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Effect of TiO_2 Inorganic Additive on the Mechanical Properties of Polypropylene

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Abstract

Plastics produced by recent technologies of surface treatment of polyolefin composites have properties comparable to those of engineering plastics. Because of their direct relevance to processing and performance in structural applications and rheological and mechanical properties, mineral filled composites have been widely studied. In the present research, inorganic additive, namely titanium dioxide was treated by adsorption of oleic acid, sodium silicate and sodium aluminate as modifiers, and the best modification type and extent for optimum compatibility with polypropylene was determined. In addition, the effect of treated and untreated additives on the mechanical properties of the prepared composites was studied. Because of the fact that filled polymers are generally used as insulators, their electrical properties deserve attention. In the present study, their dielectric relaxation property was used to provide further information about their structure.

1. INTRODUCTION

The scope of the application of polymeric materials has been widened by the incorporation of various additives into the polymer[1-5]. Such additives, when incorporated into a thermoplastic, modify certain properties such as tensile strength and moldability, with an accompanying reduction in cost. Of all the additives used for thermoplastics, the bulk consists mainly of inorganic materials such as talc, $CaC0_3$, various silicates, glass beads and glass fibers. The influence of various particulate fillers on crystallinity, tensile strength and modulus, thermal conductivity, and melt rheology of polypropylene has been extensively studied.[6-10] In general; the crystallinity is reduced upon incorporation of fillers. Modification of tensile properties depends on the polymer-filler combination, as well as on the interface of these two phase systems. While melt viscosity was found to increase with increasing filler content, melt elasticity was found to decrease. Decrease in melt elasticity adds to the processing safety of the composites by increasing the critical shear stress for melt fracture, ensuring the smooth surface of the extrudates.

In the present study, the effect of the incorporation of titanium dioxide on the mechanical properties of polypropylene (PP) has been reported. Tensile and electrical properties of PP/TiO_2 composites were studied at titanium dioxide concentrations up to 40 wt %.

2. EXPERIMENTAL WORK

2.1. Materials Used

Materials used in the present study were:

- Polypropylene of MFI (12g/min) by Montell USA Inc.
- Titanium dioxide (TiO_2), in the form of very fine powder, packed and distributed by El-Gomhouria Co.
- Oleic acid and toluene provided by El Nasr Pharmaceutical Chemicals (ADWIC)
- Potassium hydroxide and sodium alluminate supplied by Pharmaceutical Chemical Co.
- Sodium silicate (commercial grade).

2.2. Organic Surface Modification Process

The organophilization with oleic acid was carried out by preparing oleic acid solution in toluene at different concentrations ranging from 0 to 0.07 mol/l. The inorganic TiO_2 was organophilized by suspension in the oleic acid solutions in the ratio of 1:10 in stoppered cylinders. The stoppered cylinders were shaken frequently and allowed to sediment for 48 hrs at room temperature. After the adsorption equilibrium had been established, the solid particles were separated by filtration from the equilibrium solution, and then washed several times with toluene solvent. The organophilized samples were dried at 60 °C in a drying vacuum oven.

2.2.1. Determination of the Adsorption Isotherm

From the difference in concentration of the oleic acid before and after adsorption, the amount adsorbed was determined. The oleic acid concentration was determined by acid-base titration against 0.1 mol/l alcoholic KOH.

The adsorbed amount of the oleic acid per gram of titanium dioxide, (n^s), was determined according to equation (1)

$$(n^s) = V\,(C_o - C_e) / m, \text{ mol/gm} \quad \text{-------------} \quad (1)$$

Where:

C_o is the initial concentration of the oleic acid

C_e is the equilibrium concentration, after adsorption

V is the solution volume

m is the quantity of pigment

The adsorption isotherm was obtained by plotting the adsorbed amount of the surface modifier against the equilibrium concentration.

2.3. Inorganic Surface Modification Process

10 grams of titanium dioxide were added to 20 ml of water at 60 °C , followed by the addition of 25 ml of sodium aluminate (12.5 %) and finally 10gm of sodium silicate (50 %) were added. 10 min stirring was performed after each of the previous additions. The final pH was adjusted to 7 to obtain final packed pigment and to affect the complete precipitation of the further coating. The solid surface was separated by filtration and dried to constant weight at 60 °C in a drying oven.

2.4. Preparation of the Composites

After the surface modification process, the titanium dioxide was dried at 105 °C. (for the modified in aqueous medium). Polypropylene was placed in a brabender mixer at a rate of 85 rpm at 190 °C for 3 min., and then the pigment was loaded to the polypropylene and mixed for 7 min. Samples were prepared by compression moulding into 3mm and 10mm plates at 190 °C for 2 min. at 30 atm. The cooling process was controlled by transferring the mold to a cold press.

2.5. Mechanical Properties Measurements

2.5.1. Tensile properties

Tensile properties of the dumbbell shaped specimens, of 2mm thickness and 4 mm width, were measured. Both ends of the specimen were firmly clamped in the jaws of the AUTOGRAPH AG-5000B computer control system universal testing machine. The jaws were set to move apart with an elongation speed of 0.5 mm/min. pulling the sample from both ends, and the tensile yield was indicated by a cursor moving along with the stress transfer at pre-break stretch.

2.5.2. Hardness

Hardness was measured by using Wolpert hardness tester HT 2004 machine. A swinging pendulum arrangement was used for applying the impact load. The energy required to break the sample was determined from an indicator that measures how high the pendulum swings after breaking the sample.

2.6. Dielectric Measurements

The AC dielectric properties of polypropylene have been extensively studied (12-13). Polypropylene a non polar material with a low inherent dipole moment, exhibiting dielectric relaxation peaks mainly as a consequence of slight oxidation and/or the presence of small amounts of polar additives (13).

In the present study the dielectric properties of the samples of the prepared polymer composites were measured according to an ASTM D150 test procedure at room temperature using HIOKI 3531Z Hi Tester. The samples were cut into discs of 1cm diameter and 2 - 3 mm thicknesses and coated with silver paste.

Both the dielectric constant ε', and the dielectric loss ε" were measured at room temperature, at different frequencies ranging from 500 Hz to 1MHz and at different pigment loading wt.%.

3. RESULTS AND DISCUSSION

3.1. Adsorption Isotherm

The adsorption isotherm representing the change in the adsorbed amounts (n^s) with equilibrium concentrations (C_e) is shown in Figure (1).

A high increase in the adsorbed amount is detected with the increase of the equilibrium concentrations up to $5x10^{-3}$ mol/l. followed by a lower increase rate. The first step in the isotherm represents the formation of monolayer surface coverage from the oleic acid molecules onto the TiO_2 surface. The second step represents the formation of more than one layer in the TiO_2 surface from oleic acid molecules.

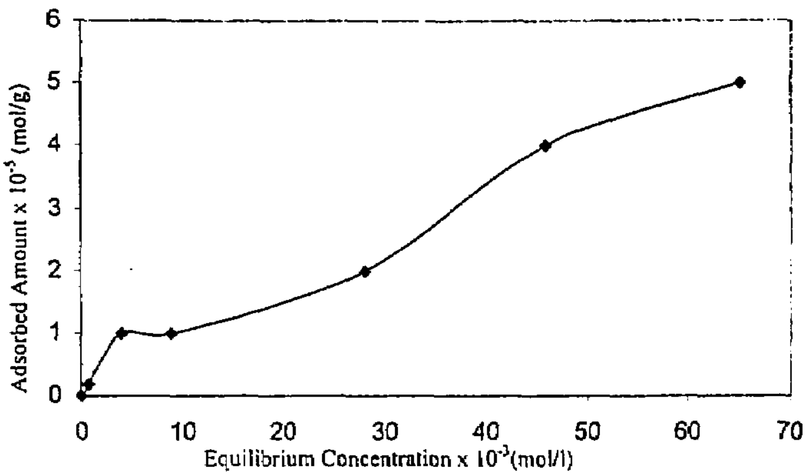

Figure (1): Adsorption isotherm of oleic acid on titanium dioxide surface

3.2. Mechanical Properties

3.2.1. Tensile properties

The tensile yields of the molded sheets were measured and presented in Figure (2). The use of treated or untreated TiO_2 generally resulted in composites with lower tensile yields. Specimens prepared using inorganic treated TiO_2 showed the highest deterioration in the tensile yield values.

Figure (3) shows that the elongation at rupture of the prepared composites was deleteriously affected by the loading of both untreated as well as treated pigments. It is very important to mention that the use of organic treated TiO_2 improves the elongation at rupture relative to untreated TiO_2 at the tested loadings (2, 5, 10, 20, 40 wt %), while the use of inorganic treated TiO_2 caused a deterioration in the elongation properties of the composites relative to the equivalent composites based on the untreated pigment.

As clear from Figure (4), the loading of polypropylene by both untreated and treated pigment induced a decrease in the toughness properties of the prepared samples with the inorganic treated showing the highest decrease and organic treated showing the lowest.

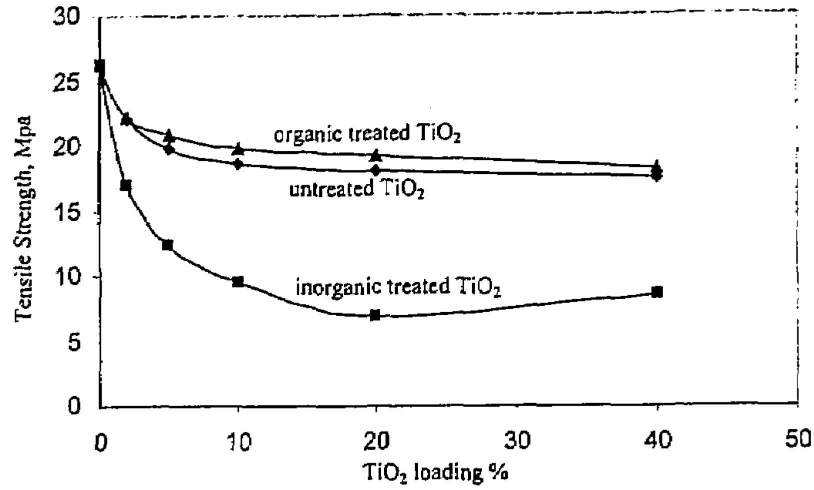

Figure (2): The effect of TiO_2 loading % on Tensile Strength

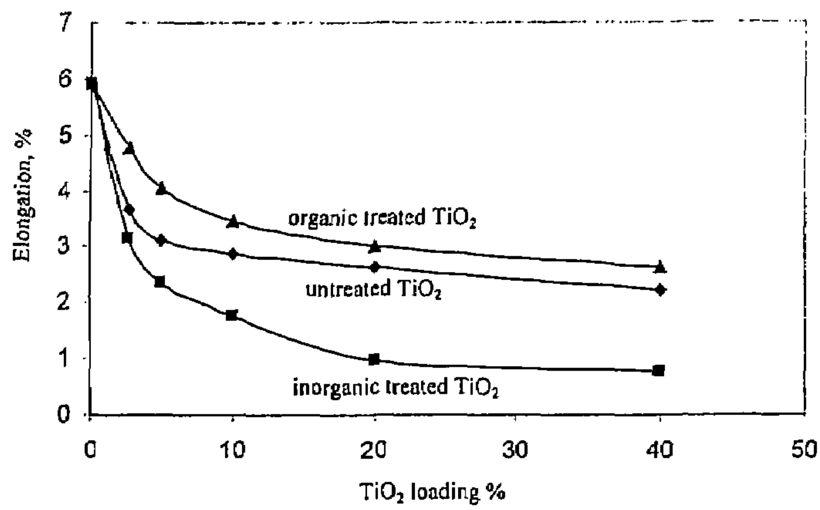

Figure (3): The effect of TiO_2 loading % on Elongation at rupture

On the other hand, it is obvious from Figure (5) that the Young's modulus of the prepared composites has increased by the use of both treated and untreated pigments. It is worth mentioning that the use of inorganic treated TiO_2 increases the Young's modulus relative to untreated TiO_2 at loading of (20 and 40 wt %), while the use of organic treated TiO_2 decreases the young's modulus of the composites relative to the equivalent composites based on the untreated pigment.

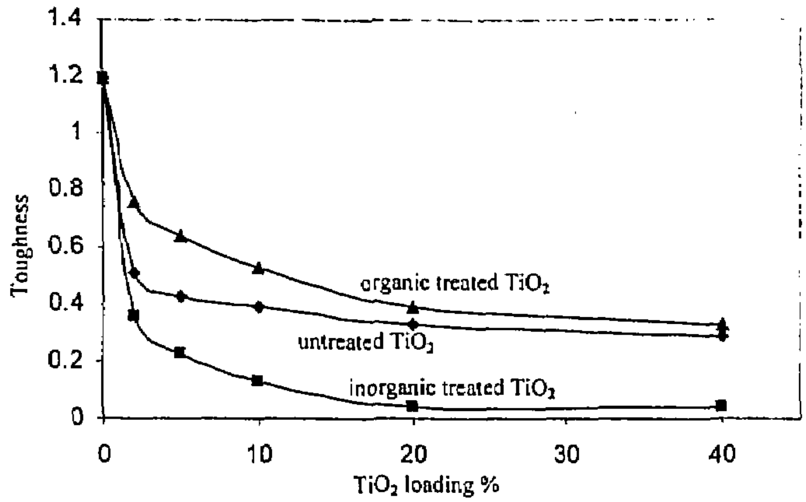

Figure (4): The effect of TiO_2 loading % on toughness

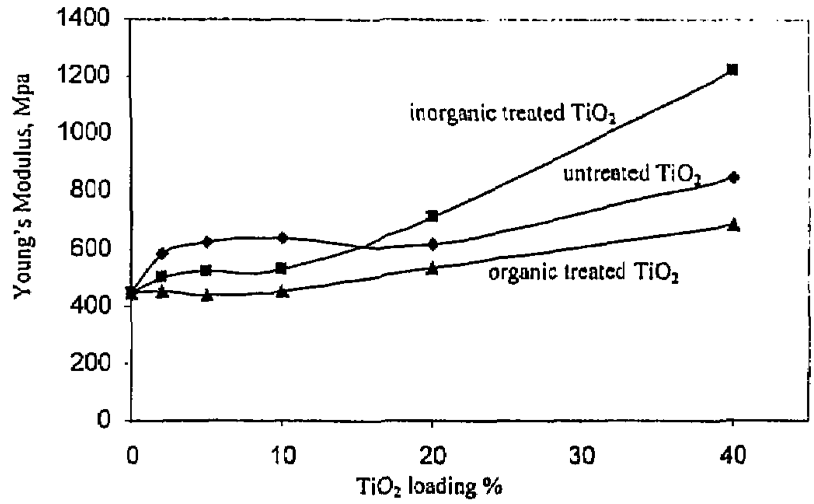

Figure (5): The effect of TiO_2 loading % on Young's Modulus

3.2.2. Hardness

It is clear from Figure (6) that the loading of both untreated and organic treated pigment generally caused an increase in the hardness of the prepared composites. However, the organic treated ones showed a higher increase in the values of the hardness. The use of inorganic treated pigments showed a decrease in the hardness of polypropylene up to 2 wt% above which an increase in the values of hardness was noticeable

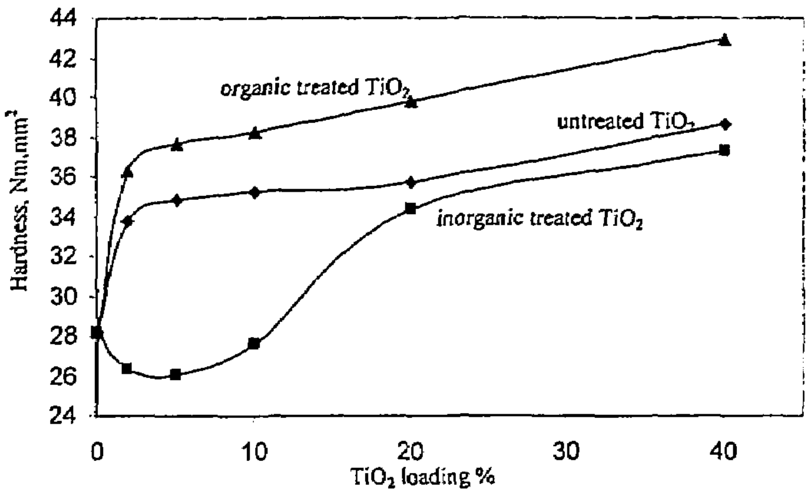

Figure (6): The effect of TiO_2 loading % on hardness

Figure (7) reveals a deterioration of the impact properties of the tested samples with the use of both treated and untreated pigment. The use of untreated TiO_2 acquired the highest impact values among all the pigment-based composites up to 40wt % of pigment. The worst impact values were obtained for polypropylene loaded with inorganic treated TiO_2.

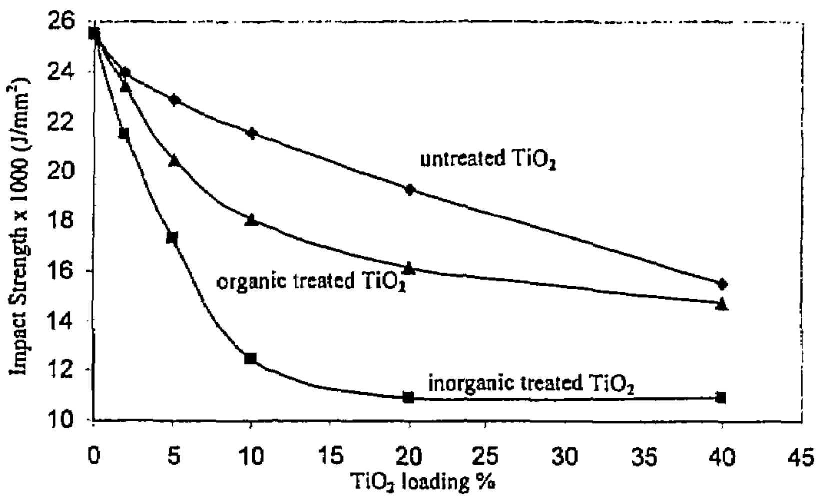

Figure (7): The effect of TiO_2 loading % on impact strength

3.3. Dielectric Properties Measurements

3.3.1. Effect of TiO_2 loading on the dielectric properties of PP

Figures (8) and (9) show the variation of dielectric constant (ε'), and dielectric loss (ε'') respectively with the loading of untreated TiO_2 at different frequencies. An increase in the values of ε' is noticed upon loading of the pigment. This may be attributed to the increase of amorphisity and decrease of crystallinity of the polymer which leads to higher permiativities.

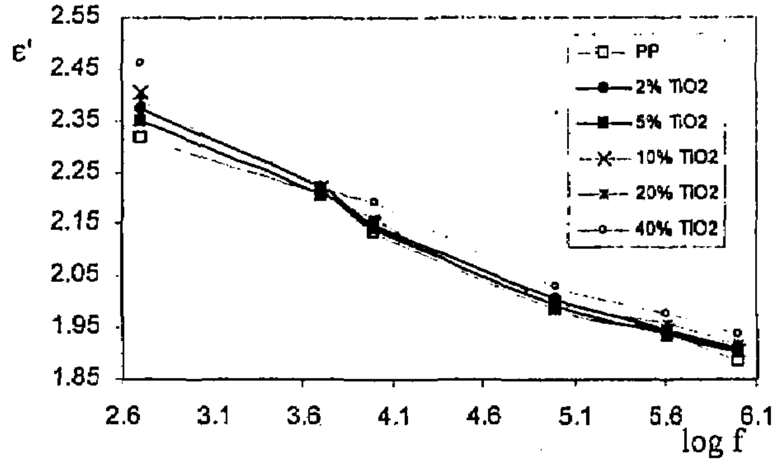

Figure 8: The variation of the dielectric constant (ε') with frequency at different concentrations for the untreated TiO_2 pigment.

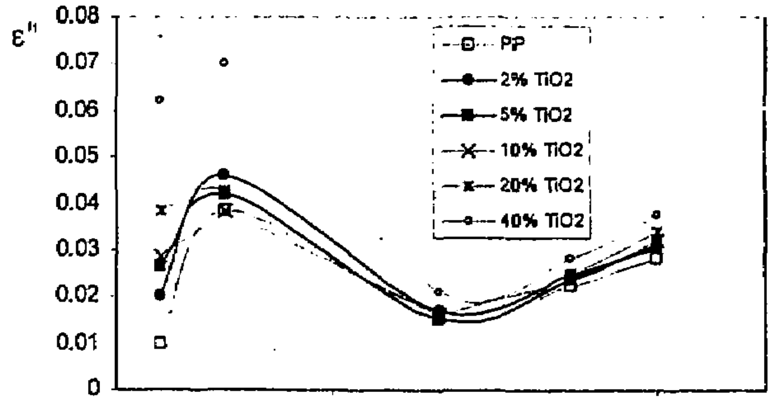

Figure 9: The variation of the dielectric loss (ε'') with frequency at different concentrations for the untreated TiO_2 pigment.

The variation of ε" with frequency followed the same pattern however; all the samples exhibited a maximum at 10000 Hz. A continuous decrease in the amplitude of the maximum is noticed on the increase of TiO2 as a result of increased permiativity.

Figure (10) shows a comparison between the untreated TiO_2 and both types of treatments on the dielectric constant at 10% pigment concentration. It is clear that at lower frequencies the difference in values of ε' is quite small, and it increases with the increase of frequency. The larger change in the value of the dielectric constant occured in case of loading of inorganic treated TiO_2 and the minimum in case of loading of untreated TiO_2.

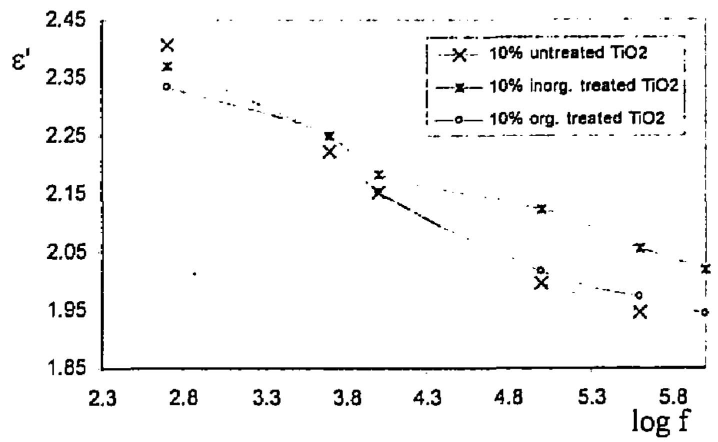

Figure 10: The variation of the dielectric constant (ε') with frequency at 10% concentration for the untreated, inorganic and organic treated TiO_2 pigment.

This may be attributed to the difference in the ability of Na_2SiO_3 and oleic acid in the absorption of water, as the former has a higher affinity to water, which raises the value of ε'.

The same effect was pronounced on the dielectric loss as shown in figure (11) where the three peaks appeared at nearly the same frequency but with different depths. The biggest depth was attributed to TiO_2 treated with Na_2SiO_3 followed by that with oleic acid then by the untreated where the difference between the two latter cases was not significant.

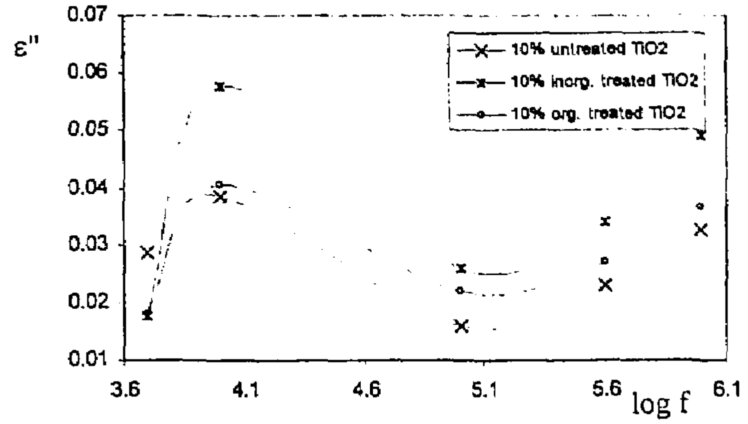

Figure 10: The variation of the dielectric loss (ε") with frequency at 10% concentration for the untreated, inorganic and organic treated TiO_2 pigment

4. CONCLUSION

Measurement of the mechanical and dielectric properties of polypropylene samples loaded by untreated and treated TiO_2 resulted in the following:-

- The loading of treated and untreated TiO_2 resulted in composites with low tensile yields. The samples loaded by the inorganic treated pigment showed the lowest values of tensile yield amongst all prepared samples.
- Elongation at rupture of all samples was deteriously affected by the loading of TiO_2 in general. However, the samples prepared using the organic treated pigment showed the highest elongation at rupture values followed by those loaded with the untreated pigment while the inorganic treated pigment resulted in the least values.
- The loading of polypropylene by both treated and untreated pigments induced a decrease in the toughness of the prepared samples with the inorganic treated showing the lowest values and the organic treated showing the highest values.
- The Young's modulus of the prepared composites has generally increased by the loading of TiO_2. The highest values were obtained upon loading with inorganic treated pigment followed by the untreated while those loaded with organic treated pigment showed lowest modulus values.
- Hardness has witnessed an increase upon loading the samples with TiO_2. The use of organic treated pigment showed the highest values of hardness while the inorganic treaded TiO_2 resulted in the lowest hardness values.

- A deterioration of impact properties was clear in all the samples prepared by loading TiO_2. The use of untreated pigment showed the highest impact strength while the inorganic treated showed the lowest.
- Both the dielectric constant and dielectric loss of the samples decreased with the loading of polypropylene with inorganic pigment.

Thus one could generally summarize the above results in the following three conclusions:-

- Incorporation of inorganic pigments particles increases the Young's modulus and hardness but reduces tensile strength and elongation at rapture, toughness, and impact strength of PP.
- Composites loaded by organic treated pigment showed better mechanical properties compared to those loaded with untreated pigment. They showed higher values of tensile yields, elongation at rupture, toughness, Young's modulus, hardness and impact strength
- Loading of polypropylene with TiO_2 in general resulted in an increase in the electrical properties.

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