

Synthesis and Characterization of Polypropylene and CTAB Modified Diatomite Composites

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.

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_3 [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. Material 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_w : 364.45 g mol^{-1}), 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^{-2} 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.

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 -CH_2 , -CH_3 bending and C-C stretching are observed at 1455.73, 1375.60 and 1167.22 cm^{-1} , respectively, from the FTIR spectrum of PP. In the same figure, peaks of -OH bending, Si-O-Si and OH vibrations are observed at 1634, 1023 and 795 cm^{-1} , respectively, from the FTIR spectrum belonging to the diatomite [13]. Characteristic peaks at 2918.8 and 2850.6 cm^{-1} in the FTIR spectrum of CTAB are due to the bending of -CH_2 and -CH_3 in the structure. However, from the spectrum of CTAB, values of 2850-2950, 1450-1490, and 900-950 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 Figure 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 cm^{-1} when the amount of D in the composite increases. Finally, the MD/PP spectrum in Figure 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 $^{\circ}\text{C}$ to 105 $^{\circ}\text{C}$, 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 $^{\circ}\text{C}$ and $350 - 550$ $^{\circ}\text{C}$, 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 Figure 5 that the thermal gravimetric curve of neat polypropylene has nearly zero mass loss at around 550 $^{\circ}\text{C}$. 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

Figure 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 Figure 6, although the surface of polypropylene appears 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

Figures 7(a) and (b) show the effect of tensile strength on the amount of D and MD added to the polymer matrix, respectively. From Figure 7(a) 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].

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 Figures 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 Figure 4, it was seen that polypropylene (PP) interacted with CTAB modified diatomite (MD) in the composites.
- It was observed in Figure 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 Figures 7(a) and (b), the highest tensile strength value of all composites was found to be 22.84 MPa for 2.5 % MD/PP sample.

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FIGURES

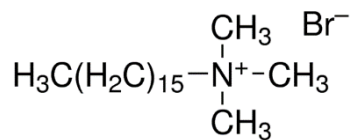


Figure 1. The molecular structure of CTAB

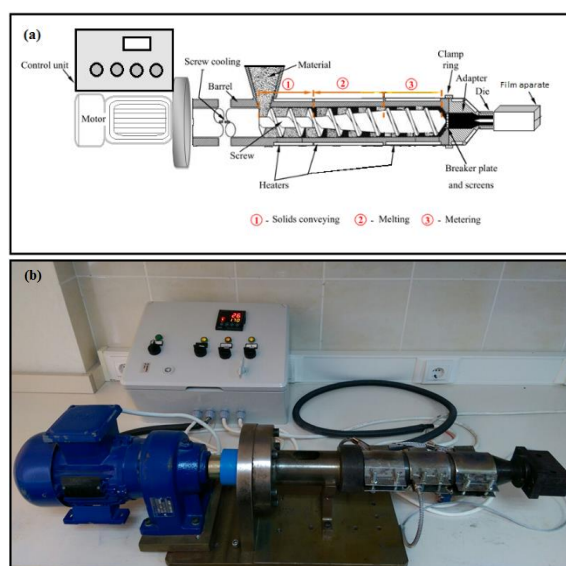


Figure 2. Schematic (a) and original (b) images of one of the designed extruders.

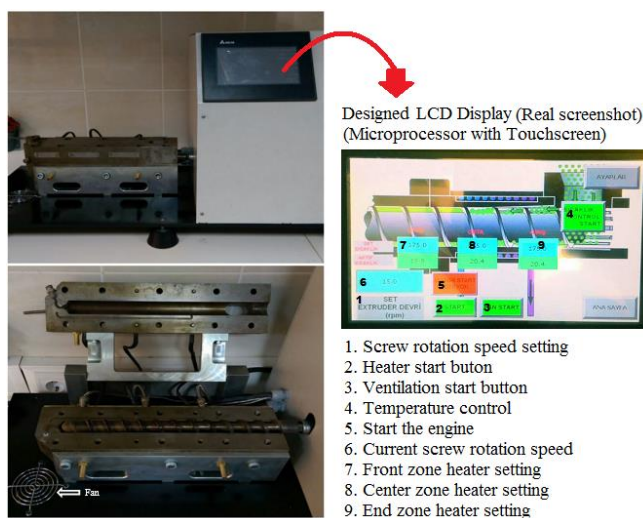


Figure 3. Images of the second of the designed extruders and its LCD display.

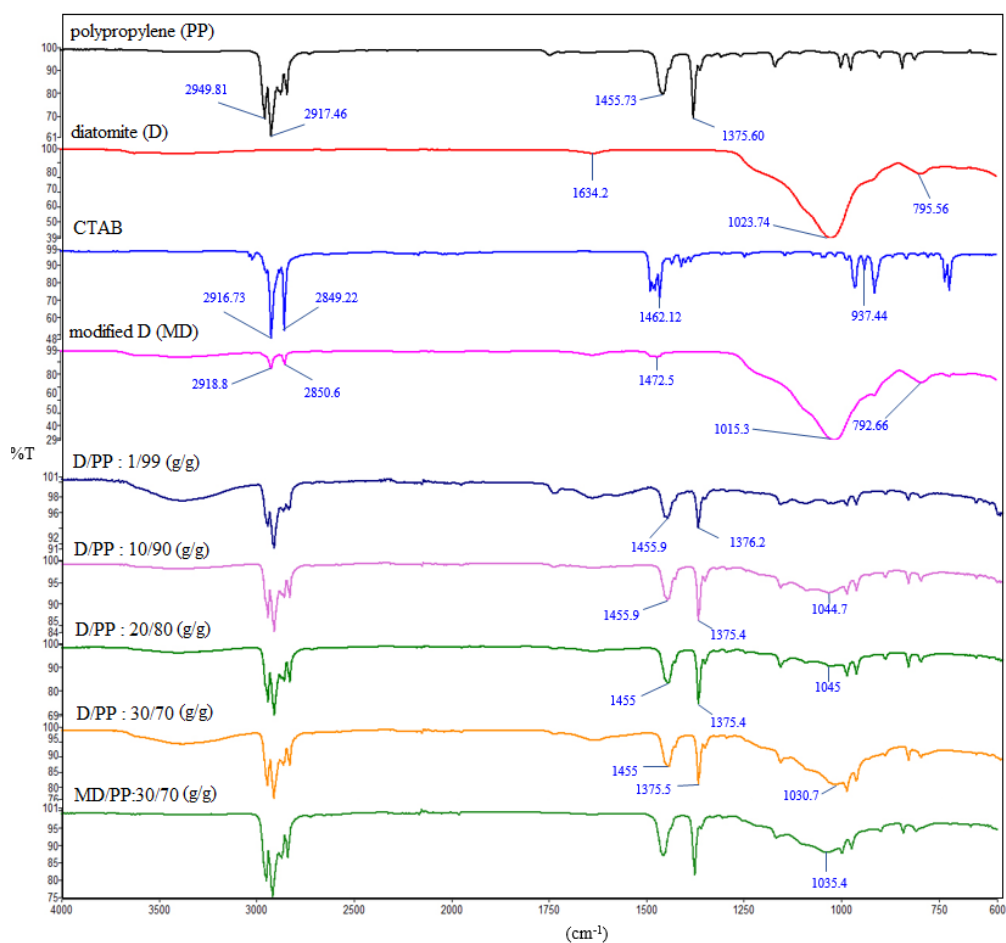


Figure 4. FTIR spectra of PP, D, CTAB, MD, and composite films

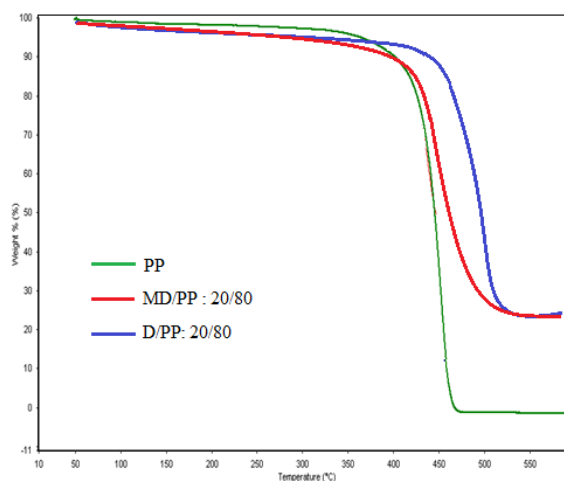


Figure 5. TGA curves of some synthesized composite films

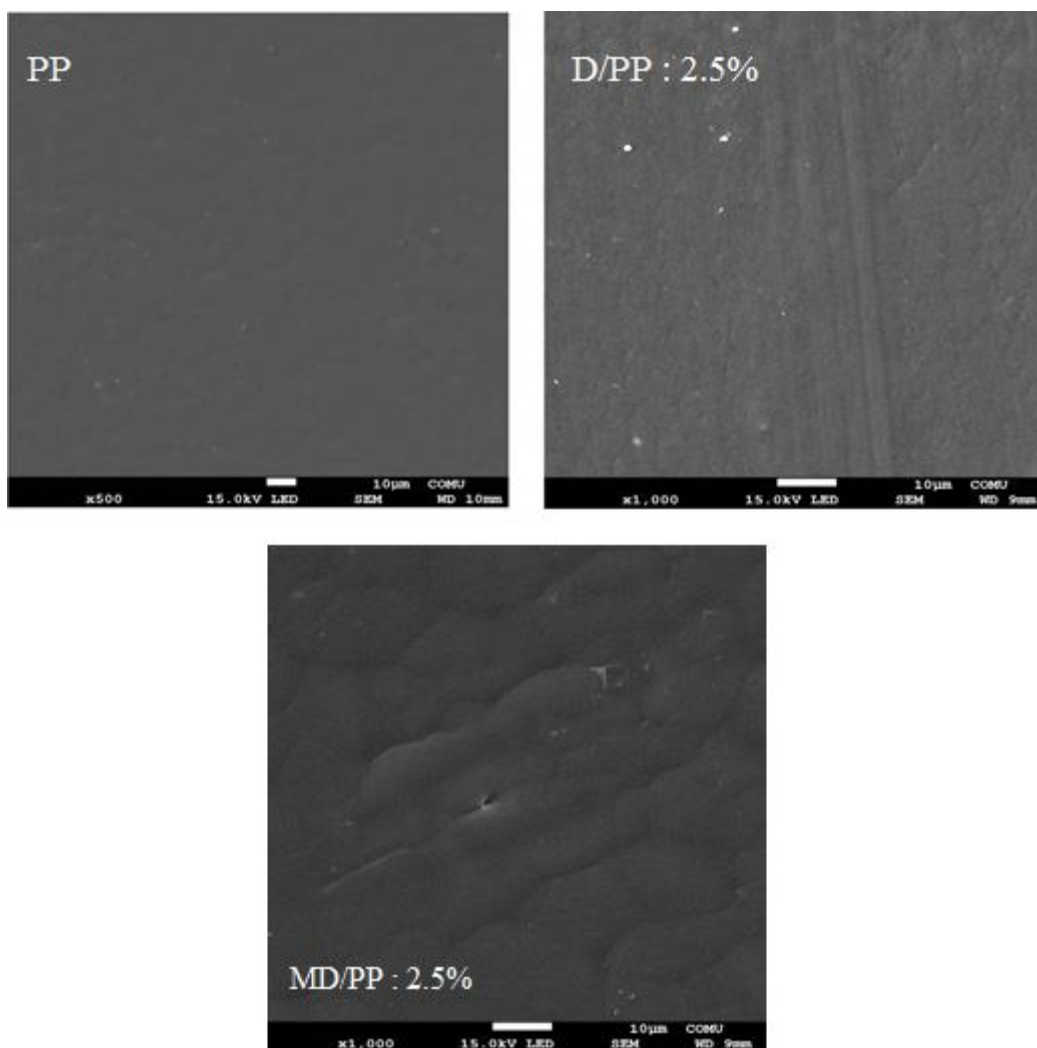
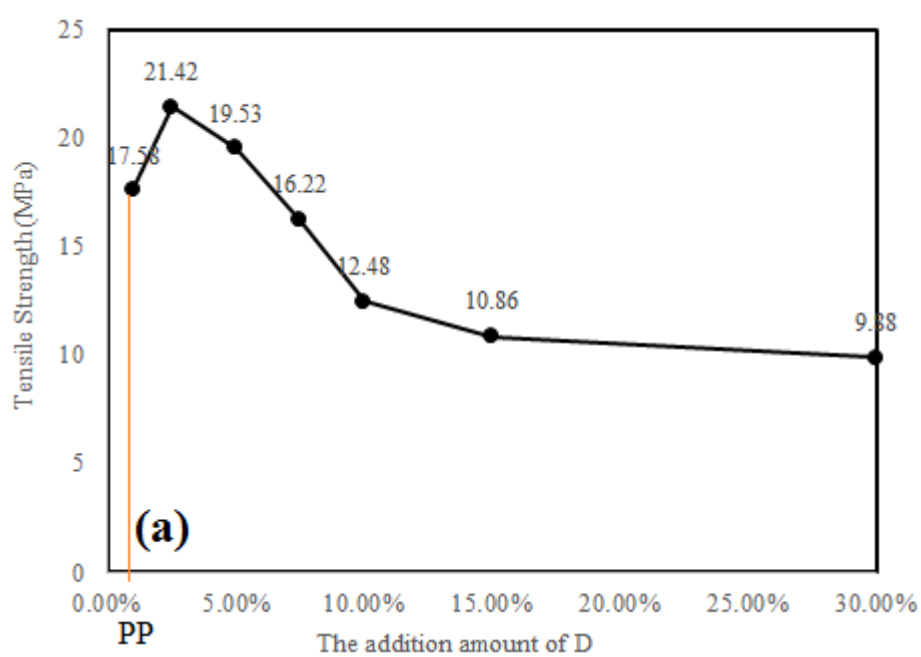


Figure 6. The SEM images of some synthesized composite films



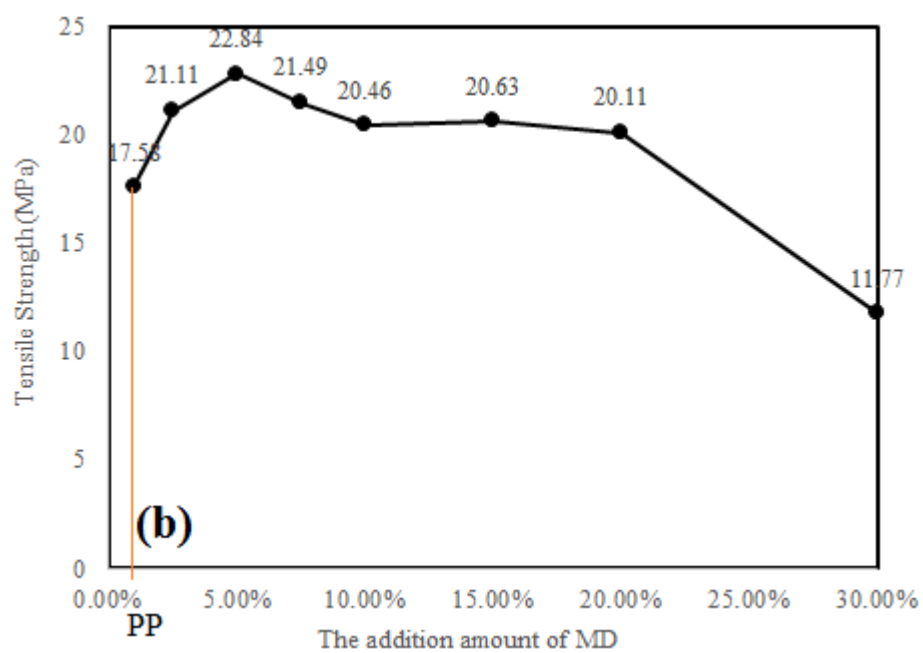


Figure 7. The variations of tensile strengths versus weight percentages of synthesized composite films.