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ARAŞTIRMA MAKALESİ

The Effects of PANI Concentration on the Mechanical Properties of PP/PANI Composites**Mehmet Kılıç¹, Ümit Alkan², Yaşar Karabul¹, Hale Berber Yamak³, Orhan İçelli¹**¹ Department of Physics, Faculty of Science and Letters, Yıldız Technical University, 34220 Istanbul, Turkey.² Department of Computer Engineering, Faculty of Engineering and Architecture, Istanbul Gelişim University, 34215, Istanbul, Turkey.³ Department of Metallurgical and Materials Engineering, Faculty of Chemistry- Metallurgical, Yıldız Technical University, 34220 Istanbul, Turkey.

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Abstract**Keywords**Polypropylene;
Polyaniline; Polymer
composites;
Mechanical properties;
stress-strain

In this study, the effect of PANI additive with different concentrations (0.3-3.0 wt.%) on mechanical properties of Polypropylene/Polyaniline (PP/PANI) film composites have been investigated. The composites films obtained from the hot pressing technique have been characterized to determine their surface properties and structural morphology (SEM and FT-IR), thermal properties (TG). The effects of PANI additive on mechanical properties of polypropylene have been examined by tensile tests. In particular, tensile strength, Young's modulus and percentage strain at break of the composites have been tested. According to our results, it has been observed that the PANI additive in polypropylene had a significant impact on its mechanical properties. The tensile strength has been reached highest value in PP/0.6 wt.% PANI composites.

PANI Konsantrasyonunun PP/PANI Kompozitlerinin Mekanik Özelliklerine Etkisi**Özet****Anahtar kelimeler**Polipropilen; Polyanilin;
Polimer kompozit;
Mekanik özellikler;
Stres-gerinim

Bu çalışmada, farklı konsantrasyonlarda (ağırlıkça %0,3-%3,0 arası) Polyanilin (PANI) katkısının Polipropilen/Polyanilin (PP/PANI) film kompozitlerinin mekanik özelliklerine etkisi araştırılmıştır. Sıcak presleme tekniği ile elde edilen kompozit filmlerin, yüzey özellikleri ve yapısal morfolojileri (SEM ve FT-IR), termal özellikleri (TG) belirlenmek üzere karakterize edilmiştir. PANI katkısının polipropilen filmlerin mekanik özelliklerine etkisi çekme testleri ile incelenmiştir. Özellikle, kompozitlerin çekme dayanımı, Elastisite modülü ve yüzde kopma uzama miktarları test edilmiştir. Sonuçlarımıza göre, PANI katkısının polipropilenin mekanik özelliklerinde belirgin bir etkisi olduğu görülmüştür. Çekme gerilimi, PP/0.6 wt.% PANI kompozitlerinde en yüksek değere ulaşmıştır.

1. Introduction

The products of thermoplastic polymer and particularly polypropylene (PP) are depleted nowadays in huge quantities. PP is one of the most commonly used in the thermoplastic industries (Pickering *et al.* 2016; Feteke *et al.* 2003; Byelov *et al.* 2007). It is widely used both in the industry and in consumer goods; it can be used both as a structural plastic and as a fiber as well, because of its easy processability, and low cost and good comprehensive properties (Kim and Kim 2015). However, the PP is largely limited by its disadvantages such as insufficient strength and poor thermal properties (Liang *et al.* 2016). Therefore, PP is generally modified by melt mixing with particulate (Wang *et al.* 2012; Wu *et al.* 2002) and fibrous (Ameli *et al.* 2013; Pickering *et al.* 2016; Chen *et al.* 1998) fillers as well as by melt blending with other polymers. Especially, these are modified with a conductive material (graphite, polyaniline, carbon fiber etc.) have been commonly studied as well (Akinci 2009; Taipalus *et al.* 1999; Saleem *et al.* 2007).

Polyaniline (PANI) is one of the representative conductive polymers due to its huge electrical conductivity, process capability, tunable properties, high environmental stability in addition to a comparatively low cost (Bhadra *et al.* 2009; Boeva *et al.* 2014). PANI is commonly used in organic electronics, supercapacitors, electrochemical catalysis (Boeva *et al.* 2014; Wen-Zhi *et al.* 2006), corrosion protection (Samui *et al.* 2003), sensors (Ates 2013) and PANI-based rechargeable battery (Ghanbari *et al.* 2006), the chemical industry etc. In recent times, the preparation of Polymer/PANI composite is a current issue because of a broad variety of potential applications.

The PANI is melt-processable, and it can be blended with numerous thermoplastics (polystyrene (PS), polyethylene (PE), polypropylene (PP) etc.). Also, it is commonly used to improve mechanical, electrical and thermal properties of polymer-based composites (Schackletta *et al.* 1993; Taipalus *et al.* 2000; Taipalus *et al.* 1999). The potential uses of Polymer/PANI blends are in the areas of electronic components, coatings and

structural bodies etc. (Abd Razak *et al.* 2013). Also, PP/PANI composites can be utilized as membranes (Piletsky *et al.* 2002). They are defined as smart materials and their binding ability is used as immobilization matrix for biomolecules such as proteins in biotechnology. Stable and thin PP/PANI membranes are also suggested to be used as films and adsorbant. Polyaniline-silica/polypropylene membrane is also generated as a flexible conductive composite to be used as an electrostatic shield, light-emitting and electronic devices (Wang *et al.* 2012). A ternary nanocomposite system of PP/PANI nanofibers is produced to be used in a high energy density capacitor (Cho *et al.* 2015).

The objective of this study is to enhance the thermal and mechanic performance of PP engineering plastics. Therefore, PP/PANI composites with different PANI contents (0.3, 0.4, 0.5, 0.6, 0.7, 1.0, 3.0 wt.%) are prepared by mechanical mixing, and then hot pressing method. Mechanical properties (Young's modulus, tensile strength, etc.) were examined by the stress-strain measurements at the room temperature. In addition, these composites were characterized by Fourier transform infrared (FT-IR) analysis, scanning electron microscopy (SEM), and thermal gravimetric analysis (TGA).

2. Experimental

2.1. Materials

Polypropylene (melting temperature: 165 °C, density: 0.905 g/cm³) was obtained from Petkim Industry in Turkey. Polyaniline (emeraldine base, average Mw ~5000, product number: 556459) was obtained from Sigma-Aldrich.

2.2. Preparation of Samples

To analyze effects of PANI additive (0.3, 0.4, 0.5, 0.6, 0.7, 1.0, 3.0 wt.%) on the mechanical attributes of PP, PP/PANI composite films were prepared by the hot pressing method. Firstly, PP/PANI mixtures were obtained by mechanically blending the PP powder with PANI powder in different weight percentages. Then the mixtures were ground and blended by IKA A11 basic analytical mill (with the

rotational speed of 10000 rpm) for 10 minutes. After these process, each mixture becomes a homogeneous powder form. Pure PP and prepared PP/PANI mixture in powder form were compression molded in an electrically heated press (Hot pressing method). Hot pressing procedures involved pre-heating at 165 °C for 20 minutes, followed by compressing for 10 min at the same temperatures under 15 MPa pressure. Finally, each melting mixture has homogeneous film, after cooled in a cold water. For the measurements, each composite has been prepared in the form of thick films of 24 mm diameter and 71–100 µm thickness. The thickness of composite films was measured by using a Mitutoyo micrometer. The preparation process of these composites has been schematically given in Figure 1.

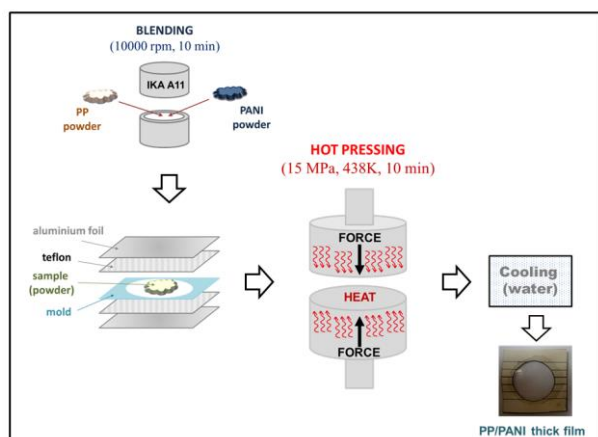


Figure 1. Schematic view of the preparation procedure of samples.

2.3. Characterization

The morphology of the PP and PP/PANI films has been determined by Scanning Electron Microscopy (SEM) measurements performed by Zeiss-EVO® LS 10. The FTIR spectrum of each sample has been determined by Spectrum 100 FTIR Spectrometer (Perkin-Elmer Inc.) operated in transmission mode with the spectral region from 4000 to 400 cm^{-1} . The thermogravimetric analyses of these samples were performed on a Perkin-Elmer Pyris Diamond thermogravimetric-dynamic temperature analyzer with programmed heating at 10 °C/min between 25 °C and 750 °C.

The mechanical properties (Young's modulus, percentage strain, tensile strength, and energy at the break, etc.) of these films were determined by stress-strain measurements performed by "Lloyd Instruments LF Plus Single Column Universal Materials Testing Machine" with a crosshead speed of 50 mm/min at 23 ± 3 °C.

3. Results

3.1. FT-IR Analysis

Figure 2 shows the FTIR spectra of the pure PP and PP/PANI composite films with different PANI content. For the PP, the characteristic strong peaks between 3000-2800 cm^{-1} indicate the asymmetric C–H stretching vibrations and the symmetric C–H stretching vibrations in CH_3 , CH_2 and CH groups. The strong peak at 1460 cm^{-1} and 1378 cm^{-1} also indicate the asymmetric and the symmetric bending deformation vibrations of the CH_3 groups respectively.

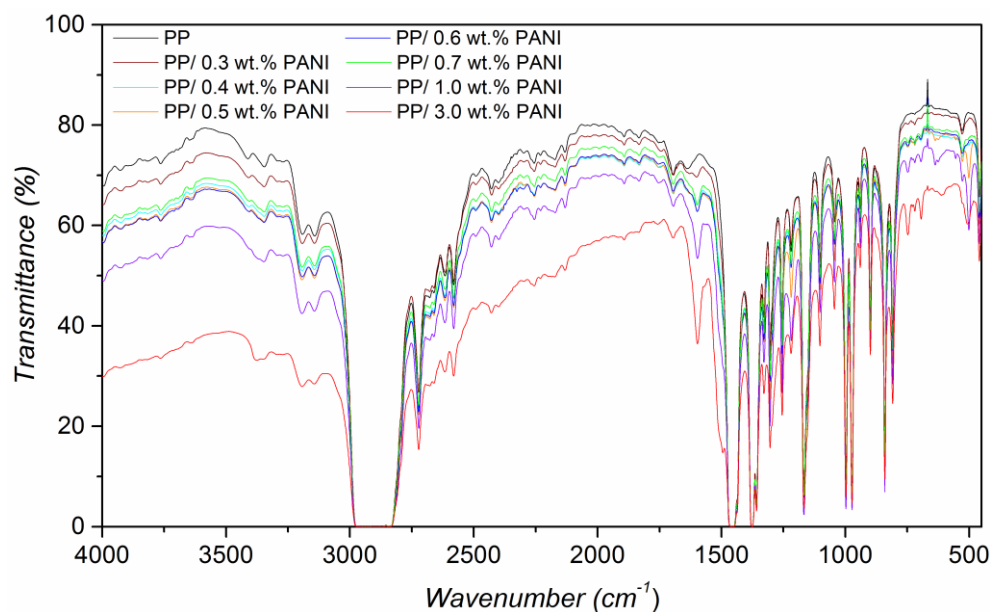


Figure 2. FT-IR analysis of PP and PP/PANI composites.

The peak observed at 1167 cm^{-1} assigned to the C–C chain stretching, C–H wagging, and CH_3 rocking vibrations. The sharp peaks at 997 , 973 and 899 cm^{-1} show the CH_3 rocking and the C–C chain stretching vibrations. The peak at 840 cm^{-1} also shows the CH_2 rocking and the C– CH_3 stretching vibrations.

The medium peak observed at 809 cm^{-1} indicates the C–C stretching and CH_2 rocking. All these peaks are the typical absorption peaks of the pure PP. With the addition of PANI to the PP, the few new peaks, which have different intensities varied depending on the PANI content in the PP based composites appear, as shown in Figure 2. The most obvious peaks belonging to the PANI are observed at 1596 cm^{-1} and 1495 cm^{-1} refer to C–C ring stretching vibrations of the quinoid and benzenoid structures in PANI. Also, the new peaks appear at 747 cm^{-1} and 694 cm^{-1} indicating C–H vibration of para coupling benzenoid and aromatic ring, respectively. It is seen in spectra that some characteristic peaks belonging to the PANI overlap with the strong peaks of the PP (Alkan *et al.* 2013; Pukánszky *et al.* 1996).

3.2. SEM Analysis

The SEM micrographs for the surface morphology of samples are shown in Figure 3. The pure PANI and pure PP are given in Figure 3a and Figure 3b respectively while Figure 3c-i shows the PP/PANI film composites. In Figure 3a, SEM images of PANI reveal the big globular agglomerates with irregular particles. The PP thick film has nearly smooth surface before PANI additive as seen in Figure 3b. In Figure 3c-e, PANI was heavily agglomerated and poorly dispersed on the 0.3-0.5 wt.% PANI additive samples. Also, PP/0.5wt.%PANI samples have a few bloating on the surface. The image of the PP/0.6 wt.% PANI composite films has nearly smooth, this implies that the adhesion between the PP and PANI was confirmed (In Figure 3f). As seen in Figure 3g-i, the increasing the PANI additives causes a porosity are formed on the surface of the films. The porosity was evident in greater than 0.7 wt.% PANI additive concentration, which was promoted by the PANI agglomerates. The obvious increase porous for the PP/PANI film composites, which have PANI content higher than 0.7%, leads to a degradation in mechanical properties.

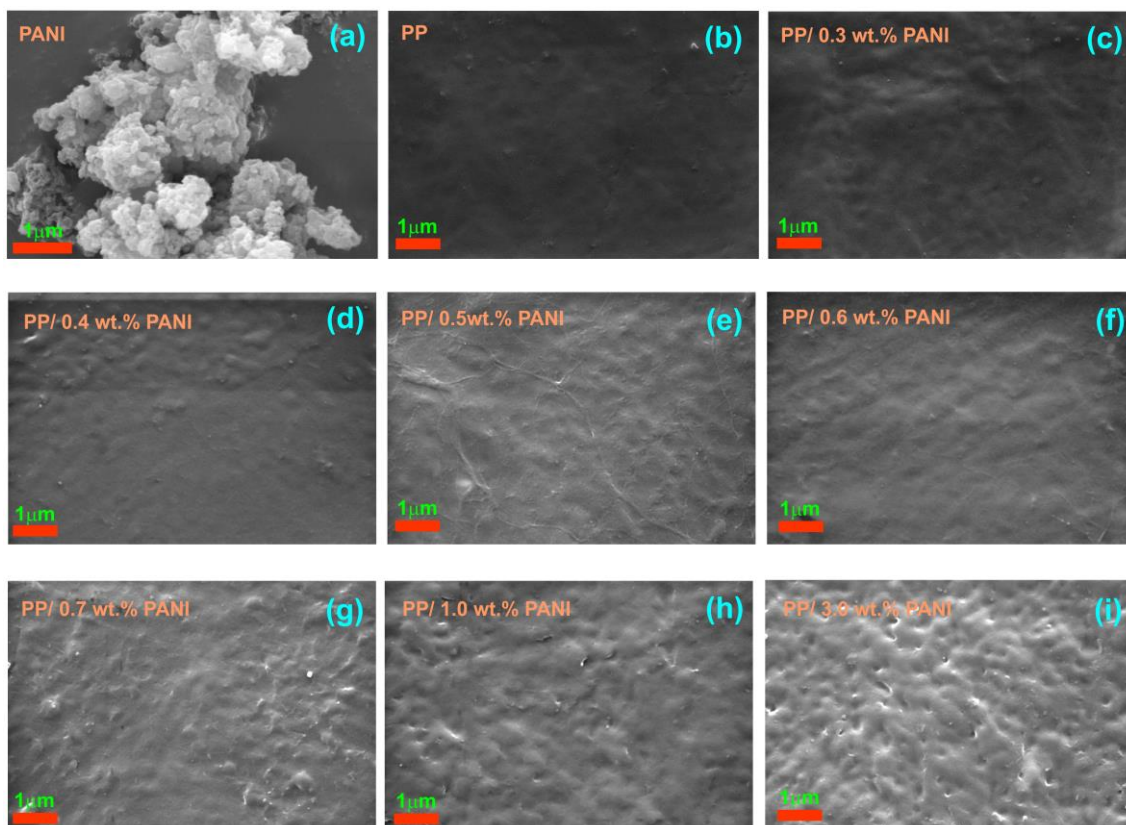


Figure 3. SEM micrographs of the PANI, PP and PP/PANI composites.

3.3. TG Analysis

As a function of % weight loss with the increase in temperature, TGA results of all samples (pure PP and PP/PANI composites) are displayed in Figure 4. A one-step pattern of thermal degradation occurring at approximately 350-490 °C was observed for all the samples. It was clearly seen in the curves that the degradation temperatures noticeably decreased with the addition of PANI to the PP matrix. The minimum degradation temperature was determined for the composite sample containing 0.5 wt.% of PANI, and then the temperatures started to increase the amount of PANI. In particular, when the amount of PANI was increased to 0.6 wt.%, a significant increase in the thermal stability of the composites was observed. As a result, it can be said that the thermal stability of the PP based composites is enhanced again above 0.6 wt.% of PANI content, particularly at the low weight loss values.

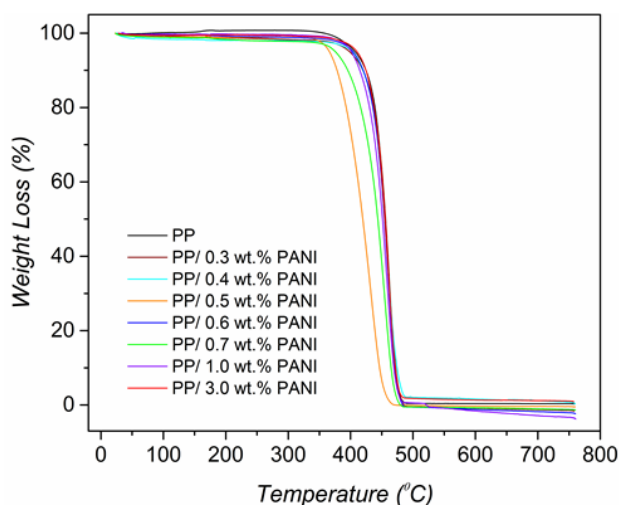


Figure 4. TGA curves of the pure PP and PP/PANI composites.

3.4. Mechanical Analysis

The mechanical properties of PP/PANI composites have been measured with a cross-head speed of 50 mm/min to determine the evolution of tensile strength, Young's modulus, energy at break and percentage strain as a function of PANI additive percentages. Stress-strain tests have been carried out under uniaxial extension and stress-percentage

strain curves of all films have been given in Figure 5.

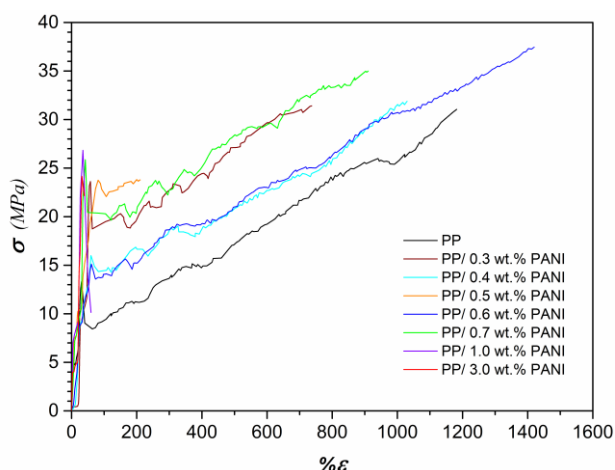


Figure 5. Stress-percentage strain curve.

Also, the value of mechanical parameters of all samples has given in Table 1. The addition of 0.6 wt.% PANI content enhanced the mechanical properties of the composites. The modified of PP with 0.6 wt.% PANI has increased the tensile strength and percentage strain by approximately 21 % and 20 %, respectively, compared to the value of neat PP (Table 1). Increasing the PANI content in the composite to 0.7 wt.% led to no significant change in the tensile strength compared to a proportion of 0.6 wt.%. While doped PANI concentration was increased from 1.0 to 3.0 wt.%, the positive effect of PANI content on the tensile strength and percentage strain at break of these composite was reduced.

The decrease in the tensile strength and percentage strain at break could be attributed to the immiscibility, characterized by a lack of interfacial adhesion, between PP and PANI. Also, SEM photographs in Figure 2(c-e) and Figure 2 (g-i) showing higher agglomerates and porous content for PP/PANI composites, while showing nearly smooth surface to PP/0.6 wt.% PANI composites

(Figure 2f) help explaining the observed tensile attributes variations. The matrix of the porous film provides the benefit of easy entry to the monomers and other agents or the conducting polymers into the composites. As seen in the literature (Yang *et al.* 1995), the porous structure of the film may also guarantee the formation of a conducting polymer system inside the main film at a lower additive of the conducting polymer in the composite. Nevertheless, when pores are formed in the film, its mechanical attributes will be reduced clearly.

Furthermore, Young's modulus determined from the stress-percentage strain curves (the initial slope of the tensile curves), as shown in Figure 5. Generally, Young's modulus of PP/PANI composite was increased by increasing PANI content. PANI was placed in the gap between PP chains and thus increased its rigidity. On the other hand, PP/0.4 wt.% PANI and PP/0.6 wt.% PANI composites have a lower Young's modulus value than pure PP sample.

As seen in Table 1, the key reason why an increasing trend on Young's modulus with the PANI content has been more notable than the decrease of the tensile strength may be for the reason that the increase of PANI content severely changes the rigidity characteristics of the composite films.

These mechanically obtained results are consistent with the literature (Taipalus *et al.* 1999; Chodak *et al.* 2001). It was determined that the tensile strength decreasing with increasing conducting polymer content, whereas the Young modulus increasing with increasing conducting polymer content.

Table 1. The mechanical characteristics of the samples.

Samples	Tensile Strength (MPa)	Young's Modulus (MPa)	Percentage Strain at Break	Energy to Break (mJ)
PP	31.05±2.68	163.08±23.21	1182.2±84.77	44.40±5.2
PP / 0.3 wt.% PANI	31.42±1.91	209.93±13.66	737.16±92.37	34.67±4.3
PP / 0.4 wt.% PANI	31.88±1.82	91.81±14.35	1029.9±53.17	42.36±3.7
PP / 0.5 wt.% PANI	23.81±2.63	147.62±15.36	210.49±18.05	8.42±1.6
PP / 0.6 wt.% PANI	37.47±3.84	82.71±12.44	1420.1±34.01	73.53±3.9

PP / 0.7 wt.% PANI	34.99±4.21	274.07±22.41	910.58±50.14	51.93±4.6
PP / 1.0 wt.% PANI	26.83±1.91	247.59±13.66	59.69±6.23	1.57±0.23
PP / 3.0 wt.% PANI	24.16±1.91	310.29±13.66	39.05±4.43	0.66±0.11

4. Conclusion

In the present study, PP/PANI film composites with different PANI concentrations (0.3, 0.4, 0.5, 0.6, 0.7, 1.0, 3.0 wt.%) have been prepared by the hot pressing method to enhance mechanical properties of polypropylene. The influence of PANI on structural and mechanical attributes of PP have been examined by FT-IR, TG, SEM and stress-strain measurements. It was found that the PANI doping in PP had a significant impact on its mechanical properties. The tensile strength and energy of break showed its highest value in the case when PP was the only 0.6 wt.% component of the composites. Finally, a good conductive composite with good mechanical and processability attributes is the demand for future composite industries.

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