

Titanium Dioxide Reinforced Polypropylene Composites: Preparation and Characterization

PP TiO₂ Composites

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Abstract— Titanium dioxide (TiO₂) is a white filler mainly used in the paint industry has been used to reinforce polypropylene via extrusion using twin screw extrusion method. The filler percentage was varied up to 30 %. The composites were characterized using several techniques such as Fourier Transform Infra red spectroscopy (FTIR), differential scanning calorimeter (DSC), Thermogravimetric analysis (TGA), microcalorimetry and mechanical properties.

Keywords— Polypropylene; titanium dioxide; composites; mechanical properties; flame retardancy

I. INTRODUCTION

Polymers have changed the lifestyle of human beings to comfortable zones of unimaginable heights these days. Among the polymers thermoplastics materials has occupied a large share of the commodities available now. Among these polyolefin materials such as polyethylene and polypropylene contribute more than 50% of applications. One can easily assume that polypropylene (PP) is the first polymer to have achieved industrial importance because of the vast variety of products available. The properties of PP are extra ordinary and have been used for many technical applications due to its low cost and high tensile strength to name a few. PP can be converted to different forms too. Among them PP fibers has been used in variety of applications such as upholstery, floor coverings, geotextiles, car industry, automotive textiles, various home textiles, appareletc [1]. There have been a lot of attempts to reinforce PP with rigid fillers in order to reduce cost of production, improve the properties and make useful artifacts [2]. Among the different fillers used such as calcium carbonate, clays, silicas, nanotubes, inorganics etc, titanium dioxide (TiO₂) possess a special mention [3].

It has received a great amount of applications due to its strong oxidizing power of the photogenerated holes, chemical inertness, non-toxicity, low cost, high refractive index and other advantageous surface properties. It is used as a white pigment in paints, plastics, paper and cosmetic products which represent the major end-use sectors of TiO₂. TiO₂ is also added to opacify the plastic materials and improve photodurability. The requirements for TiO₂ are good dispersibility in polymer system, blue undertone, and good heat stability. The consumption of TiO₂ increased in the last few years in a number of minor end-use sectors such as photocatalyst, catalyst support or promoter, gas sensor, in electric and electrochromic devices, and so on [4-6].

The present paper examined the effect of TiO₂ on polypropylene with respect to varying filler loading. TiO₂ is a natural resource found in many countries like India, Saudi Arabia etc. TiO₂ can be incorporated in resin systems by processing dry blending of TiO₂ with powdered resins or added in masterbatch concentrate. The resulting composites may be fabricated by standard thermoplastics processing methods, e.g., injection molding, blow molding, thermoforming, extrusion, rotomolding, etc. The prepared composites will find end use applications in automotive products and in plastic casings requiring outstanding stiffness and/or sound and vibration dampening. The current studies are related to the mechanical and structural aspects of PP with respect to different loading of TiO₂, the filler.

II. EXPERIMENTAL

A. Materials and Methods

Polypropylene pellets, which are commercially available from NATPET (RMLT40), and TiO₂ powder, made available by CRYSTAL Company, Saudi Arabia, were dry-mixed in the desired compositions. Four compositions with TiO₂ content of 0, 10, 20 and 30 wt (%) were prepared using modular co-rotating 24 mm twin screw extruder with an L/D ratio of 25:1 (Haake Rheodrive 16 OS-16kW). The temperature profile was (140-160-180-200-200-210-220-220-230-230°C) and the screw speed was 200 rpm. The obtained strands were pelletized and injection molded using a minijet II (Thermo) at 230°C. The molds were kept at 40°C and air pressure was 7 bar. The samples were designated as PP0, PP10, ... and so on where PP stands for PP and the number stands for the amount of TiO₂ incorporated into the matrix.

The mechanical properties of PP and PP/TiO₂ were studied in tensile stress, and impact tests. Tensile testing was performed using an Instron (3365) universal testing machine of 10 kN load cell. ISO methods 527 and 178 were used respectively for impact study. FTIR measurements were done on Thermo iS5 FTIR with diamond ATR accessory in the range of 400-4000 cm⁻¹. The melting and crystallization behavior of the composites were studied on Shimadzu DSC 60 machine under nitrogen atmosphere. 5 mg of the samples were kept in aluminum pans and the heating rate was 10°C. The temperature profile for the measurements is, 1) first heating to 230°C and 2 minutes hold, 2) cooling to room temperature (27°C) and 2 minutes hold and 3) second heating to 230°C. The first cooling and second heating data were utilized to plot the curves and analysis. Thermogravimetric analysis was performed on HITACHI STA7000 at a heating rate of 10°C/min starting from room temperature to 700°C under nitrogen atmosphere.

Small-scale flammability tests were carried out on the Federal Aviation Administration's Pyrolysis Combustion Flow Calorimeter, and samples were tested in triplicate according to ASTM D7309-07. Samples were 5 mg (± 0.5 mg) in weight and were obtained from the center of the composite plaques detailed below. The heating rate was 60°C/min in an 80 cm³/min stream of nitrogen; the maximum pyrolysis temperature was 900°C. The anaerobic thermal degradation products in the nitrogen gas stream were mixed with a 20 cm³/min stream of oxygen prior to entering the combustion furnace at 900°C. The heat release was determined by oxygen consumption calorimetry. PHRR data were reproducible within $\pm 0.5\%$.

III. RESULTS AND DISCUSSION

A. FTIR results

Figure 1 shows the FTIR curves for virgin PP and the TiO₂ reinforced composites obtained from the ATR measurements. The characteristic peaks of PP were shown at 2949, 2865, 1652, 1455, 1375, 1167, 1016, 972, 840 and 808 cm⁻¹ respectively. On incorporation of TiO₂ the peaks such as 2865, 1652, 1455, 1375 cm⁻¹ were shifted marginally. Moreover, a few peaks of 2837, 1596, 1358, 997 and 898 were seen in the composites showing TiO₂ incorporation. The intensity of the peaks changed based on increase in loading. However, the interaction between the polymer matrix and the filler is minimal as there is no appreciable change in the characteristic peaks for PP and TiO₂ in the composites.

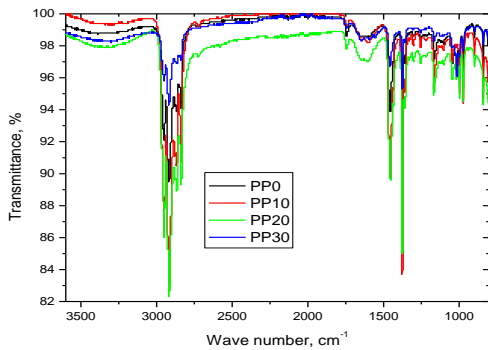


Figure 1: FTIR spectra of PP/TiO₂ composites

B. Mechanical properties

Mechanical properties of the composites are very important to assess the suitability of applications for the prepared composites. In this regard, stress-strain measurements and impact testing were carried out for the composites.

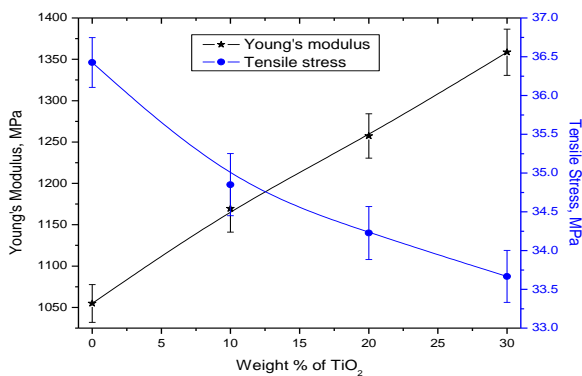


Figure 2: Tensile properties of PP TiO₂ composites

a) Stress-strain measurements

Figure 2 shows the behavior of Young's modulus and tensile stress with respect to filler loading. Tensile stress shows a decrease as the weight percent of TiO₂ increases. In this static test, and due to weak interaction between TiO₂ fillers and PP materials, the matrix is dominating and therefore the TiO₂ increase is not strengthening the system. The modulus increased as the TiO₂ weight present increase. This is due to the system which becomes more elastic as an absence of interaction between TiO₂ and PP matrix materials.

b) Theoretical modeling of Young's modulus

Young's modulus can be modeled by using different mathematical equations. There are a number of parameters which affect the mechanical properties of particulate filled polymer composites especially filler orientation, filler/matrix adhesion and filler shape. A number of equations were developed to predict the properties based on filler volume percentage and several reports are available in the literature [7-9].

The theories proposed to model Young's modulus can be classified based on the nature of the matrix and reinforcements. The matrix can be non-rigid or rigid ones. The commonly used equations are those developed by Einstein, Guth, Mooney, Kerner and Nielson [10-14].

Einstein and Guth equations

These equations are mainly used for the theoretical calculations of the properties of particulate (spherical) reinforced polymer composites. According to the Einstein equation

$$M_c = M_m(1 + 1.25V_p)$$

Where M_c and M_m are the Young's modulus of composite and matrix, respectively, and V_p is the particle volume fraction. Einstein's equation is applicable only for materials filled with low concentrations of non-interactive spheres. Einstein's equation implies that the stiffening or reinforcing actions of filler is independent of the size of the filler particles. This equation shows that the volume occupied by the filler is independent of the size of the filler particles and can be considered as the important variable in determining Young's modulus of the composite. The equation also assumes that filler is more rigid than the matrix.

Guth equation

$$M_c = M_m(1 + 1.25V_p + 14.1V_p^2)$$

Guth's equation is an expansion of Einstein, to account for the inter-particle interactions at higher filler concentrations.

Kerner equation

Young's modulus of spherically shaped particulate-filled polymer composites is given by Kerner's equation

$$M_c = M_m \left[1 + \frac{V_p 15(1 - \sigma_m)}{V_m(8 - 10\sigma_m)} \right]$$

Where V_m is the matrix volume fraction and σ_m is the Poisson's ratio of the matrix.

Quemeda equation

$$M_c = M_m \frac{1}{(1 - 0.5KV_p)^2}$$

where K is a constant normally 2.5. This variable coefficient is introduced to account for the inter-particle interactions and differences in particle geometry.

Thomas equation

$$M_c = M_m(1 + 2.5V_p + 10.05V_p^2 + 0.00273e^{16.6V_p})$$

Thomas equation is an empirical relationship based on the data generated with dispersed spherical particles.

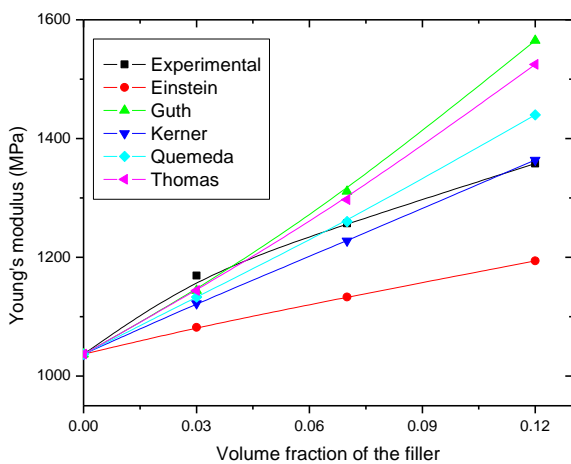


Figure 3: Theoretical modeling of Young's modulus of the composites

The experimental results were compared with theoretical predictions and the plots are given in figure 3. All these predictions assume that matrix and filler have no appreciable degree of interaction. The experimental results at lower filler loading matches with Quemeda equation and 30 wt% matches with Kerner model. Both the models were predicted taking into account of the inter-particle interaction too. The tensile modulus for higher loading of fillers is more similar to Kerner equation which considered the particle geometry too. Owing to the spherical structure of TiO₂, the chances of inter-particle interaction is more at higher loadings which contributed to the decrease in modulus in that region.

c) Impact tests

Impact tests were conducted as per ASTM/ISO standards. For each sample, 5 specimens were used and the average is given in the tables as the numerical results. Both unnotched and notched samples were tested. The obtained results are given in tables 1 and 2 respectively.

TABLE I. UNNOTCHED SAMPLES; WIDTH: 10 MM AND THICKNESS: 4 MM; IMPACT VELOCITY: 3.03 M/S

Sample	Energy (J)	Resilience (J/m)	Absorption energy (%)
PP	3.661 ± 0.526	997.2 ± 43.1	79.74 ± 8.2
PP + 10% TiO ₂	2.997 ± 0.408	824.5 ± 49.6	69.88 ± 8.7
PP + 20% TiO ₂	2.502 ± 0.412	797.6 ± 41.4	63.78 ± 7.3
PP + 30% TiO ₂	2.286 ± 0.347	721.7 ± 39.6	55.695 ± 5.9
PP + 40% TiO ₂	1.936 ± 0.272	687.6 ± 38.4	48.72 ± 4.3

TABLE II. NOTCHED SAMPLES; WIDTH: 8 MM AND THICKNESS: 4 MM; IMPACT VELOCITY: 3.03 M/S

Sample	Energy (J)	Resilience (J/m)	Absorption energy (%)
PP	0.1425 ± 0.012	35.55 ± 4.7	2.84 ± 0.31
PP + 10% TiO ₂	0.1465 ± 0.019	36.565 ± 6.5	2.925 ± 0.29
PP + 20% TiO ₂	0.1465 ± 0.015	37.09 ± 5.3	2.89 ± 0.38
PP + 30% TiO ₂	0.143 ± 0.015	35.23 ± 5.7	2.76 ± 0.37
PP + 40% TiO ₂	0.1455 ± 0.0098	33.34 ± 3.8	2.71 ± 0.3

As the TiO₂ weight percent increases, the impact strength decreases. This behavior is expected because the PP is incompatible with TiO₂ as the phase is non-polar, hydrophobic and has low surface energy for PP while polar, hydrophilic and high surface energy for TiO₂. As a composite system under impact strike, the TiO₂/PP interface is weak and thus creating stress concentration points or like voids and therefore the load is not being transmitted from PP to TiO₂ to enforce the system.

It is clear that the impact strength decreases with filler addition. This is mainly due to the reduction of elasticity [15,16] of material due to filler addition, thereby reducing the deformability of matrix and in turn the ductility, so that the composite tends to form a weak structure. An increase in concentration of filler reduces the ability of matrix to absorb energy and thereby reducing the toughness, so impact strength decreases.

C. Thermal properties

Figures 4 and 5 show the heating and cooling curves for the composites from DSC study. The heating curves show similar patterns for virgin PP and the composites. It can be seen from the curves that the melting point of the composites increases upon TiO₂ addition. The virgin PP has a melting point of 162°C and the TiO₂ addition slightly increases it to 164°C. In short, the melting point of the composites hasn't improved much on addition of the present filler.

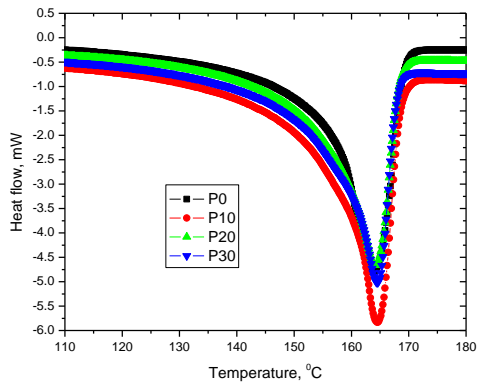


Figure 4: Heating curves of PP TiO₂ composites

From figure 5, the crystallization behavior of the composites can be analyzed on addition of TiO₂ filler to PP. The crystallization temperature for PP is 117°C. The composites show a gradual increase in crystallization temperature and the increment is worth approximately 8°C for 20wt% composites. This increase in crystallization temperature can be attributed to the nucleation effect of the added filler in the system.

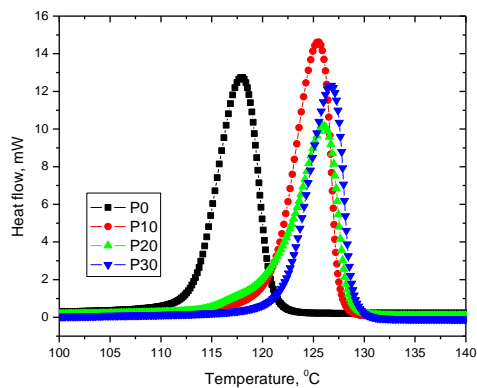


Figure 5: Cooling curves of PP TiO₂ composites

The thermogravimetric analysis of the composites was done to understand the effect of filler on the thermal degradation of the polymer materials. Figure 6 shows the thermograms of PP and the composites and a remarkable change in the thermal stability can be observed in them. The onset of degradation for PP is at 350°C and on addition of filler it has been moved to higher temperatures, close to 420°C for the different composites. One can argue that the composites became thermally stable due to the good dispersion of the spherical particles of TiO₂. The maximum degradation temperature of the virgin polymer and the composites were 457, 468, 475 and 479°C respectively. The filler addition increased the maximum degradation temperature by 11-22 °C for 10-30 wt% which is a remarkable improvement and can be utilized for exterior applications for these composites. This improvement in the thermal stability is believed to be due to the good dispersion of the filler in the matrix. The char residue showed consistent results with respect to the percentage filler loading as TiO₂ do not degrade at 500-600°C region.

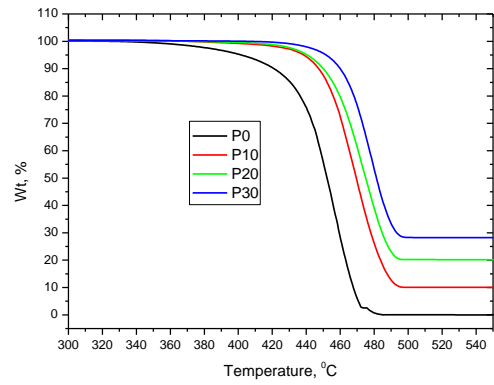


Figure 6: Thermograms of PP TiO₂ composites

The flammability of composite samples was measured using a pyrolysis combustion flow calorimeter, also known as a microscale combustion calorimeter (MCC). Figure 7 shows the heat release rate (HRR) curves of the composites with respect to temperature.

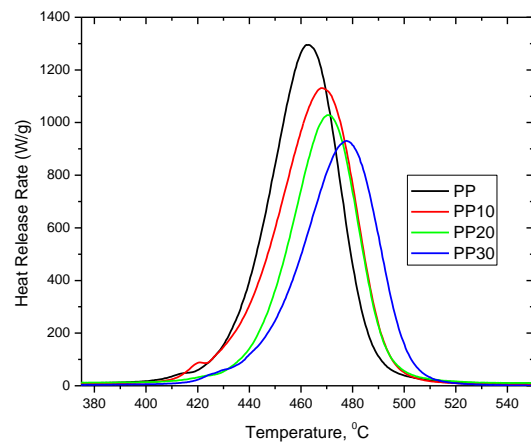


Figure 7: Heat release rate behavior of PP TiO₂ composites

All samples present a single peak of HRR between temperatures of 462°C and 480°C. The abstracted primary parameters obtained by MCC are heat release capacity (HRC), peak heat release rate (PHRR), total heat release (THR), and reduct-MCC (Table 3). The HRC is defined as the ratio of maximum heat release rate to the constant heating rate in the test. This is one of the measures of the fire hazard of a material [17, 18]. It is seen from the table that the HRC is influenced by the addition of TiO₂ in the polymer composites and is found to decrease with the increase with respect to loading in the composites. In fact, the thermal conductivity of the filler is greater than that of the polymer matrix. Thus the addition of TiO₂ assists in conducting the heat throughout the polymer matrix. With the increase in filler loading in the polymer matrix, this heat conduction throughout the matrix is increased, which minimizes the localized decomposition. This leads to the decrease in HRC with the increase in filler addition in the present composites [19].

TABLE III. MICROCALORIMETRY DATA OF PP TiO₂ COMPOSITES

Sample	HRC(J/gK)	PHRR (W/g)	THR (kJ/g)	Reduct-MCC (%)
PP	1358 ± 5	1297 ± 6	47.69 ± 0.17	-
PP + 10% TiO ₂	1230 ± 4	1132 ± 5	48.06 ± 0.13	13
PP + 20% TiO ₂	1209 ± 4	1029 ± 5	47.92 ± 0.11	21
PP + 30% TiO ₂	1173 ± 4	933 ± 5	47.79 ± 0.16	28

PHRR is one of the most important parameters to characterize the fire hazard (20). The PHRR decreases with the increase in TiO₂ loading in the composites. However, the total heat release, which is the integral of the HRR curve over the duration of the experiment, increases marginally with the increase in TiO₂ loading in the composites. Reduct-MCC (%) is the percent deduction in PHRR of the composites with respect to neat PP. Table 3 shows that the percent reduction in PHRR increases with the increase in TiO₂ loading in the composites.

IV. CONCLUSION

Based on the structural analysis and thermo-mechanical analysis of the TiO₂ incorporated PP composites one can conclude that the extrusion followed by injection molding is a good method to prepare polymeric composites. Here the material used are from natural resources of Saudi Arabia and it is potential has not been exploited yet. Thermal stability showed appreciable improvement as evidenced from thermogravimetry and microcalorimetric studies. The mechanical properties did not show drastic improvements, even though; TiO₂ is believed to have higher inherent properties such as high elastic modulus and thermal stability. This behavior is believed to be due to the less interaction between the polymer matrix and the filler corroborated by the IR results. Therefore, suitable modification of TiO₂ to form better bonding between the polymer and filler is recommended as future prospect.

V. REFERENCES

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