

## Synthesis and Characterization of Polypropylene and CTAB Modified Diatomite Composites

Özkan Demirbaş<sup>1\*</sup> and Onur Ulus<sup>1</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science and Literature, University of Balıkesir, 10145 Balıkesir, Turkey.

### Authors' contributions

This work was carried out in collaboration between both authors. Author OD designed the laboratory-type extruder devices and their parts used for the preparation of the composite materials. In addition to these, author OD designed the study, wrote the protocol and the first draft of the manuscript. Author OU performed the lab experiments and statistical analysis, managed the literature search. Both authors read and approved the final manuscript.

### Article Information

DOI: 10.9734/IRJPAC/2016/30960

#### Editor(s):

(1) Li Cai, Department of Chemistry, University of South Carolina Salkehatchie, USA.

#### Reviewers:

(1) Bhagwan F. Jogi, Dr. B. A. Technological University, Lonere-Raigad MS Pin 402103, India.

(2) Kamol Dey, University of Chittagong, Bangladesh.

Complete Peer review History: <http://www.sciencedomain.org/review-history/17428>

Original Research Article

Received 11<sup>th</sup> December 2016  
Accepted 26<sup>th</sup> December 2016  
Published 3<sup>rd</sup> January 2017

### ABSTRACT

Polypropylene (PP) has been used extensively in many parts of the industry. The main reason for the frequent use of polypropylene is low cost, easy processing and high performance. Diatomite (D) has superior properties in terms of surface area, thermal conductivity, porosity, particle size, permeability than other siliceous sedimentary rocks. Due to these properties, preparation of composite materials containing polypropylene and diatomite with better properties was considered in the study. Furthermore, the surface of diatomite particles was modified by cetyltrimethylammonium bromide (CTAB). Composite materials were formed by mixing diatomite and modified diatomite samples with polypropylene at a weight percentage range from 0 to 30 %. The prepared composites were made into films or strips by melt blending using a designed single screw extruder. The characterizations of the samples were carried out with Fourier transform infrared spectroscopy with an attenuated total reflectance (FTIR-ATR), thermogravimetric analysis (TGA), and scanning electron microscope (SEM) devices. In addition, tensile strength tests of composite materials were conducted in accordance with ASTM D882 standards.

\*Corresponding author: E-mail: [ozkandemirbas@gmail.com](mailto:ozkandemirbas@gmail.com);

**Keywords:** Polymer; extrusion; modification; surfactant; clay; ASTM D882.

## 1. INTRODUCTION

Polypropylene (PP) has been used extensively in many sectors of the industry. The main reason for the frequent use of polypropylene is low cost, easy processing and high performance. These sectors include automotive, rubber and plastic, household and garden products, packaging [1]. However, restrictions have been placed on the use of polypropylene in some sectors. In the literature, composites of polypropylene were synthesized with many fillers in order to improve the mechanical properties and reduce the production costs. In the literature, considerable improvements have been achieved on the physical and mechanical properties of polymers by filling them with additives such as CaCO<sub>3</sub> [2-5], talc [6], mica [7], kaolin [8], montmorillonite [9], layered silicate [10].

The natural appearance of diatomite is a soft rock-like. It consists of the remains of various single-cell microscopic plants known as diatoms. Diatomites are amorphous with their hydrated silica content as the main component and may contain impurities in various quantities such as silica sand, clay, metal salts and organic matter. Diatomite has superior properties in terms of surface area, thermal conductivity, porosity, particle size, permeability than other siliceous sedimentary rocks [11].

In this study, binary mixtures were formed at different mass ratios between diatomite, CTAB modified diatomite and polypropylene. The prepared binary mixtures were made into thin films or strips using laboratory-type extruder devices. Meanwhile, the laboratory-type extruder devices used in this study are designed by Dr. Özkan Demirbaş, University of Balıkesir, Turkey. In addition, the characterization of the obtained thin films or strips was carried out using the FTIR, SEM, TGA and mechanical test devices.

## 2. MATERIALS AND METHODS

### 2.1 Materials

Polypropylene used as a matrix for the preparation of thin films was purchased from PETKIM Co., TR. Diatomite, a component of composite materials, was purchased from producers who traded commercially for diatomite. Prior to use in this study, grinding and sieving were performed to bring the particle size of the

diatomite to a range of 45-109 µm. The molecular structure of cetyltrimethylammonium bromide (CTAB), obtained from Merck (purity >99%, M<sub>w</sub>: 364.45 g mol<sup>-1</sup>), for use in the modification process is given in Fig. 1.

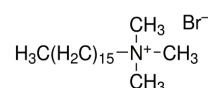
### 2.2 Modification of Diatomite with CTAB

First, master CTAB solution with concentration of 12.5 g/L (about 0.034 M) was prepared by uniformly adding CTAB powder to the deionized water and mixing via the magnetic stirrer for 2 h. Then, lower CTAB concentrations were attained by appropriate dilution of master CTAB concentration (12.5 g/L) using deionized water [12]. 10<sup>-2</sup> M CTAB solution was prepared from master CTAB solution and shaken with 5 g of the dried diatomite mineral for 3 h at 45°C using a shaker water bath. After 60 minutes, the solid particles were separated by centrifugation from the suspension and then filtered. Filtered particles were washed with 500 ml of 1:1% volume of deionized water and methanol in order to remove any impurity. Furthermore, the solid particle, modified diatomite (MD), was dried in oven at 80°C for overnight.

### 2.3 Preparation of Composites Films

All samples used in the preparation of the composite films were dried at 80 C for 4 hours before the experimental procedure. PP was added to the composite materials such that the percentages of D or MD samples in the mixture were 0-30%. The prepared mixtures were pressed at 170-220°C using single screw extruder to form melts suitable for film formation. Immediately after the pressing process, these melted mixtures were made into thin films or strips by means of the apparatus attached to the end of the extruder.

The laboratory-type extruder devices and their parts used in this work are designed by Dr. Özkan Demirbaş, University of Balıkesir, Turkey. However, other works in the production stage of extruder (CNC lathe, welding, montage etc.) have been made by various firms. Schematic and original views of the designed extruders are shown in Figs. 1 and 2.



**Fig. 1. The molecular structure of CTAB**

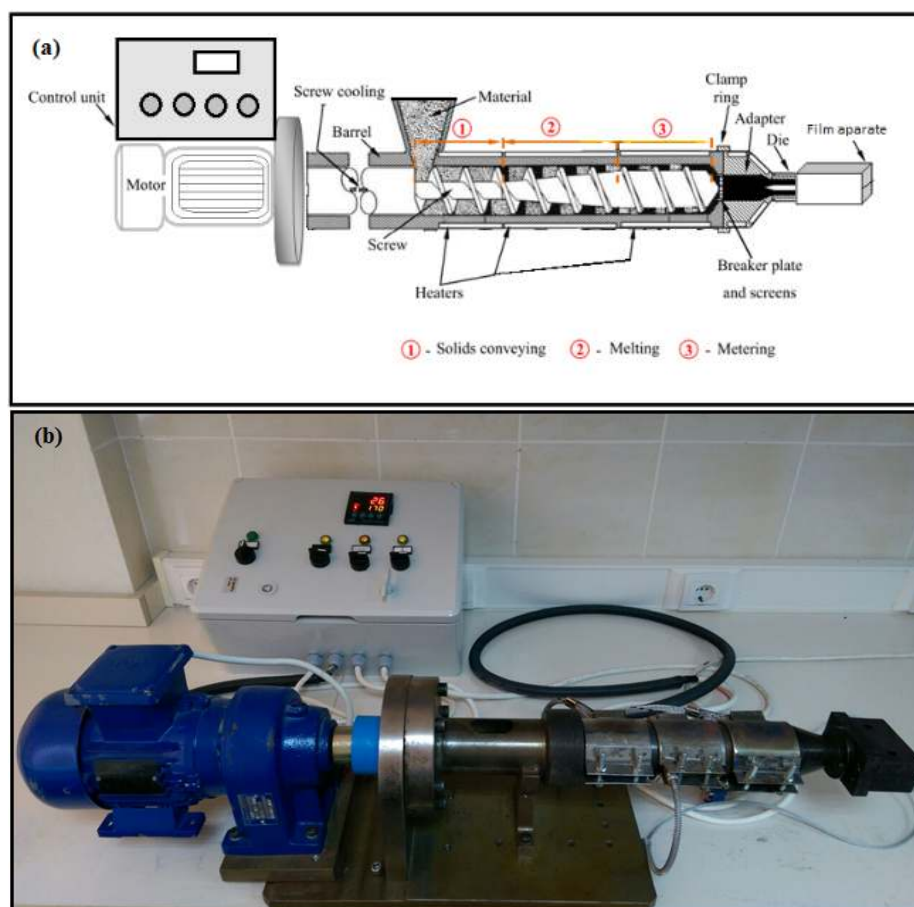


Fig. 2. Schematic (a) and original (b) images of one of the designed extruders

## 2.4 Characterizations and Tests of the Composite Films

Characterization of synthesized composite films or strips in the study was carried out using FTIR-ATR, TGA and SEM instruments. The morphology of the surface of the films was examined by Hitachi's scanning electron microscope. Fourier transformation infrared spectra (FTIR-ATR) were recorded with a Perkin Elmer FTIR spectrometer attached to ATR apparatus. Thermal gravimetric analysis (TGA) of the film samples used in the experiments was performed using a Perkin Elmer instrument. Diatomite and modified diatomite of composite loadings were ranged from 0, 1, 2.5, 5, 7.5, 10, 15, 20 and 30 wt%. The prepared composites was melt blended with in a single screw extruder. The melted composites were made into film strips using the apparatus attached to the end of the extruder. Strip form specimens were cut from the films and strained at a rate of 120 mm/min at

room temperature. A Universal Testing Machine Zwick / Roell was used to determine the tensile properties of the film samples according to ASTM D882 standard.

## 3. RESULTS AND DISCUSSION

### 3.1 FTIR Spectra of the Samples

The FTIR-ATR spectra of PP, D, CTAB, MD and their composite films used and synthesized in this study are observed in Fig. 4. In Fig. 4, peaks of  $-\text{CH}_2$ ,  $-\text{CH}_3$  bending and C-C stretching are observed at  $1455.73$ ,  $1375.60$  and  $1167.22 \text{ cm}^{-1}$ , respectively, from the FTIR spectrum of PP. In the same figure, peaks of  $-\text{OH}$  bending, Si-O-Si and OH vibrations are observed at  $1634$ ,  $1023$  and  $795 \text{ cm}^{-1}$ , respectively, from the FTIR spectrum belonging to the diatomite [13]. Characteristic peaks at  $2918.8$  and  $2850.6 \text{ cm}^{-1}$  in the FTIR spectrum of CTAB are due to the bending of  $-\text{CH}_2$  and  $-\text{CH}_3$  in the structure.

However, from the spectrum of CTAB, values of 2850-2950, 1450-1490, and 900-950  $\text{cm}^{-1}$  are C–H stretching vibration, methylene scissoring vibration and asymmetric bending mode of the head  $[\text{N}(\text{CH}_3)_3]$  methyl group, and C–N stretching vibration, respectively. Characteristic peaks of both CTAB and diatomite (such as 2918.5, 2850.6 and 1015.3 etc.) are observed in the CTAB-modified diatomite (MD) spectrum. These observed peaks may mean that there are some interactions between CTAB and diatomite. In addition to the above, the spectra of composite films between D and PP appear at increasing mass ratios in Fig. 4. These are indicated by the D/PP symbol. The most conspicuous feature of the D/PP spectra is the increase in peak intensities of Si–O–Si vibrations in the range of 1018-1045  $\text{cm}^{-1}$  when the amount of D in the composite increases. Finally, the MD/PP spectrum in Fig. 4 is quite similar to the D/PP spectra. This spectrum shows the presence of interactions between MD and PP.

### 3.2 Thermal Properties

As seen in Fig. 5, the thermal gravimetric analyses of PP, D/PP and MD/PP were measured by thermal gravimetric analyser (TGA). From the TGA curves of a representative sample, we conclude that:

- In the temperature range from 25°C to 105°C, the weight loss due to absorbed

water are 3.1 % for PP, 4.8 % for D/PP and 5.0 % for MD/PP.

- It can be observed from the profiles of the TGA curves, both D/PP and MD/PP are practically similar. As illustrated in Fig. 5 curves, there are two weight loss stages at room temperature –350°C and 350 – 550°C, respectively. For the PP, D/PP and MD/PP, the first stage is attributed to the absorbed and structural water; the second stage is assigned to the decomposition of PP.

As a result, it is observed in Fig. 5 that the thermal gravimetric curve of neat polypropylene has nearly zero mass loss at around 550°C. Here, we can talk about the decomposition of the polymer, which is almost completely burned up to this temperature. Similarly, large mass losses in the D/PP and M/DP curves are due to the decomposition of the PP in the composite [14].

### 3.3 Morphological Analysis

Fig. 6 shows SEM images of neat polypropylene and 2.5 wt. % D/PP and MD/PP composites. From these SEM images, some information about the morphological properties and fractures of composite materials can be obtained. There are two cases in the literature regarding the fracture of composites. These are ductile fractures and brittle fractures [15]. In Fig. 6, although the surface of polypropylene appears

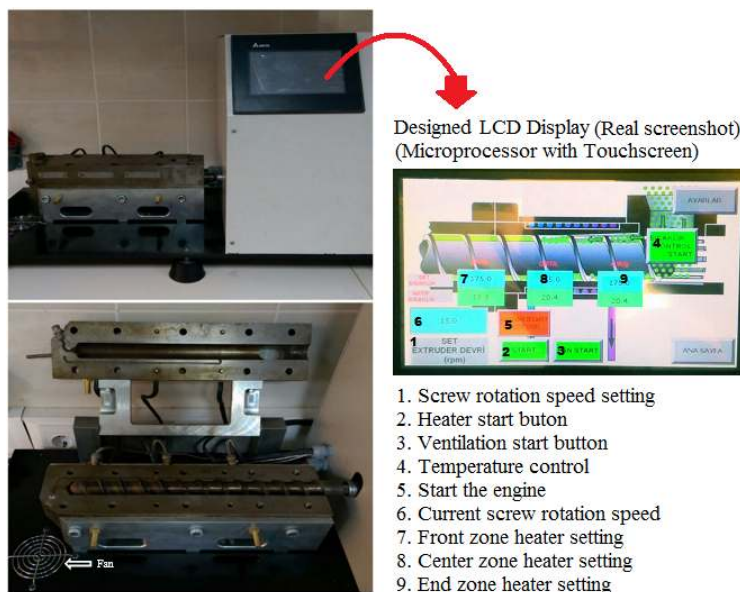


Fig. 3. Images of the second of the designed extruders and its LCD display

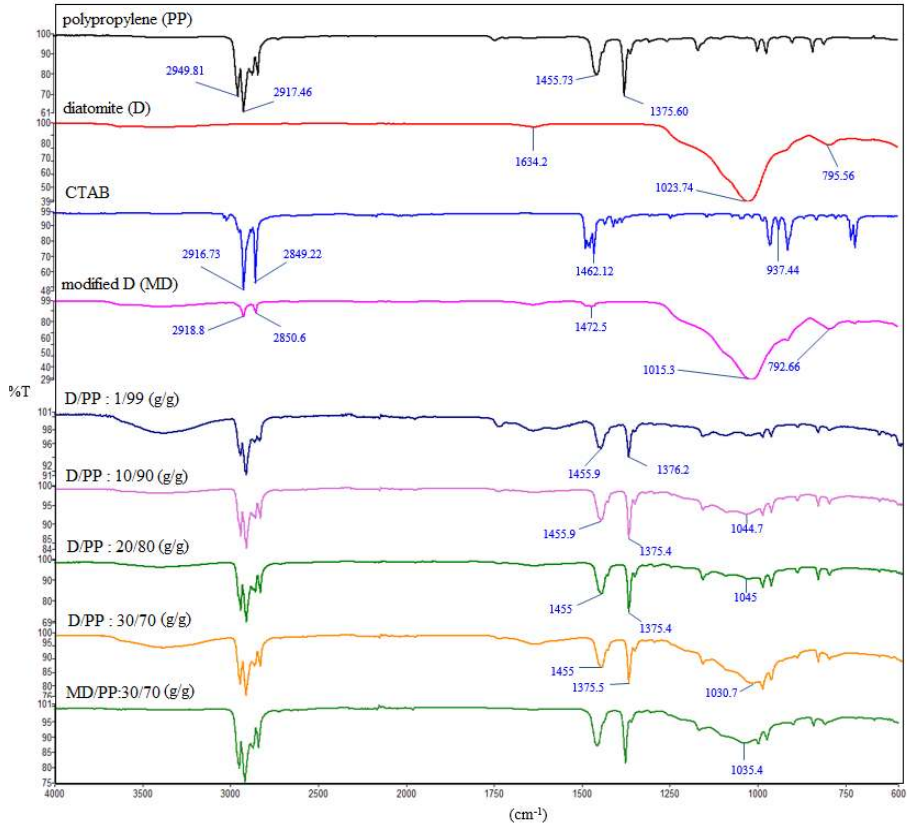


Fig. 4. FTIR spectra of PP, D, CTAB, MD, and composite films

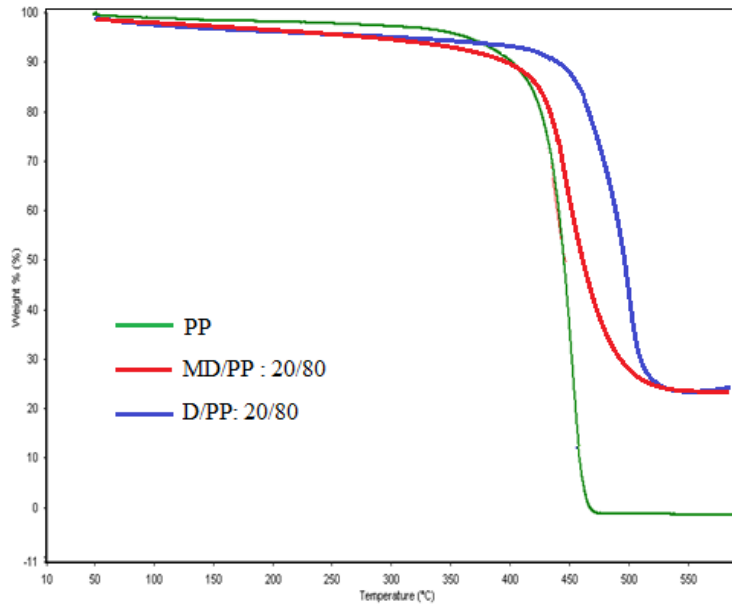


Fig. 5. TGA curves of some synthesized composite films

smooth, the surface of the D/PP composite appears rigid and brittle. In the SEM image, on the surface of the MD/PP composite, small-wave-like shapes and a few MD particles are

seen. These small wave-like shapes and MD particles on the surface absorb the energy applied to the deformation and fracture of the composite structure [15]. Thus, the tensile strength of the composite increases and the mechanical properties are improved.

### 3.4 Mechanical Properties

Fig. 7a and b show the effect of tensile strength on the amount of D and MD added to the polymer matrix, respectively. From Fig. 7a and b, it was observed that when MD was added to polypropylene matrix, tensile strength of

composite increased more than D. One of the reasons for this is related to the fracture properties of the composites as mentioned in the SEM morphology. The formation of stronger bonds such as interactions of apolar groups between MD and polypropylene molecules increases the tensile strength of the composite. It can be said that the apolar interaction is caused by the interaction of polymer molecules with CTAB, which is a modifier substance in the composite structure. There are some studies in the literature about mechanically good properties of composites prepared with modifier materials [15-17].

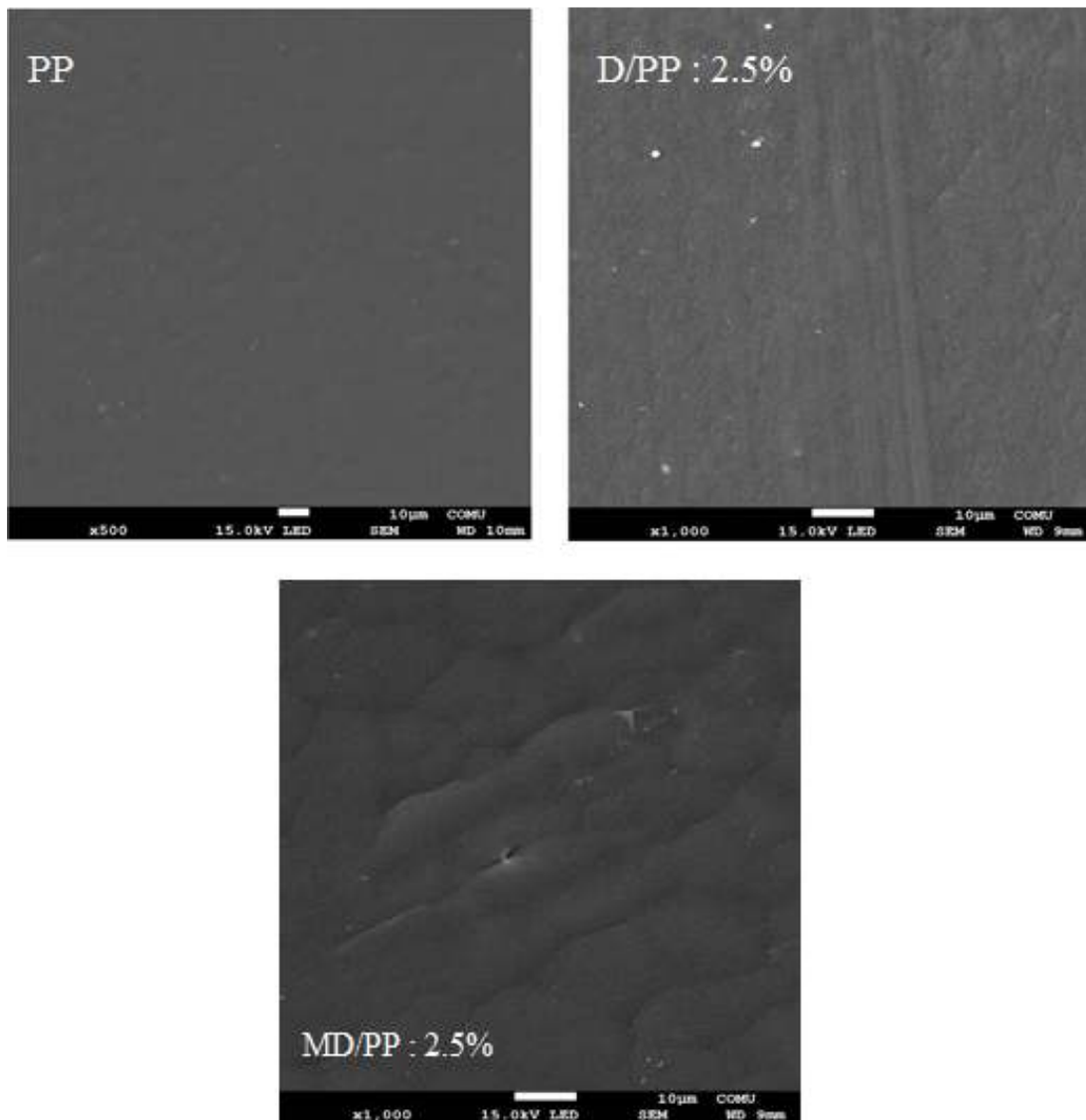
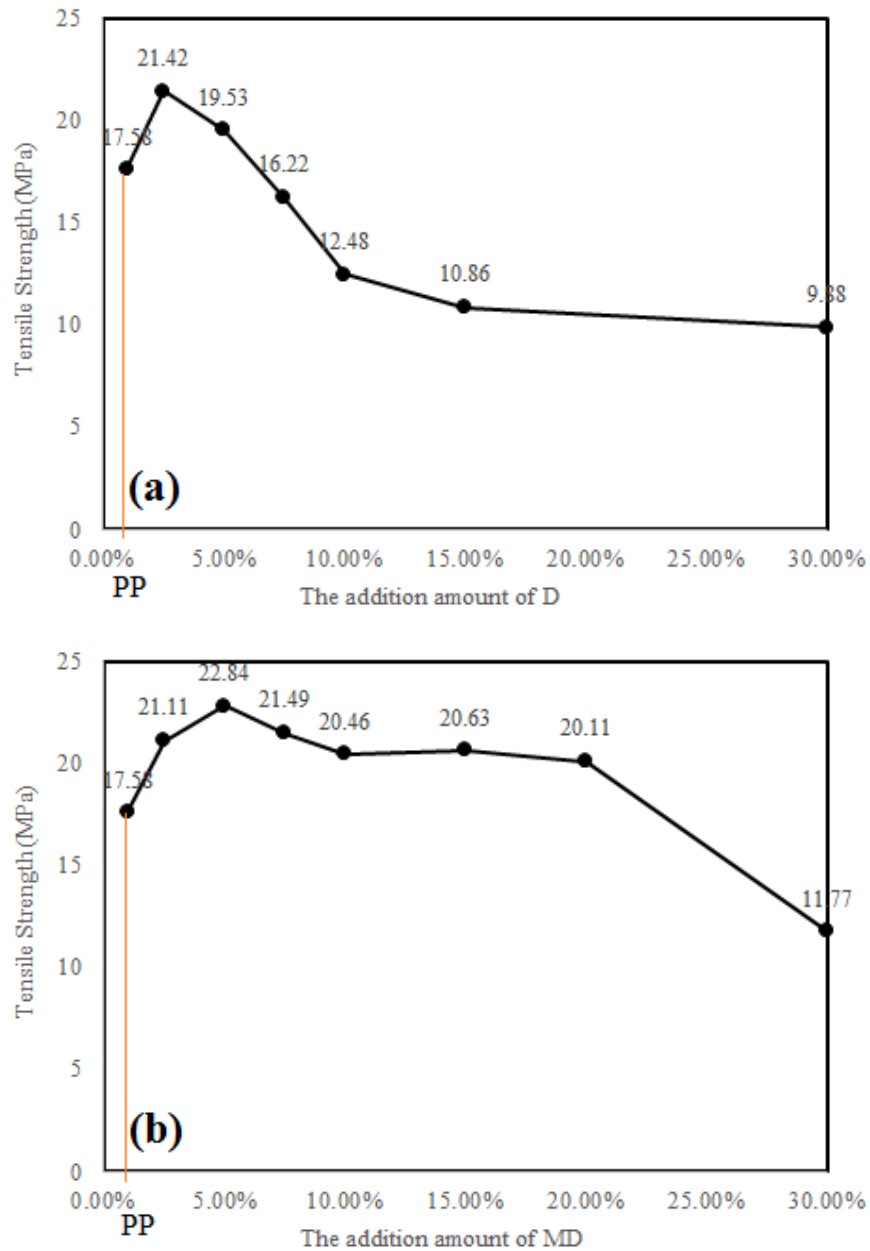


Fig. 6. The SEM images of some synthesized composite films



**Fig. 7. The variations of tensile strengths versus weight percentages of synthesized composite films**

**4. CONCLUSIONS**

The significance of this study is summarized with the following conclusions:

- In the present study, PP was one of the composite components and was selected as a matrix, while D and MD were selected as fillers.
- CTAB has been modified to the diatomite surface for use in composite materials. Thus, the effect of the modification on the characterization of composite materials was investigated.
- Laboratory-type extruders and apparatus were designed for use in similar studies, and their schematic and original images were shown in Figs. 2 and 3.

- The FTIR-ATR spectra of PP, D, CTAB, MD and their composite films used and synthesized in this study are observed in Fig. 4.
- According to Fig. 4, it was seen that polypropylene (PP) interacted with CTAB modified diatomite (MD) in the composites.
- It was observed in Fig. 5 that the thermal gravimetric curve of neat polypropylene has nearly zero mass loss at around 550°C. Similarly, large mass losses in the D/PP and M/DP curves were due to the decomposition of the PP in the composite
- In the SEM image, on the surface of the MD/PP composite, small-wave-like shapes and a few MD particles were seen. These small wave-like shapes and MD particles on the surface would absorb the energy applied to the deformation and fracture of the composite structure.
- Finally, the tensile test results were discussed in accordance with the morphology of the composites. From the Fig. 7a and b, the highest tensile strength value of all composites was found to be 22.84 MPa for 2.5 % MD/PP sample.

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

## REFERENCES

1. Rimdusit S, Smittakorn W, Jittarom S, and Tiptipakorn S. Highly filled polypropylene rubber wood flour composites. *Eng. J.* 2011;15(2):17–30.
2. Sadeghi M, Esfandiari A. The effects of micro and Nano CaCO<sub>3</sub> on the rheological and physico/mechanical behavior of an SBS/ CaCO<sub>3</sub> composite. *Mater. Sci. Technol.* 2012;46(6):695-703.
3. Zhang Z, Wang C, Meng Y, Mai K. Synergistic effects of toughening of nano-CaCO<sub>3</sub> and toughness of β-polypropylene. *Compos. Part A: Appl. Sci. Manuf.* 2012; 43(1):189-197.
4. Zuiderduin WCJ, Westzaan C, Huétink J, Gaymans RJ. Toughening of polypropylene with calcium carbonate particles. *Polymer.* 2003;44:261-275.
5. Eteläaho P, Haveri S, Järvelä P. Comparison of the morphology and mechanical properties of unmodified and surface-modified nanosized calcium carbonate in a polypropylene matrix. *Polym. Compos.* 2011;32:464-471.
6. Rotzinger B. Talc-filled PP: A new concept to maintain long term heat stability. *Polym. Degrad. Stab.* 2006;91:2884–2887.
7. Parvaiz MR, Mahanwar PA, Mohanty S, Nayak SK. Morphological, mechanical, thermal, electrical and rheological properties of polycarbonate composites reinforced with surfaces modified mica. *J. Miner. Mater. Charact. Eng.* 2010;9(11): 985-996.
8. Ariffin A, Mansor AS, Jikan SS. Mechanical, morphological, and thermal properties of polypropylene / kaolin composite. Part I. The effects of surface-treated kaolin and processing enhancement. *J. Appl. Polym. Sci.* 2008; 108(6):3901-3916.
9. Mittal V. Polypropylene-layered silicate nanocomposites: filler matrix interactions and mechanical properties. *J. Thermoplast. Compos. Mater.* 2007;20: 575–599.
10. Esfandiari A, Nazokdast H, Rashidi AS, Yazdanshenas ME. Review of polymer – Organoclay nanocomposites. *Journal of Applied Sciences.* 2008;8:545-561.
11. Lemonas JF. Diatomite. *Am. Ceram. Soc. Bull.* 1997;76:92–95.
12. Moslemizadeh A, Aghdam SK, Shahbazi K, Aghdam HK, Alboghobeish F. Assessment of swelling inhibitive effect of CTAB adsorption on montmorillonite in aqueous phase. *Applied Clay Science.* 2016;127–128:111–122.
13. Iliä IK, Stamatakis MK, Perraki TS. Mineralogy and technical properties of clayey diatomites from north and central Greece. *Cent. Eur. J. Geosci.* 2009;1:393-403.
14. Sun T, Dong X, Du K, Wang K, Fu Q, Han CC. Structural and thermal stabilization of isotactic polypropylene/ organo-montmorillonite/poly(ethylene-co-octene) nanocomposites by an elastomer component. *Polymer.* 2008;49:588–598.
15. Aguilar H, Yazdani-Pedram M, Toro P, Quijada R, Ángel M, Machado L. Synergic effect of two inorganic fillers on the mechanical and thermal properties of hybrid polypropylene composites. *J. Chil. Chem. Soc.* 2014;59(2):2468-2473.



16. Demirbaş Ö. Synthesis and characterization of polymeric composite films by designed extruders. International Journal of Engineering and Applied Sciences. 2016;3(11):104-107.
17. Kumar R, Dhaliwal DS, Kapur GS, Shashikant. Mechanical properties of modified biofiller-polypropylene composites. Polymer Composites. 2013; 35(4):708-714.

© 2016 Demirbaş and Ulus; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

*Peer-review history:*

*The peer review history for this paper can be accessed here:  
<http://sciencedomain.org/review-history/17428>*