

Synthesis and Characterization of Polypropylene and CTAB Modified Diatomite Composites

Abstract

Polypropylene (PP) is extensively used in many industrial areas due to its good performance and processing properties as well as low cost. Diatomite (D) is a siliceous sedimentary rock. It has high porosity, high permeability, small particle size, large surface area and low thermal conductivity. 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) and the diatomite and modified diatomite (MD) filled polypropylene composites (D/PP and MD/PP) with a weight percentage range of the filler from 0 to 30% were prepared by means of melt blending in a designed single-screw extruder. The characterizations of the composite films synthesized by the laboratory type extruder were performed 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 were also performed for the mechanical properties of the synthesized films.

Keywords: Polypropylene, Characterization, Composite, Diatomite, Extruder, CTAB

1. Introduction

Polypropylene is one of the most commonly used polymers in many sectors such as automobile, household goods, packaging and electronic appliance properties applications due to its good performance and processing properties as well as low cost [1]. However, the use of polypropylene in the some industry is limited under certain circumstances. In the literature, composites of polypropylene were synthesized with many fillers in order to improve the mechanical properties and reduce the production costs. For this purpose, the physical and

mechanical properties of polymers are being greatly improved by filling with rigid inorganic additives, such as CaCO_3 [2-5], talc [6], mica [7], kaolin [8], montmorillonite [9] and layered silicate [10].

30

Diatomite in its natural state is a soft rocklike material consisting essentially of the skeletal remains of a variety of single celled microscopic plants known as diatoms. They are generally amorphous, hydrated or opaline silica, $\text{SiO}_2 \cdot n\text{H}_2\text{O}$, with various amounts of impurities such as silica sand, clay minerals, metal salts and organic matter. Diatomite is a low-cost, environment-friendly and natural micro/nanostructured material derived from sedimentary silica, and has cylindrical and plate morphologies with well-developed mesoporous/macroporous structures [11].

37

In this study, the diatomite was modified with cetyltrimethylammonium bromide (CTAB) and mixed with polypropylene at different mass percentages. Thin films were synthesized with the prepared mixtures by using designed laboratory type of extrusion machines. Meanwhile, the laboratory type of extrusion machines used for the preparation of composite films have been designed and manufactured by Özkan Demirbaş. Characterization of the synthesized films was performed using FTIR, SEM, TGA, and mechanical test devices.

43

2. Material and Methods

45

Materials

Polypropylene (PP) used as a matrix material in the synthesis of composite film is supplied from PETKİM Co., Turkey. The diatomite used as a filler material is of analytical purity and is obtained from commercially sold companies. The particle size of the diatomite was reached to 45-109 μm by grinding and sieving. Cetyltrimethylammonium bromide (CTAB) was purchased from Merck and its molecular structure was given in Figure 1.

52

Modification of Diatomite with CTAB

10^{-2} M CTAB solution was prepared 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.

Preparation of composites

Before mixing, PP and diatomite (D) and MD samples were dried at 80 °C for 4 h and then cooled to room temperature in a desiccator. After mixing at different mass percentages (0-30%), the PP with D and MD samples were combined in a single-screw extrusion apparatus. The mixture was carried out at a temperature range of 170-220 °C and a screw speed of 15 rpm.

The laboratory type extrusion devices and their parts used for preparing composite films are shown in Figure 2 and 3. Design of these original laboratory-type-extruders were made by Ö. Demirbaş. However, other works in the production stage of extruder (CNC lathe, welding, montage etc.) have been made by various firms.

Characterization and Tests

The characterizations of the composite films synthesized by the laboratory type extruders were performed with FTIR, TGA, and SEM devices. The morphologies of samples were observed in scanning electron microscopy (SEM) of Hitachi. Fourier transform infrared (FTIR) spectra were recorded on a Perkin Elmer FTIR spectrometer using ATR device. The Thermo-Gravimetric analysis (TGA) was obtained simultaneously using a Perkin Elmer instrument. Tensile strength tests were also performed for the mechanical properties of the synthesized films. A mechanical test was conducted according to the ASTM standard.

3. Results and Discussion

FTIR Spectra

Figure 4 shows the FTIR spectra of PP, D, CTAB, MD, and their composite films. As seen in Figure 4, spectrum of PP, values of 1455.73, 1375.60, and 1167.22 cm⁻¹ are -CH₂ bending, -CH₃ bending, and C-C stretching, respectively. From Figure 4, spectrum of diatomite, the band at ~1634 cm⁻¹ is due to OH bending vibrations of adsorbed water in sheet silicate minerals. The ~ 1023 cm⁻¹ band arises from the Si-O-Si vibration. The ~795 cm⁻¹ band occurs because of the OH translational vibration [12]. 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 [N(CH₃)₃] methyl group, and C-N stretching vibration,

87 respectively. The CTAB modified diatomite (MD) spectrum has characteristic peaks both CTAB and diatomite.
 88 This spectrum may show that CTAB interacts with diatomite. The peaks of the FTIR spectra of the D/PP
 89 composite films prepared from 1% to 30% by weight (w/w) are -CH₂ and -CH₃ bending at about 1455 and 1375
 90 cm⁻¹, respectively, Si-O-Si vibrations of diatomite were observed at 1030.27 cm⁻¹. As the amount of D in the
 91 D/PP composites increases, the peaks of the Si-O-Si vibrations (in the range of 1018-1045 cm⁻¹) naturally
 92 become more apparent in the FTIR spectra. The spectrum of MD/PP composite film is similar to that of D/PP
 93 (ratio of 30/70) composite film. However, in the MD/PP spectrum, characteristic peaks of CTAB were observed
 94 in the range of 650-750 cm⁻¹. This result indicates the presence of interaction between MD and PP in the
 95 composite films.

96 ***Thermal Properties***

97 Thermogravimetric analysis (TGA) was used to study the thermal stability of the samples. Figure 5 shows the
 98 weight loss temperature curves (TGA) of PP and containing either D or MD. According to the thermal behavior
 99 observed for these composites the decomposition mechanism could be attributed principally to the
 100 functionalization process of PP occurring in one step located around 400-550°C. The polar organic compound
 101 present in modifier and the MD could be the principal decomposition events to explain the thermal stability of
 102 composites. In the case of PP the thermal degradation is known to occur principally by a random scission
 103 mechanism [13].

104 ***Morphological analysis***

105 Figure 6 displays respectively the SEM images of PP, D/PP, MD/PP systems with mass fraction of the fillers.
 106 There are two fracture modes in polymeric composites: ductile fracture and brittle fracture. The neat PP belongs
 107 to a typical brittle fracture, where the fracture section was flat [14]. In Figure 6, the SEM image of neat
 108 polypropylene film looks smooth. The surfaces of D/PP composite films are rough and brittle. However, the
 109 SEM image of a 2.5% MD/PP composite films looks like small waves. In addition, particles of modified
 110 diatomite are observed onto composite surface. These small waves and particles will absorb relevant impact
 111 deformation energy or fracture energy, leading to improving obviously the impact fracture toughness of the
 112 composite systems.

113 ***Mechanical Properties***

114 In this study, the variation of the mass percentages of the filler materials (D or MD) versus the tensile strengths
 115 of the PP, D / PP and MD / PP composite films synthesized is shown in Figure 7 (a) and (b). The tensile strength
 116 of MD-filled composites at lower percentages is slightly greater than that of D-filled composites. The reason of

this, the poor adhesion between D filler and the polymer may be the major reason for the poor tensile strength performance and created weak interfacial regions, resulting in debonding and frictional pullout. However, in low percentages, especially 2.5%, the maximum tensile strength was tested for the composite film between CTAB modified diatomite (MD) and polypropylene (see Figure 7b). We can explain the reason for this situation by having stronger interactions between MD and polymer. The decrease in the polymer matrix content in the composite as a function of the filler content was also responsible for the low tensile strength.

CONCLUSIONS

In this study, polypropylene (PP) used as a matrix material in the synthesis of composite film. The diatomite was modified with CTAB and mixed with polypropylene at different mass percentages. Thin films were synthesized with the prepared mixtures by using laboratory type of extrusion machines. Characterization of the synthesized films was performed using FTIR, SEM, TGA and mechanical test devices. FTIR spectra show that diatomite is modified with CTAB, polypropylene is interacting with diatomite and MD. Thermal analyzes indicate that the thermal stability of the composite specimens increases at least. SEM images showed that the surface morphology of the composite films changed. Finally, from the mechanical test results, the highest tensile strength was found to be 22.84 MPa for MD films at 2.5% (w/w). As a result, diatomite and BC modified diatomite fillers were shown to be usable with polypropylene matrices.

REFERENCES

- [1] S. Rimdusit, W. Smittakorn, S. Jittarom, and S. Tiptipakorn. (2011). Highly filled polypropylene rubber wood flour composites. *Eng. J.* 15(2), 17–30.
- [2] M. Sadeghi and A. Esfandiari. (2012). The Effects of Micro and Nano CaCO_3 on the Rheological and Physico/Mechanical Behavior of an SBS/ CaCO_3 Composite. *Mater. Sci. Technol.* 46(6), 695-703.
- [3] Z. Zhang, C. Wang, Y. Meng, K. Mai. (2012). Synergistic effects of toughening of nano- CaCO_3 and toughness of β -polypropylene. *Compos. Part A: Appl. Sci. Manuf.* 43 (1), 189-197.
- [4] W. C. J. Zuiderduin, C. Westzaan, J. Huétink, and R. J. Gaymans. (2003). Toughening of polypropylene with calcium carbonate particles. *Polymer*, 44, 261-275.
- [5] P. Eteläaho, S. Haveri, and P. Järvelä. (2011). Comparison of the Morphology and Mechanical Properties of Unmodified and Surface-Modified Nanosized Calcium Carbonate in a Polypropylene Matrix. *Polym. Compos.* 32,464-471.

- [6] B. Rotzinger. (2006). Talc-filled PP: a new concept to maintain long term heat stability. *Polym. Degrad. Stab.* 91, 2884–2887.
- [7] M. Rahail Parvaiz, P. A. Mahanwar, Smita Mohanty, Sanjay K. Nayak. (2010). Morphological, Mechanical, Thermal, Electrical and Rheological Properties of Polycarbonate Composites Reinforced with Surfaces Modified Mica. *J. Miner. Mater. Charact. Eng.* 9(11), 985-996.
- [8] A. Ariffin, A.S. Mansor, S.S. Jikan (2008). Mechanical, morphological, and thermal properties of polypropylene/kaolin composite. Part I. The effects of surface-treated kaolin and processing enhancement. *J. Appl. Polym. Sci.* 108 (6), 3901-3916.
- [9] V. Mittal. (2007). Polypropylene-layered silicate nanocomposites: filler matrix interactions and mechanical properties. *J Thermoplast Compos Mater.* 20, 575–599.
- [10] A. Esfandiari, H. Nazokdast, A. S. Rashidi, and M. E. Yazdanshenas. (2008). Review of Polymer - Organoclay Nanocomposites. *Journal of Applied Sciences.* 8, 545-561.
- [11] J.F. Lemonas. (1997). Diatomite, *Am. Ceram. Soc. Bull.* 76, 92–95.
- [12] I.K. Iliia, M.G. Stamatakis, T.S. Perraki. (2009). Mineralogy and technical properties of clayey diatomites from north and central Greece. *Cent. Eur. J. Geosci.* 1, 393-403
- [13] T. Sun, X. Dong, K. Du, K. Wang, Q. Fu, C.C. Han. (2008). Structural and thermal stabilization of isotactic polypropylene/organo-montmorillonite/poly(ethylene-co-octene) nanocomposites by an elastomer component. *Polymer* 49, 588–598.
- [14] H. Aguilar, M. Yazdani-Pedram, P. Toro, R. Quijada, M. Ángel, L.-Manchado. (2014). Synergic Effect of Two Inorganic Fillers on the Mechanical and Thermal Properties of Hybrid Polypropylene Composites. *J. Chil. Chem. Soc.* 59(2) 2468-2473

FIGURES

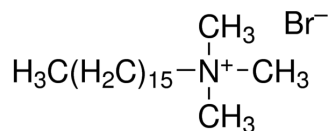


Figure 1. Molecular structure of CTAB

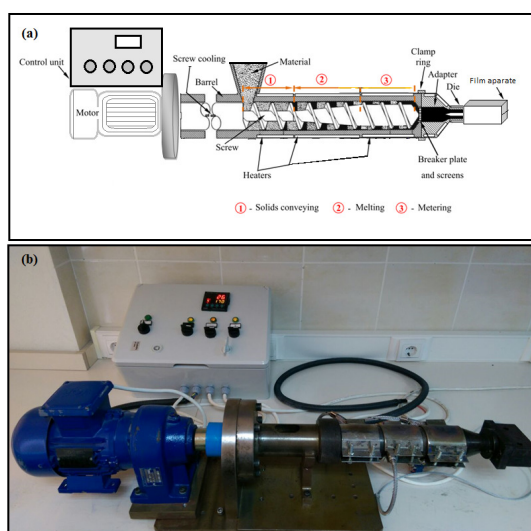


Figure 2. (a) Schematic and (b) original device representation of a laboratory-type-extruder used in the preparation of polypropylene composite films.

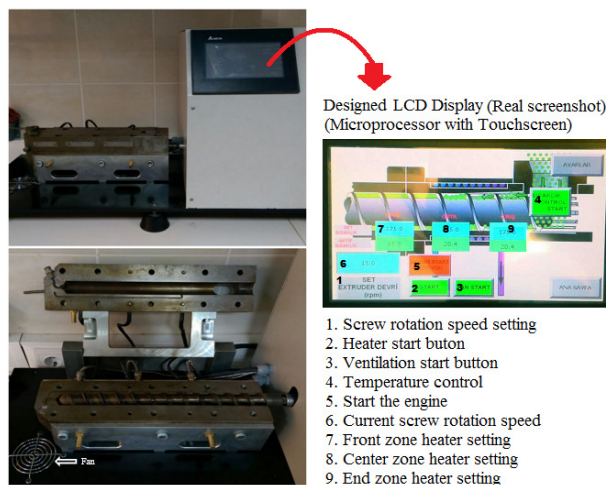


Figure 3. Microprocessor controlled second original laboratory-type-extruder and parts of the designed LCD screen.

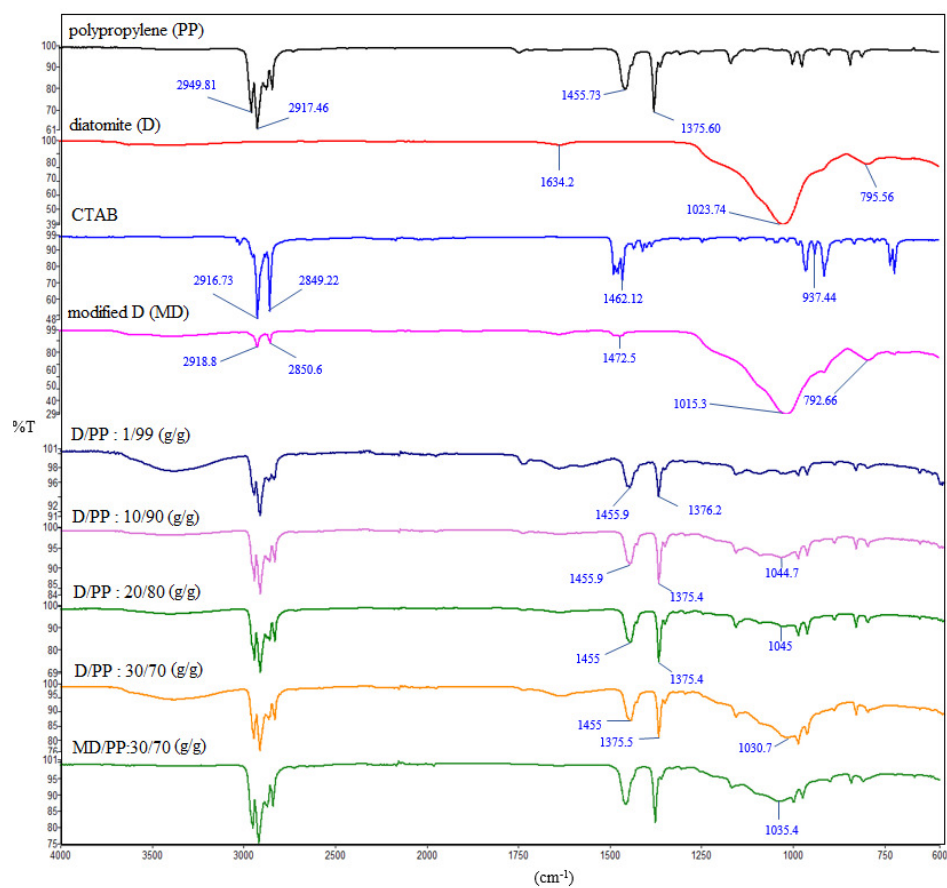


Figure 4. FTIR spectra of PP, D, CTAB, MD, and composite films

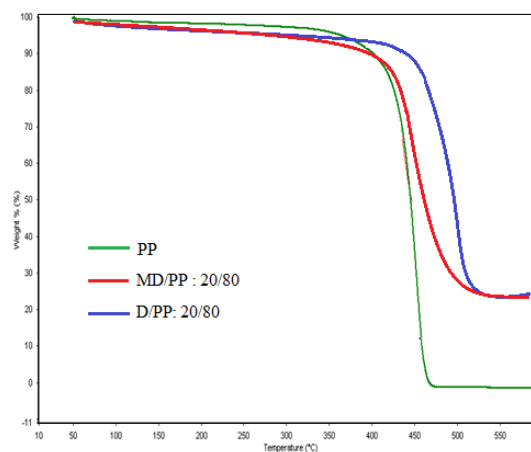


Figure 5. Thermogravimetric analysis of PP and selected their composite films

206

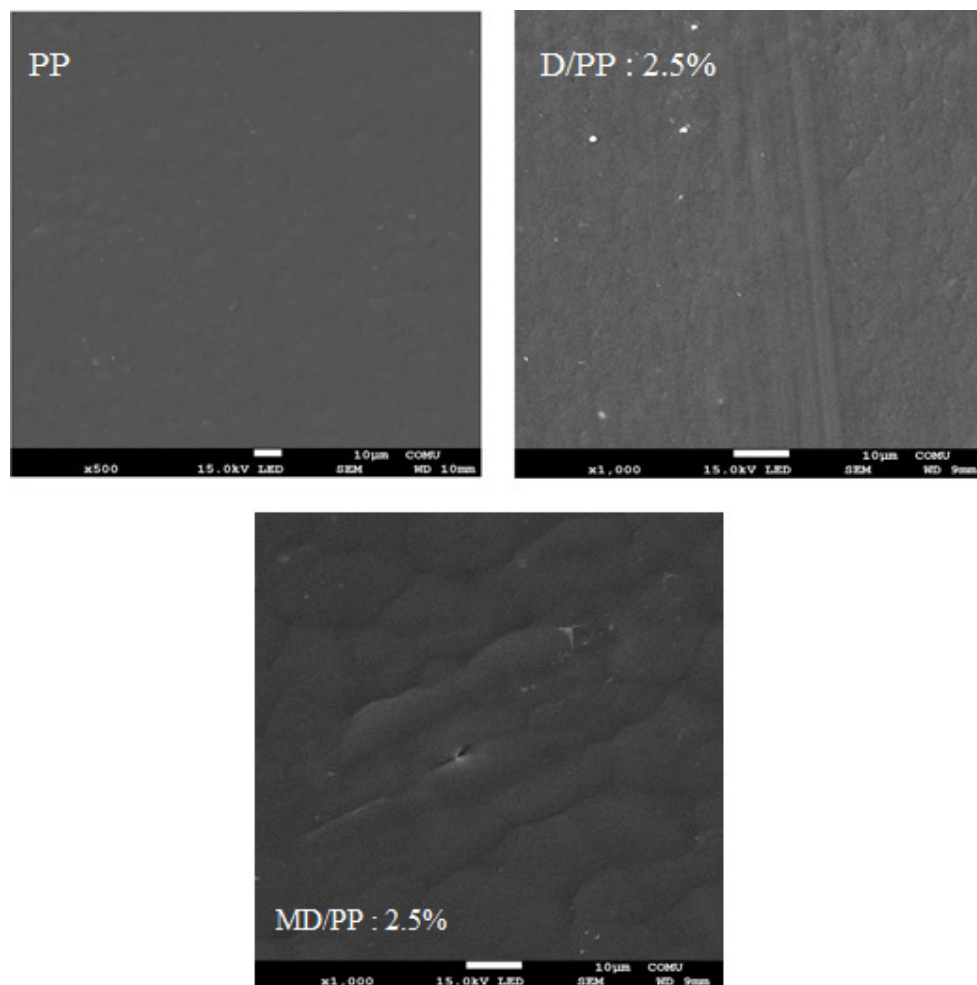


Figure 6. The SEM images of samples

207
208
209
210
211
212

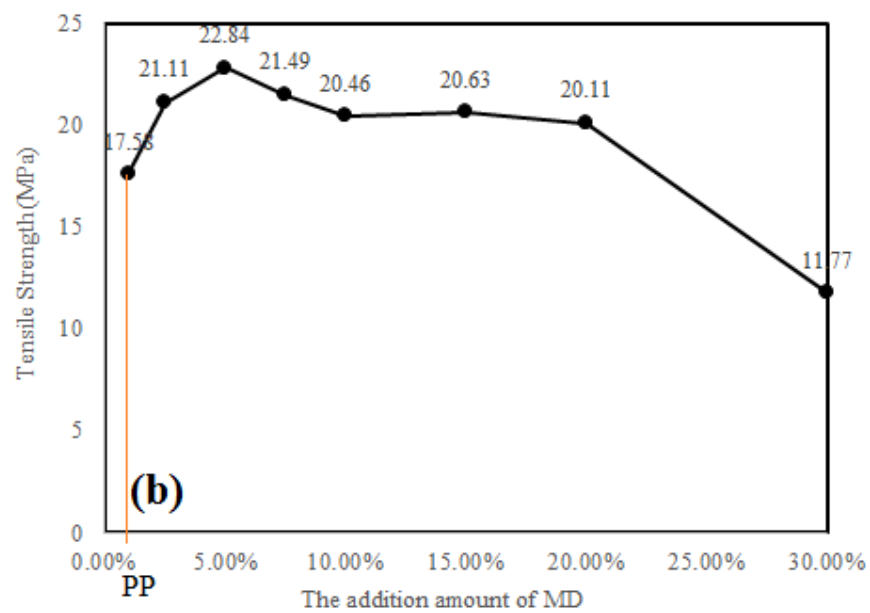
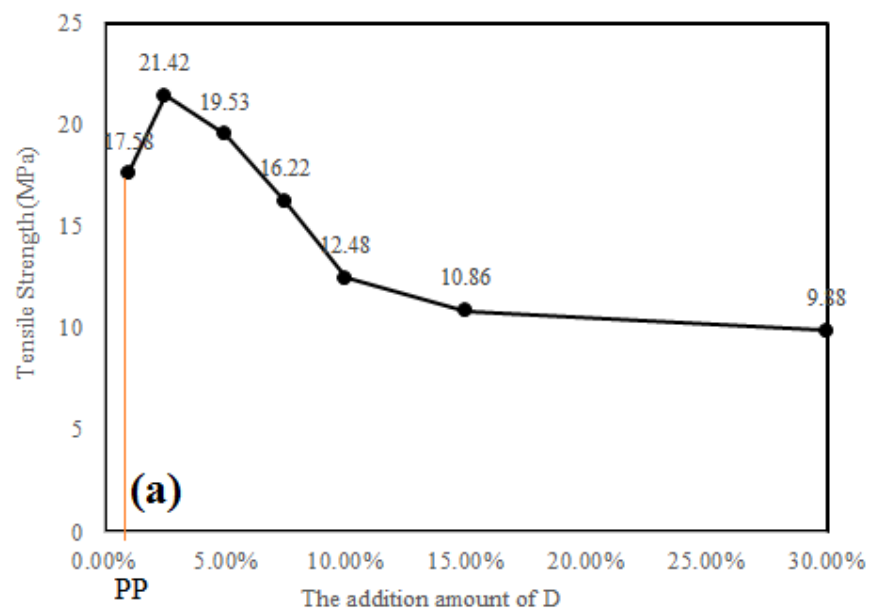


Figure 7. Tensile strength of PP, D/PP and MD/PP samples