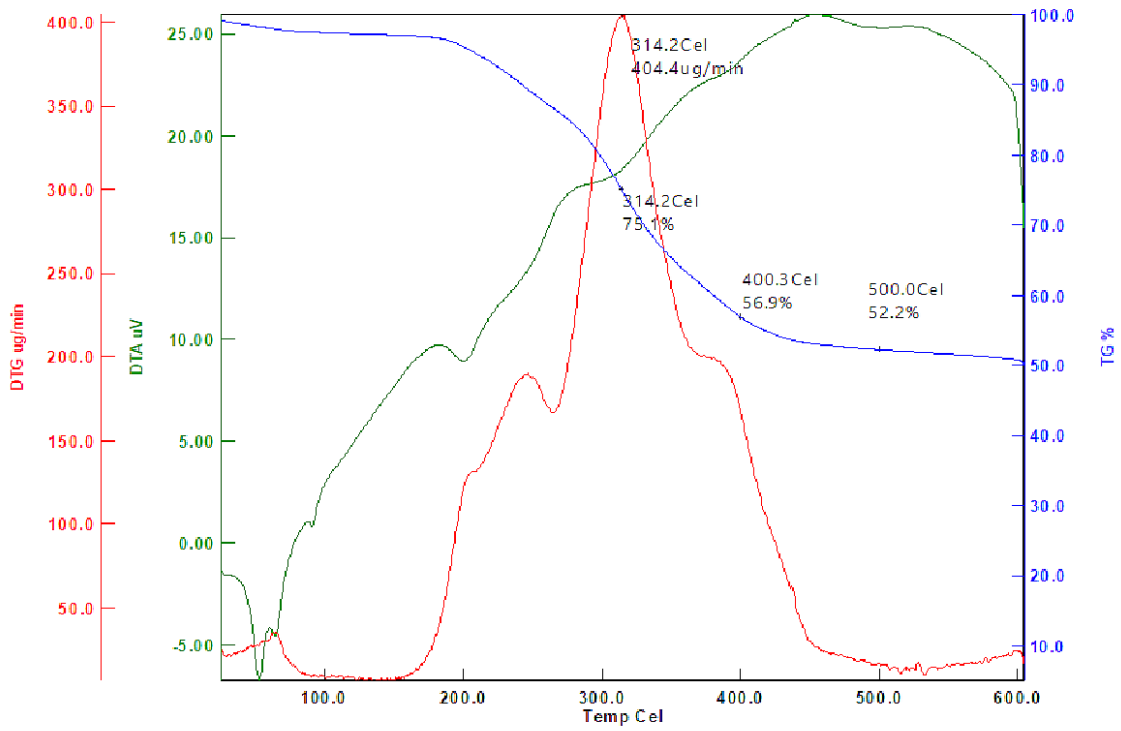
When the thermal behavior of nanocomposite and organoclay is compared, it is observed that the composite has better thermal stability than organoclay. This thermal change shows us that polymer chains can penetrate between layers of clay and that nanocomposite is properly synthesized. The dispersibility of polymers between the layers of clay limits thermal stability and thereby increases thermal stability [9-11,15-18,21-29]. Simultaneous device TGA / DTA / DTG has calculated the thermal properties of the components. The degradation of the organoclay and composite from the thermogram were observed at one level. Thermogram are given in Figure 5, and some thermal data are given in Table 1.

**Table 1:** Some thermal data of organoclay and nanocomposite.

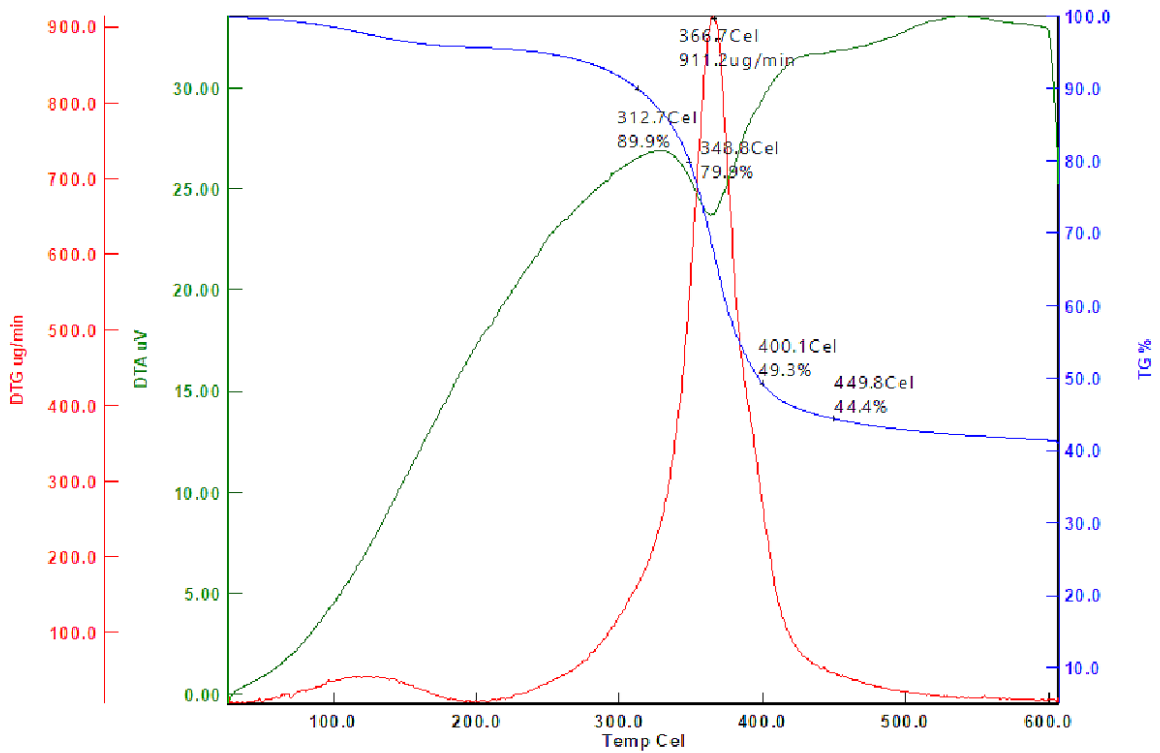
Sample	Max. Decomp. Temp. (°C)	Temp. of 10% weight loss at (°C)	Temp. of 20% weight loss at (°C)	Temp. of 25% weight loss at (°C)	Temp. of 50% weight loss at (°C)	%Weight loss at	Max. Decomp. Temp. (°C)
OVHAC	314	243	299	314	-	48	50
MPAEMA/OVHAC	366	313	349	314	398	57	41

## 4. CONCLUSION

In this research, MPAEMA (2-(4-methoxyphenyl amino)-2-oxoethyl methacrylate) monomer and OVHAC organoclay were re-synthesized according to the literature for composite synthesis. Characterization of polymer/organoclay nanocomposite synthesized by in-situ polymerization method was performed by FTIR, XRD, SEM techniques and also, thermal behaviors were investigated. From XRD, SEM and thermal measurements, it was observed that the morphology of



a)



b)

**Figure 5:** The TGA/DTA/DTG curves of the a) OVHAC b) nanocomposite, respectively.

nanocomposite was intercalated when the clay content is made high. In addition, the poly (MPAEMA)/OVHAC nanocomposite shows higher thermal stability than the OVHAC organoclay. Given that polymer/clay composites are used in various fields such as innovative synthesis methods, aviation, automobile, construction, packaging, petroleum, biomedical and wastewater treatment, we hope that this study will lead the literature and companies.



## 5. AVAILABILITY OF DATA AND MATERIAL

Data can be made available by contacting the corresponding authors.

## 6. ACKNOWLEDGEMENT

The authors wish to thank the Uşak University Research Fund for providing financial support for this research (2016/TP001).

## 7. REFERENCES

- [1] Bhattacharya, M. (2016). Polymer Nanocomposites-A Comparison between Carbon Nanotubes, Graphene, and Clay as Nanofillers. *Materials*. 9(4), 262.
- [2] Roelofs, J.C.A.A., Berben, P.H. (2006). Preparation and performance of synthetic organoclays. *Applied Clay Science*. 33(1), 13-20.
- [3] Okamoto, M., Ray, S.S., Edited by Nalwa, H.S. (2004). Polymer/Clay Nanocomposites. *Encyclopedia of Nanoscience and Nanotechnology*. 8, 1-52.
- [4] Gilman, J.W. (1999). Flammability and thermal stability studies of polymer layered-silicate (clay) nanocomposites. *Applied Clay Science*. 15(1-2), 31-49.
- [5] Paiva, L.B., Morales, A.N., Valenzuela, F.R. (2008). Organoclay: properties, preparation and applications. *Applied Clay Science*. 42, 8-24.
- [6] Liu, P., (2007). Polymer modified clay minerals: A review. *Applied Clay Science*. 38, 64-76.
- [7] Ray, S.S., Okamoto, M., Polymer/Layered Silicate Nanocomposites: A Review from Preparation to Processing, *Progress in Polymer Science*, (2003), 28, 1539-1641.
- [8] Çankaya, N., Şahin, R. (2019). Chitosan/Clay Bionanocomposites: Structural, Antibacterial, Thermal and Swelling Properties. *Cellulose Chemistry and Technology*. 53(5-6), 537-549.
- [9] Kurt, A., Yavuz, R., Bozdağ, G. (2013). Synthesis of Polystyrene-Clay Nanocomposites, Investigation of Thermal and Optical Properties. *Adıyaman University Journal of Science*. 3(2), 58-70.
- [10] Kurt, A., Yilmaz, P. (2016). Thermal decomposition kinetics of benzofuran derived polymer/organosilicate nanocomposites. *Kuwait J. Sci*. 43(2), 172-184.
- [11] Kurt, A., Koca, M. (2015). Optical Properties of Poly(2-(5-bromo benzofuran-2-yl)-2-oxoethylmethacrylate)/Organoclay Nanocomposites. *Arab. J. Sci. Eng*. 40, 2975-2984.
- [12] Çankaya N., Besci G. (2018). Synthesis, characterization, thermal properties and reactivity ratios of methacrylate copolymers including methoxy group. *Journal of the Faculty of Engineering and Architecture of Gazi University*. 33 (3), 1155-1170.
- [13] Acikbas, Y., Çankaya, N., Capan, R., Erdogan, M., Soykan, C. (2016). Swelling behaviour of the 2-(4-methoxyphenylamino)-2-oxoethyl methacrylate monomer LB thin film exposed to various organic vapours by quartz crystal microbalance technique. *Journal of Macromolecular Science, Part A, Pure and Applied Chemistry*. 53(1), 18-25.
- [14] Daşbaşı, T., Saçmacı, Ş., Çankaya, N., Soykan, C. (2016). A New Synthesis, Characterization and Application Chelating Resin for Determination of Some Trace Metals in Honey Samples by FAAS. *Food Chemistry*. 203, 283-291.
- [15] Zhang, W.A., Chen, D.Z., Xu, H.Y., Shen X. F., Fang, Y.E. (2003). Influence of four different types of organophilic clay on the morphology and thermal properties of polystyrene/clay

nanocomposites prepared by using the c-ray irradiation technique. *European Polymer Journal*. 39(12), 2323-2328.

- [16] Li, Y., Zhao, B., Xie, S., Zhang, S. (2003). Synthesis and Properties of Poly(Methyl Methacrylate)/Montmorillonite (PMMA/MMT) Nanocomposites. *Polymer International*. 52(6), 892.
- [17] Kurt, A., Topsoy, O.K. (2017). Preparation of Novel Coumarin Cyclic Polymer/Montmorillonite Based Nanocomposites. *Russian Journal of Applied Chemistry*. 90(12), 2019-2027.
- [18] Soykan, C., Akbay, M. (2019). In-Situ Synthesis of Polymer-Clay Nanocomposites: Exfoliation of Organophilic Montmorillonite Nanolayers in Poly 2-Thiozyl Methacrylamide. *Journal of Material Science and Technology Research*. 6, 22-33.
- [19] Doğar, Ç., Gürses, A., Köktepe, S., Mindivan, F., Güneş, K., Aktürk, S. (2014). Synthesis and Characterization of Phenol/Urea/Formaldehyde and Clay Composites. *Acta Physica Polonica A*. 125(2).
- [20] Nikolaidis, A.K., Koulaouzidou, E.A., Gogos, C., Achilias, D.S. (2019). Synthesis and Characterization of Dental Nanocomposite Resins Filled with Different Clay Nanoparticles. *Polymers*. 11, 730.
- [21] Longo, S., Mauro, M., Daniel, C., Galimberti, M., Guerra G. (2013). Clay exfoliation and polymer/clay aerogels by supercritical carbondioxide. *Frontiers in Chemistry*. 1(28), 1-9.
- [22] Campos L.M.P. et al. (2016). Evaluation of polymerization shrinkage in dental restorative experimental composites based: BisGMA/TEGDMA, filled with MMT. *J. Appl. Polym. Sci*. 43543, 1-10.
- [23] Mansa, R., Detellier, C. (2013). Preparation and Characterization of Guar-Montmorillonite Nanocomposites. *Materials*. 6, 5199-5216.
- [24] Doğar, Ç., Gürses, A., Karaca, S., Köktepe, S., Mindivan, F., Güneş, K. (2014). Investigation of thermal properties of PUF/clay nanocomposites. *Applied Surface Science*. 318, 59-64.
- [25] Kiersnowski, A., Kozak, M. Jurga, S. Pięłowski, J. (2004). Structure and Crystallization Behaviour of Poly( $\epsilon$ -caprolactone)/Clay Intercalated Nanocomposites. *Polymers&Polymer Composites*. 12(8), 727-737
- [26] Campos, L.M.P. et al. (2014). Polymerization Shrinkage Evaluation on Nanoscale-Layered Silicates:Bis-GMA/TEGMA Nanocomposites, in Photo-Activated Polymeric Matrices. *J. Appl. Polym. Sci*. 40010, 1-6.
- [27] Campos, L.M.P. et al. (2017). Thermal and mechanical behavior evaluation of dental composites filled with irradiated montmorillonite. *J. Appl. Polym. Sci*. 45063, 1-6.
- [28] Nikolaidis, A.K., Koulaouzidou, E.A., Achilias, D.S. (2019). Synthesis and Characterization of Novel Organomodified Nanoclays for Application in Dental Materials, *Current Nanoscience*. 15, 1-12.
- [29] Nikolaidis, A. K., D. S. Achilias, G. P. Karayannidis (2012). Effect of the type of organic modifier on the polymerization kinetics and the properties of poly(methyl methacrylate)/organomodified montmorillonite nanocomposites. *European Polymer Journal*. 48, 240-251.



Dr. Nevin Çankaya is an Associate Professor at Department of Chemistry, Uşak University, Uşak, Turkey. She got a Doctoral degree in Chemistry from Fırat University of Elazığ, Turkey. Her research focuses on Polymer, Biopolymer, Nanocomposite, Physical Chemistry.