

Study of Dielectric Behavior of Titanium Dioxide-Filled Polypropylene Composites

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Abstract: Titanium dioxide (TiO₂)-filled isotactic polypropylene (iPP) composites with various contents of TiO₂ were prepared using an extrusion molding machine. Scanning electron micrograph shows that the surface of iPP is smoother in comparison to those of iPP/ TiO₂ composites with varying TiO₂ concentration. The composite of 40 wt% TiO₂ contains more agglomerates or larger particles, than the composite of 20 wt% TiO₂. With increasing filler content amount of voids and holes is increased on the composite surfaces. The DTA shows two endothermic peaks that represent melting temperatures at 169, 167, 163 and 167°C and thermal degradation temperatures at 435, 437, 448, 462°C of various TiO₂ concentrations. While the melting peak of the neat iPP is sharp, the TiO₂-loaded composites rather show diffuse melting peaks along with a shift of peaks towards lower temperatures. In AC electrical measurement it is demonstrated that with the increase of frequency, conductivity (σ) increases but dielectric constant (ϵ') decreases of these composites. With varying TiO₂ concentration, there is no noticeable change observed in σ where as ϵ' value is decrease of these composites. Both σ and ϵ' are weakly dependent on temperature. At lower frequency region loss tangent ($\tan\delta$) increases with frequency and attains a maximum peak after that $\tan\delta$ decreases rapidly at higher frequency region. This reverse and usual behavior of $\tan\delta$ at high frequency can be explained in accordance with Koop's theory.

Keywords: Dielectric Behavior, Titanium Dioxide, Composite

1. Introduction

Filler-reinforced polymer composites have gained much attention to scientific investigations, with an aim to develop novel materials for various applications. Incorporation of fillers alters the structural, mechanical, thermal and electrical properties of the composites [1-5]. These properties are affected by the degree of dispersion of filler into the polymer matrix and the interaction between filler and polymer [2]. Commonly used fillers in isotactic polypropylene (iPP) are talc, calcium, clay etc. [1, 5] but titanium dioxide (TiO₂) can be one of the important fillers in producing composites with improved properties [2]. Semko et al. [6] investigated the effect of TiO₂ nanoparticles on the resistivity and gas-sensing

performance of Poly (vinylchloride) (PVC)-expanded graphite composites. The results demonstrated that by varying the composition of the composites, one can control their percolation threshold, electrical properties, and gas sensing performance. Zhang et al. [7] studied the influence of surface-modified TiO₂ nanoparticles on fracture behavior of injection molded polypropylene (PP). The transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images showed homogeneous dispersion of nano-TiO₂ at 1 vol.% filler content and weak nanoparticle matrix interfacial adhesion. El-Midany et al. [8] studied the effect of mineral surface nature on the mechanical properties of mineral-filled PP composites. In their study, they found that the difference in mechanical properties for two mineral fillers; namely, silica and talc, differs in their surface properties. Talc

containing composites showed the better results in terms of Young's modulus and impact strength, where as silica containing composites showed higher yield strength. Preparation and characterizations of TiO₂/organically modified silane composite materials produced by the sol-gel method were reported by Que et al. [9]. The TGA/DTA results showed that the organic compounds in the film would tend to decompose in the temperature range from 200 C to 500 C. Afroze et al [10] investigated elastic and electrical properties of graphite and talc filler reinforced polypropylene composites. They observed that the graphite filler content composites show better electrical properties than talc filler content composites. Investigation on the dielectric properties of nano titanium dioxide-low density polyethylene composites were carried out by Shengtao et al. [11] at the temperature ranging from 293K to 343K with the frequency ranging from 0.1Hz to 100 kHz. They observed two peaks in the spectrums; one appears in both pure and incorporated LDPE (abbreviated as peak A) while the other appears only in the samples with nano-TiO₂ content exceeding 1wt% (abbreviated as peak B). The activation energies calculated from dielectric spectrum for peak A and peak B are 1.09eV and 0.8eV respectively; they are independent of the concentration of TiO₂nanofiller. Finally they conclude that Peak B is an intrinsic peak corresponding to the response of LDPE while peak A is a new peak may originate from the traps at the "Interaction Zone" around the nanoparticles. Surface morphology, thermal and mechanical properties of bamboo fiber reinforced epoxy composites were studied by Zhang et al. [12]. SEM images show that the surface of untreated bamboo fibers were relatively smooth where as the surface of composites is covered with many lump materials. These surface materials could consist of hemicelluloses, lignin, pectin, wax, and other impurities. TGA demonstrated that Bamboo fibers treated with 6 wt% NaOH solutions had better thermal stability than untreated fibers. Bamboo-fiber composites, therefore, have potential for engineering applications. Enhancement in mechanical and electrical properties of polypropylene (PP) /graphene oxide (GO) nanocomposites were studied by Chammingkwan et al. [13]. The best improvement in the tensile strength was obtained using PP-GO at 1.0 wt%. The addition of all the types of graphitic fillers more or less increased the electrical conductivity to 1.0 wt%, while the further addition to 3.0 wt% hardly improved the conductivity.

Due to practical and technological importance of composites, in this paper we have focused the surface morphology, thermal and dielectric properties of iPP/ TiO₂ composites for understanding the influence of TiO₂ on the different properties of final products.

2. Experimental Details

2.1. Sample Preparation

Granular-shaped iPP was purchased from a company (BASF, Germany) and TiO₂ was procured from local market. Physical properties of original material (iPP) are presented in

Table 1. A neat iPP sample and 10, 20, 30, and 40 wt% TiO₂ loaded iPP/ TiO₂ composites were prepared by passing their mixtures with appropriate ratios into a locally fabricated extrusion machine. The extruder has 3 heating zones with blending temperature profiles of 220, 230 and 240°C by which different mixtures of iPP/ TiO₂ were melted. During preparation of samples, the screw rotating speed was 100 rpm, and a cylindrical die having 0.008 m diameter and 0.02 m length was placed at the outlet of the extruder. The molten extruders were cooled in ambient condition, producing rod-shaped extrudents. These were cut into pieces and melt-pressed in a die at 180°C using a hot-pressed machine with a load of 100 kN. The melt-pressed materials were again cooled to room temperature within 15–20 min by circulating water. Plane composite sheets of nearly equal thicknesses were obtained and subjected to characterization by the following techniques.

Table 1. Physical properties of original material (iPP).

Molecular Formula	(C ₃ H ₆) _n
Molecular Weight	184.7 kg/mol
Density	900 kg/m ³
Melting temperature	165°C

2.2. Characterization Techniques

2.2.1. Scanning Electron Microscopy

The surface morphology of neat iPP and composites was studied using a scanning electron microscope (SEM) (Hitachi S-3400, Japan) with an operating voltage of 15 kV. Sample surface was coated with a thin gold layer using a sputtering machine prior to SEM observation.

2.2.2. Thermal Measurements

Melting and degradation temperatures of the samples were monitored using a DTA/TGA [Seiko-Ex-STAR-6300, Japan] machine. The measurements were carried out from 30 to 700°C at a heating rate of 20°C min⁻¹ under nitrogen gas flow. The DTA traces give the melting and degradation temperatures which are determined from the exotherm versus temperature curves.

2.2.3. AC Electrical Measurement

Disc shaped samples were prepared for AC electrical measurement. The AC measurement was performed in the frequency range from 100 to 1x10⁶ Hz and temperature range 300-375 K, by an Agilent 4192A LF Impedance analyzer, 5Hz-13MHz (Agilent Technologies Japan Ltd, Japan). The temperature was recorded by a Chromel-Alumel thermocouple placed very closed to the sample which was connected to a Keithley 197A digital micro voltmeter (DMV). All measurements were carried out in a vacuum of about 1.33 Pa.

3. Results and Discussion

3.1. Surface Morphology

SEM micrographs provide us useful information about the micro voids or holes that increase in the composites

with increasing the amount of filler. Figure 1 represents the SEM micrographs of the iPP sample and composites with 20% and 40 wt% TiO_2 content. Clearly, the iPP sample shows the smoothest surface in comparison to other two composites. The composite of 40 wt% TiO_2 contains more agglomerates or larger particles, which seem to form lumps on the surface, than

the composite of 20 wt% TiO_2 . Increasing TiO_2 content develops slight roughness, darkness and some hole on the composite surfaces. The reason of the presence of more holes in the composites containing higher TiO_2 concentration may be due to the development of interface around the particles because of their incompatibility between TiO_2 and iPP matrix.

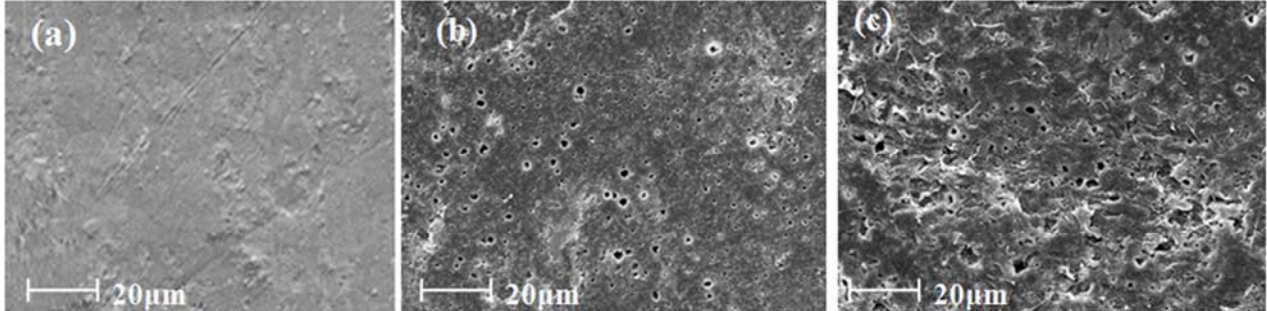


Figure 1. The SEM micrographs of (a) neat iPP (b) 20 wt% and (c) 40 wt% iPP/ TiO_2 composites.

3.2. Thermal Analysis

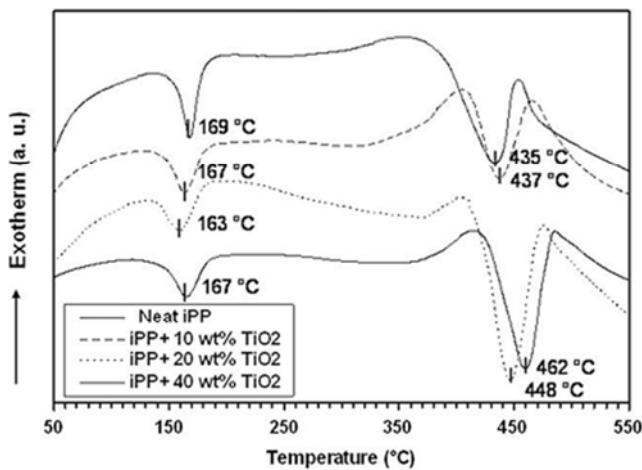


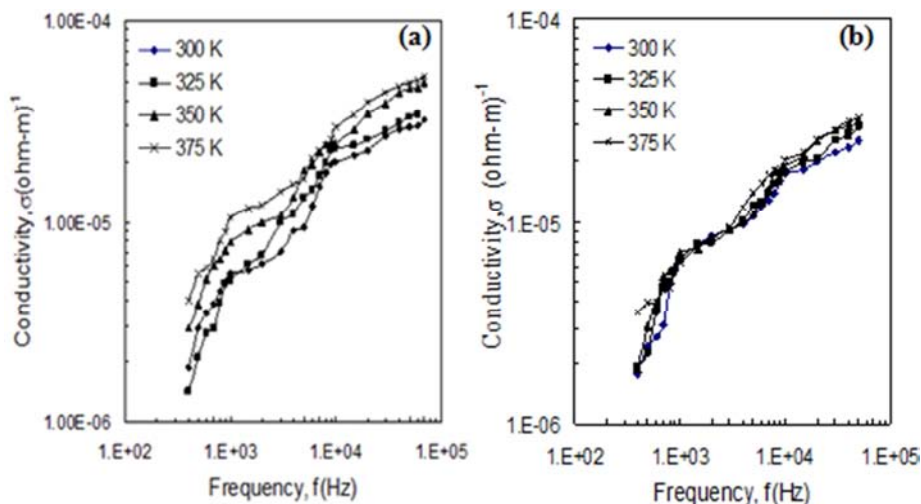
Figure 2. DTA thermograms of the neat iPP sample and iPP/ TiO_2 composites having various contents of TiO_2 .

The DTA curves of the neat iPP sample and composites of 10, 20 and 40 wt% TiO_2 content are presented in Figure 2. Each DTA run shows two endothermic peaks those represent melting temperatures (T_m) at 169, 167, 163 and 167°C and thermal degradation temperatures (T_d) at 435, 437, 448, 462°C. While the melting peak of the neat iPP sample is sharp, the TiO_2 -loaded composites rather show diffuse melting peaks along with a shift of peaks towards lower temperatures.

3.3. AC Electrical Properties

3.3.1. Variation of AC Conductivity with Frequency and Temperature

The measured values of the conductance and capacitance were used to calculate the AC conductivity (σ), dielectric constant (ϵ') and loss tangent ($\tan\delta$) of the samples with different filler contents.



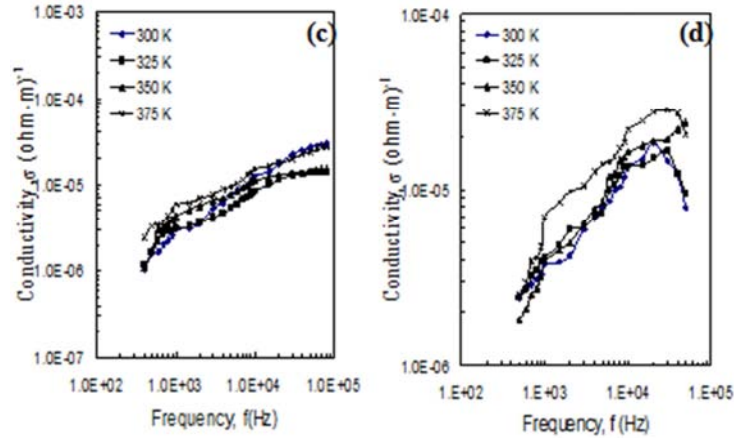


Figure 3. Variation of AC conductivity with frequency for iPP/TiO₂ composite with (a) 10% (b) 20% (c) 40% (d) 50% TiO₂ content at different temperatures.

Effect of frequency on the AC conductivity (σ) of iPP/TiO₂ composites for different wt% of TiO₂ content at temperatures 300, 325, 350 and 375 K can be depicted from Figure 3. It is observed that the σ increases with the increase of frequency for all measurement temperatures, which corresponds to interfacial polarization. It also displays that σ value is weakly dependent on temperature within the present experimental condition. On the other hand with varying TiO₂ concentration there is no significant variation of conductivity is observed.

3.3.2. Variation of Dielectric Constant with Frequency at Different Temperatures

Figure 4 shows the variation of ϵ' with frequency of

iPP/TiO₂ composites for different wt% of TiO₂ content at different temperatures. From the plots it is demonstrated that the ϵ' decreases with the increase in frequency and not much dependent on temperature. As the frequency increases the dipoles in the composite cannot follow the field and thus lag behind the applied field. So the value of ϵ' decreases with the increase of frequency. The value of ϵ' becomes more or less uniform above 10² kHz frequency. On the other hand, ϵ' value decreases of these composites with increasing TiO₂ content. In TiO₂/polypyrrole composites, Ahmed et al. [14] reported that ϵ' decreases gradually with increasing frequency but with increasing TiO₂ content of the composites the ϵ' value increases.

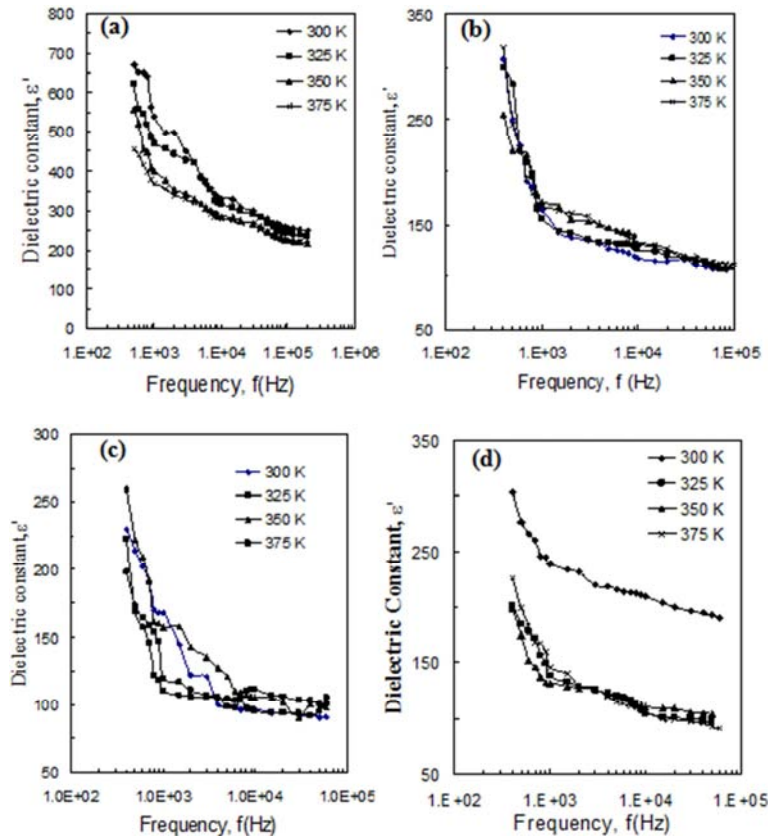


Figure 4. Variation of dielectric constant with frequency for iPP/TiO₂ composite with (a) 10% (b) 20% (c) 40% and (d) 50% TiO₂ content at different temperatures.

3.3.3. Variation of Loss Tangent with Frequency and Temperature

Figure 5 shows the variation of $\tan\delta$ with frequency of iPP/TiO₂ composites for different wt% of TiO₂ content at different temperatures. It is exhibited that as the frequency increases $\tan\delta$ increases and at a particular frequency $\tan\delta$ attains a maximum value. After reaching the maximum, $\tan\delta$ decreases with the increase in frequency. It is also observed that for a particular frequency, $\tan\delta$ is higher at higher temperature. This low frequency relaxation peak may be an intrinsic peak originates from the interfacial polarization between the electrode and the sample. It's generally believed

that new traps/defects will be introduced into composite material by adding microparticles. Some observations have been reported [15]. Such traps/defects play a dominant role in AC electrical performance. Therefore, the interfacial effect contributes to the dielectric properties at lower frequency. In high frequency region the behavior of $\tan\delta$ can be explained in accordance with Koop's theory [16]. According to this theory, when the frequency is increased, the probability of electrons reaching the grain boundaries decreases and hence a decrease in permittivity is observed. This in turn decreases the dielectric parameters at high frequencies.

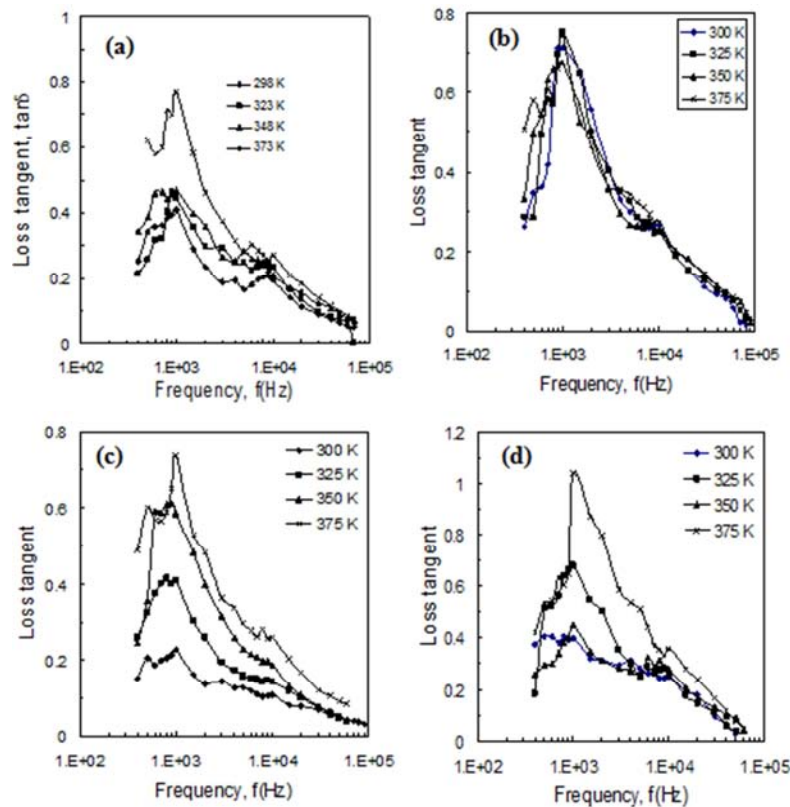


Figure 5. Variation of loss tangent with frequency at different temperatures for iPP/TiO₂ composite with (a) 10% (b) 20% (c) 40% and (d) 50% TiO₂ content at different temperatures.

4. Conclusions

iPP-TiO₂ composites in four different weight of ratios have been studied with a view to investigate their SEM, thermal properties and electrical properties. The iPP shows the smoothest surface in comparison to other two composites. The composite of 40 wt% TiO₂ contains more agglomerates or larger particles, which seem to form lumps on the surface, than the composite of 20 wt% TiO₂. Each DTA curve of the samples displays two endothermic peaks for T_m and T_d . T_m shows a little variation with increasing filler content whereas T_d is found to increase significantly with the addition of filler. The σ is found to increase rapidly with frequency where as ϵ' decreases with increasing frequency. Slight alteration is observed in both σ and ϵ' due to temperature variation. With

increasing TiO₂ content, σ value is not significantly changes but ϵ' value is reduces of these composites. Both σ and ϵ' are weakly dependent on temperature. The $\tan\delta$ increases in the lower frequency side up to about 10³ Hz, attains a maximum peak then it decreases with the increase of frequency. Interfacial polarization relaxation peaks observed in these composites.

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