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# Synthesis, characterization and thermal properties of oxo methacrylate-containing polymer/clay nanocomposites

*Okso metakrilat içeren polimer/kil nanokompozitlerin sentezi, karakterizasyonu ve termal özellikleri*

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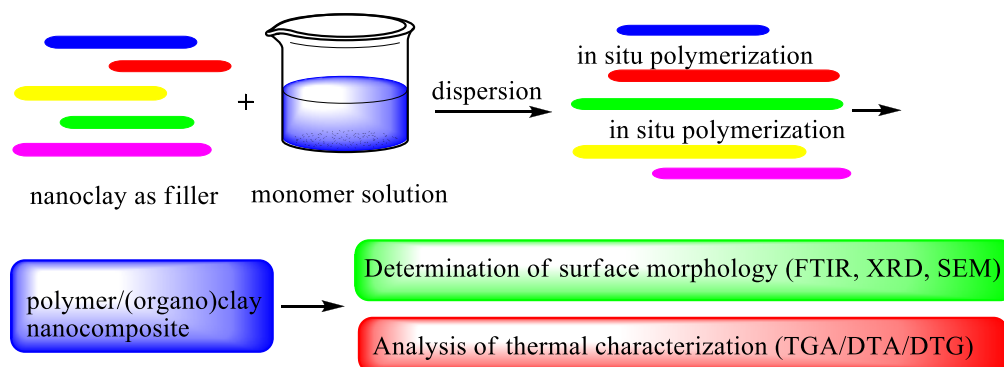
# Synthesis, Characterization and Thermal Properties of Oxo Methacrylate-Containing Polymer/Clay Nanocomposites

## Highlights

- ❖ Synthesis of polymer/organoclay nanocomposites by *in situ* polymerization method.
- ❖ Using FTIR, XRD, SEM and TGA/DTA/DTG as characterization techniques.
- ❖ Polymer/organoclay nanocomposites are exfoliated structure.
- ❖ From thermal analysis of nanocomposites, there is a positive correlation between clay ratio and their thermal stability.

## Graphical Abstract

In this research, polymer/organoclay 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 thermal techniques were used in the characterization of composites, and it was found that the composites were exfoliated from these analyzes.



**Figure.** Graphical abstract

## Aim

The aim of this research is to investigate the synthesis, characterization and thermal properties of polymer/organoclay nanocomposites.

## Design & Methodology

In the synthesis of nanocomposites, *in situ* polymerization method by 3% and 5% clay additive was used, and FTIR, XRD, SEM and TGA/DTA/DTG techniques were used for characterization.

## Originality

In this research, unlike polymer/organoclay composites made in the literature, MPAEMA polymer and C10A organoclay were used.

## Findings

It was found that the composites synthesized by the *in situ* polymerization method were exfoliated. In addition, it has been observed from thermal analysis that thermal stability increases as the amount of clay increases.

## Conclusion

It is thought that the newly synthesized synthetic polymer / clay nanocomposites with natural clay content will serve many different areas, due to their environmentally friendly and biodegradable nature.

## Declaration of Ethical Standards

The author(s) of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

# Okso Metakrilat İçeren Polimer/Kil Nanokompozitlerin Sentezi, Karakterizasyonu ve Termal Özellikleri

*Araştırma Makalesi / Research Article*

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## ÖZ

Bu çalışmada, polimer/kil bazlı nanokompozitlerin sentezi ve karakterizasyonu, 2-(4-metoksifenil amino)-2-oksoetil metakrilat (MPAEMA) ve organokil kullanılarak gerçekleştirilmiştir. İn situ (yerinde) polimerizasyon yöntemi ile sentezlenen nanokompozitlerde organokil miktarı %3 ve %5 olarak belirlenmiştir. Karakterizasyon teknikleri olarak FTIR, XRD ve SEM kullanılmıştır. Nanokompozitlerin morfolojisinin eksfoliyeye yapıda olduğu XRD ve SEM sonuçlarından belirlenmiştir. Daha sonra, nanokompozitlerin termal özellikleri TGA/DTA/DTG eşzamanlı sistem kullanılarak incelenmiştir. Termal analizde kil miktarı arttıkça ısıl kararlılığın arttığı görülmüştür. Doğal kil içerikli bu yeni sentezlenen sentetik polimer/kil nanokompozitlerin çevre dostu, biyolojik olarak parçalanabilir özelliklerinden dolayı farklı alanlara hizmet edeceği düşünülmektedir.

**Anahtar Kelimeler:** Polimer/organokil nanokompozit, organokil, termal kararlılık, yerinde polimerizasyon.

# Synthesis, Characterization and Thermal Properties of Oxo Methacrylate-Containing Polymer/Clay Nanocomposites

## ABSTRACT

In this study, synthesis and characterization of polymer/clay based nanocomposites was performed using 2-(4-methoxyphenyl amino)-2-oxoethyl methacrylate (MPAEMA) and organoclay. The amount of organoclay in nanocomposites synthesized by in situ polymerization method was determined as 3% and 5%. FTIR, XRD, and SEM were used as characterization techniques. It was determined from XRD and SEM results that the morphology of nanocomposites exfoliated. Then, the thermal properties of nanocomposites were investigated using the TGA/DTA/DTG simultaneous system. In thermal analysis, it was seen that the thermal stability increased when the clay amount increased. It is thought that this newly synthesized synthetic polymer/clay nanocomposites with natural clay content will serve different areas due to its environmentally friendly-biodegradable properties.

**Keywords:** Polymer/organoclay nanocomposite, organoclay, thermal stability, in situ polymerization.

## 1. INTRODUCTION

Polymer/clay nanocomposites are structures formed by dispersing inorganic particles in a polymer matrix [1, 2]. Thanks to the added inorganic materials, it is aimed to increase the strength of nanocomposites without increasing the hardness of the polymer matrix, and also to improve the thermal and mechanical properties and to reduce the gas permeability value, etc. [1-7]. Thanks to these advantages provided by nanocomposites, its use is becoming more and more common. On the other hand, with the increase of plastics and polymeric raw materials depending on the usage areas of traditional polymers, synthetic polymers in nature cause an important environmental problem since they cannot be biodegraded [8]. One of the novel and harmless ways of preventing plastics from damaging nature and the environment is to

include plastics in the natural cycle, that is to make plastics degradable [8-10]. For this purpose, using naturally occurring clays with synthetic polymers and making polymer/clay composites are among the academic studies of the last 25 years. Polymers with hydrophobic properties are not compatible with hydrophilic clays. Therefore, to make it compatible, clays, ammonium salts, etc. are used. They are converted into organoclays by ion exchange reaction [10-15].

Clay layers can be intercalated type or exfoliated type throughout the polymer matrix. Intercalated structure occurs when high clay rates are used, or polymerization does not occur between clay layers if the clay layers do not separate much during polymerization. In the exfoliated structure, it usually occurs at low clay rates (~1%-15%) and by separating the clay layers as much as possible. In this case, the polymer/clay composite has been found to have the good thermal and mechanical properties. Achieving this situation is very important due

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to the strong electrostatic forces that hold the clay layers together [9-15].

In this study, C10A organoclay which was expanded with organic modifiers between Na+MMT clay species layers was used. Organoclay amount was used as low as 3% and 5%. The nanocomposites formed by the C10A organoclay and the MPAEMA (2-(4-methoxyphenyl amino)-2-oxoethyl methacrylate) monomer that we synthesized in our laboratory, were synthesized by using in situ polymerization and characterized. In addition, the morphology and thermal properties of nanocomposites were investigated.

## 2. EXPERIMENTAL SECTION

### 2.1. Materials

Nanoclay 1-135 (C10A) was provided from Esan-Eczacıbaşı. The organic modifier of Nanoclay 1-135 is dimethyl, benzyl, hydrogenated tallow, quaternary ammonium cation with the particle size range of <15  $\mu$ , where tallow is ~65% C18, ~30% C16, ~5% C14 [10]. For the synthesis of MPAEMA monomer, 4-methoxyaniline, triethylamine, chloroacetyl chloride and sodium methacrylate (Aldrich) were used. For nanocomposite synthesis, benzoyl peroxide (BPO) was used as initiator and 1,4-Dioxane and ethyl alcohol as solvent.

### 2.2. Instrumental Measurements of Nanocomposite

The FTIR (Fourier Transform Infrared) spectra of all samples were performed with a PerkinElmer Spectrum Two (UATR) IR spectrometer in the range of 4000-450  $\text{cm}^{-1}$ . XRD (X-Ray Diffraction) patterns were obtained using a Bruker Axs D8 Advance diffractometer with a back monochromator and a Cu target and  $K\alpha$  ( $\lambda=1.5418$  nm) in  $2\theta=10-45^\circ$  (step of  $0.01^\circ$ , at room temperature). SEM (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 (Thermal Gravimetric Analysis/Differential Thermal Analysis/Differential Thermogravimetric Analysis) simultaneous system a heating rate of  $10^\circ\text{C min}^{-1}$ , under nitrogen gas flow (0.2 L/min).

### 2.3. Preparation of Poly(MPAEMA)/C10A Nanocomposites

MPAEMA monomer was re-synthesized according to the literature (Fig.1) [16, 17]. Poly(MPAEMA)/organoclay nanocomposites were prepared with in situ method. 3% and 5% amount of C10A organoclay was dispersed in 1,4-dioxane and stirred by magnetic stirrer at  $70^\circ\text{C}$  for 24 h. 1 M MPAEMA monomer was dissolved in 1,4-dioxane at room temperature in another flask. BPO 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  $73^\circ\text{C}$  for 48 hours. The composites were precipitated in excess ethyl alcohol,

removed from impurities, dried in the oven, and sifted through a 20micron sieve.

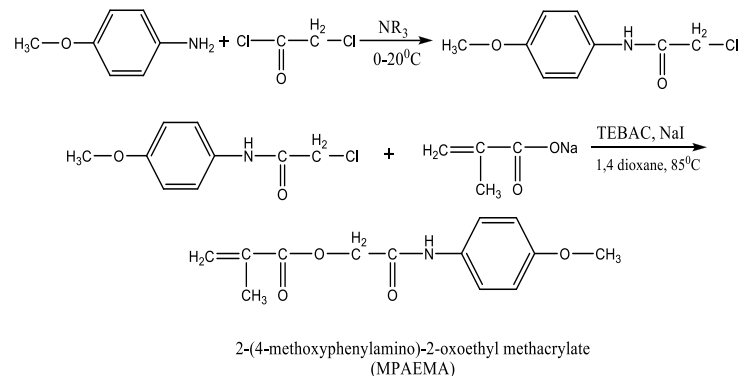
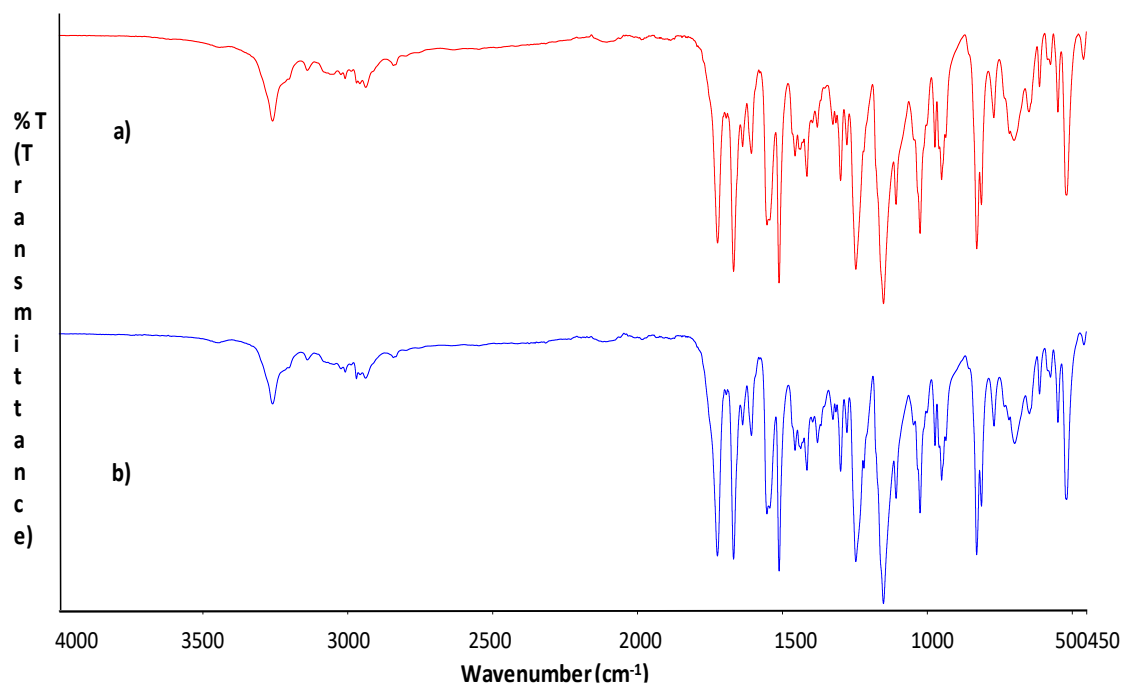


Figure 1. Synthesis of MPAEMA monomer [16, 17]

## 3. RESULTS and DISCUSSIONS

### 3.1. FTIR Spectroscopy

Figure 2 shows FTIR spectra of poly(MPAEMA)/ 3% C10A and poly(MPAEMA) / 5% C10A nanocomposites. The characteristic feature of the clay is that it contains molecules such as  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ . When the FTIR spectra of Na+MMT clay are examined, it was observed that the O-H stretch vibration peaked at  $3624$  and O-H bending vibration at  $1450$   $\text{cm}^{-1}$ , Si-O stretch at  $1010$  and bending vibration at  $514$   $\text{cm}^{-1}$ , Al-OH vibration at  $913$   $\text{cm}^{-1}$  and Mg-O vibration at  $475$   $\text{cm}^{-1}$  [9, 13-15, 17-19]. The clay peaks are observed in the C10A organoclay as mentioned above. Also, includes dimethyl benzyl alkyl chain quaternary ammonium chloride structures used in the modification. The following are the peaks from the chemical modifier; aliphatic N-CH<sub>3</sub> vibration at  $2840$   $\text{cm}^{-1}$ , aliphatic CH<sub>2</sub> vibration at  $1465$   $\text{cm}^{-1}$ , symmetric and asymmetric C-H stretching vibration at  $2920$   $\text{cm}^{-1}$  and aromatic C=C stretching vibration at  $1644$   $\text{cm}^{-1}$  [10, 18, 19]. The most characteristic bands observed for poly(MPAEMA) units are seen in ( $\text{cm}^{-1}$ )  $3260$  (N-H),  $3444$  (C Ar-H),  $\sim 2940$  (aliphatic C-H),  $1724$  (C=O ester stretch),  $1668$  (C=O amide stretch),  $1606$  (C=C stretch on aromatic ring),  $1246$  and  $1510$  (symmetrical and asymmetrical C-O-C) [16, 17]. In nanocomposites, all these peaks from the homopolymer are observed. On the other hand, some peaks characteristic of clay are also seen in composites. From these results, it can be said that the organomodified clay presents in polymer matrix as is reported by other articles [9-15].



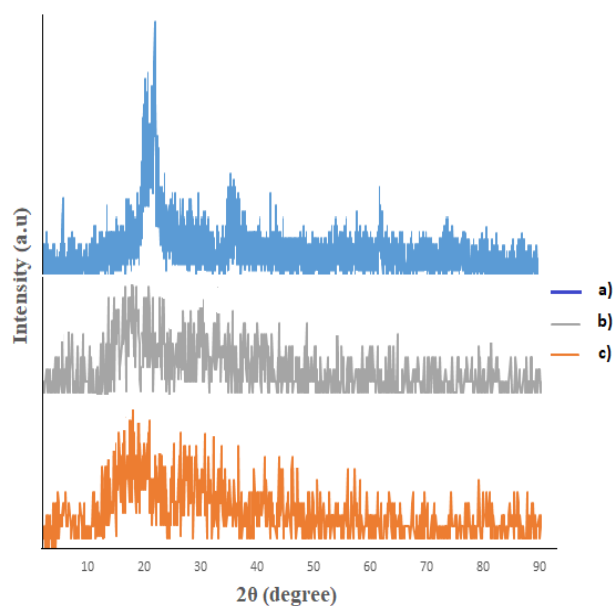
**Figure 2.** FTIR spectra of a) poly(MPAEMA)/3%C10A b) poly(MPAEMA)/5%C10A nanocomposites

### 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 the diffraction angle of C10A organoclay was  $2\theta = 5.4^\circ, 20^\circ, 22^\circ$  ( $d=1.64, 0.44, 0.40$  nm) [10, 18, 19]. Nanocomposites synthesized by the in situ polymerization method are obtained by polymerizing the monomer in these layers when the clay layers are spaced apart, so XRD peaks may appear amorphous. 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 [10-15, 17-21], clear XRD peak is not observed, and therefore it can be considered as an exfoliated structure. In addition, 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-c.

### 3.3. SEM Measurements

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, and particle sizes are close to each other. This exfoliated structure was observed in the XRD results and confirmed with the help of SEM effects [10, 15, 17, 19-21].



**Figure 3.** XRD patterns of a) C10A b) poly(MPAEM)/3%C10A c) poly(MPAEMA)/5%C10A

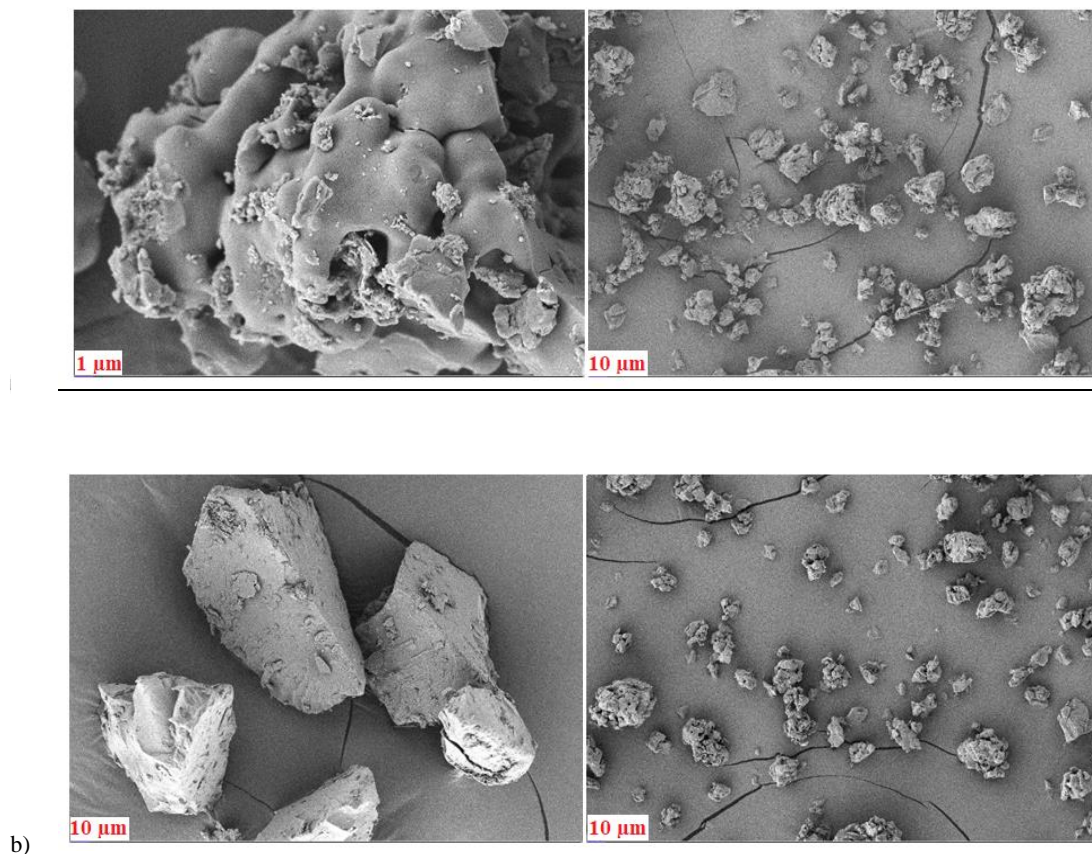


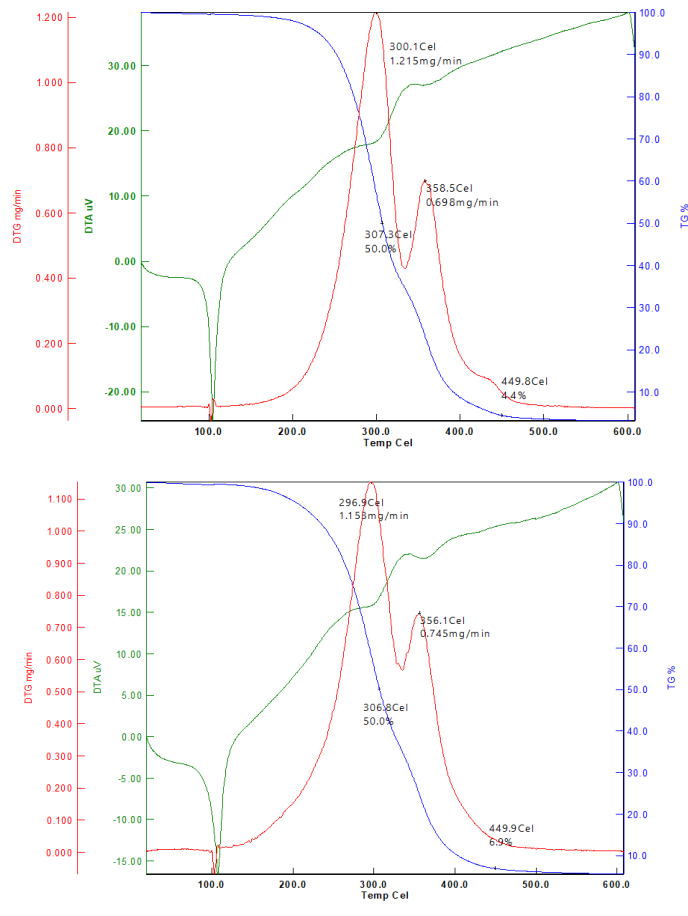
Figure 4. SEM micrographs of a) poly(MPAEMA)/3%C10A b) poly(MPAEMA)/5%C10A

### 3.4. Thermal Measurements

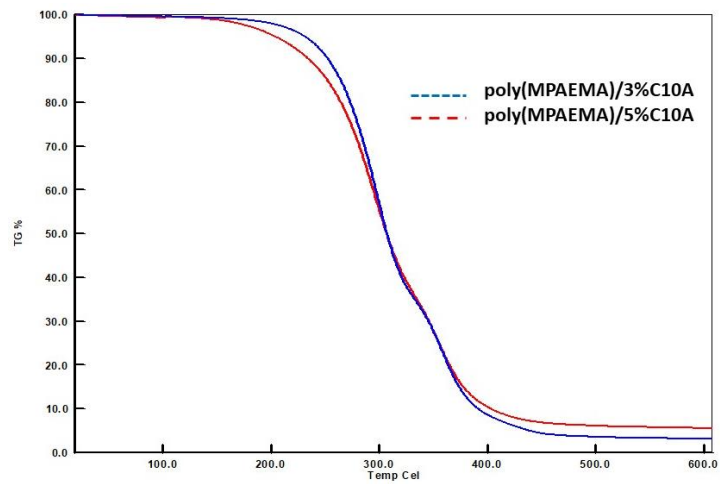
Thermal stabilities of polymer/clay nanocomposite were determined by TGA/DTA/DTG simultaneous method. For 3% and 5% clay additive nanocomposites at 10 °C/min heating rate, weight loss% decreased as the temperature increased. On the other hand, it is observed that the residue content increases with the increase of clay content in composites. Ash formation is very important for flame resistance and insulates the underlying polymer, thus it prevents flame feeding and air ingress [22, 23]. These thermal results showed that the clay additive increased the thermal stability by increasing the activation energy level required for thermal decomposition. It was also observed that degradation occurred at two levels for both composites. Thermal curves of nanocomposites are given in Figure 5, and comparatively in Figure 6. Table 1 summarizes some of the thermal data of nanocomposites at different temperatures, such as weight loss% and residual ash. Similar approaches observed for polymer/clay nanocomposites have been reported in different studies [10, 13-15, 17-24].

### 4. CONCLUSION

In this research, polymer/organoclay 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, SEM and thermal measurements, 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. Considering that environmentally friendly and biodegradable polymer/clay composites are used in various fields such as aviation, automobile, construction, packaging, petroleum, biomedical and wastewater treatment, it is hoped that this study will guide the literature and companies.



**Figure 5.** SEM micrographs of a) poly(MPAEMA)/3%C10A b) poly(MPAEMA)/5%C10A



**Figure 6.** The TGA/DTA/DTG curves of the a) poly(MPAEMA)/3%C10A b) poly(MPAEMA)/5%C10A, respectively

**Table 1.** Some thermal data of nanocomposites

Sample	Temp. of 50% weight loss at (°C)	Weight loss at% (400°C)	Weight loss at% (450°C)	Weight loss at% (500°C)	Residue at % (550°C)	Residue at % (600°C)
poly(MPAEMA) /3%C10A	307	91	95	96	3.3	3.2
poly(MPAEMA) /5%C10A	307	89	93	94	5.8	5.6

## ACKNOWLEDGEMENT

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## DECLARATION OF ETHICAL STANDARDS

The author(s) of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

## AUTHORS' CONTRIBUTIONS

**Nevin Çankaya:** Conducted the experiments, analyzed the results, and carried out the writing process of the article.

## CONFLICT OF INTEREST

There is no conflict of interest in this study.

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