



Investigation of Properties ZnO, CuO, and TiO₂ Reinforced Polypropylene Composites

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Nanotechnology is a multidisciplinary science and its popularity is increasing day by day. Nanotechnology could be applied to processing of many materials. Textile is one of such applications. Textile products which are produced by nanotechnology are more functional and superior than other products. It can improve material finishing, product processing or yarn production. Some examples of Nanotechnology mediated improvement are high strength and electrical properties. Polymer matrix nanocomposites are suitable for textile industry applications. For last several years lots of studies have focused on polymer matrix nanocomposites. Polypropylene (PP) is example of one of the polymers, being engaged for such purpose. Polypropylene fibers have high mechanical strength and light weight with widespread usage starting from automotives to packaging. In the light of these information on this study polypropylene was used as matrix and TiO₂, ZnO and CuO used as reinforcement. In our study eighty five dtex thickness nanocomposites were produced by melt-mixing. According to results 0.5% CuO/PP nanocomposites increased electrical properties by 13%. TiO₂/PP and ZnO/PP composites showed better mechanical properties than CuO/PP samples. When test results were evaluated together, considered reasons such as ease of application and production, accessibility of raw materials, it was decided that 0.5% TiO₂/PP nanocomposite is most suitable.

Keywords: Electrical resistance, Fiber, Melt-mixing, Polymer nanocomposites, Reinforcement

Introduction

Plastic materials have increased their usage ratio day by day with good physical and chemical properties and also technological development. These properties are advantages of polymers for preferring industrial applications. When glass fiber, graphite or metal oxide reinforcements are added on polymer surface, the products get more functional advantages than conventional plastics. These materials are named as composite and they have started to replace metal, ceramic and glass materials. They can be used in many industrial applications.^{1,2}

With the improvement of nanotechnology, nanocomposite materials are used widely and production ratio are rising. Nanocomposite described as one of phases under 100 nm size multiphase material system. Nanocomposite materials have high area/volume ratio because of their very small size filler particles. Nanocomposite has some advantages such as chemical corrosion resistance, mechanical strength, easy production, and being light weight. These excellent properties have widened their area of usage.³

There are many methods of production of nanocomposite materials. The most populars are in-situ polymerization, melt mixing or melt blending, and solution mixing. Most suitable method is melt mixing. Melt blending is the method for preparing polymer nanocomposites. Firstly, the polymer is melted and combined with the desired amount of the nanoparticles using an extruder. Alternatively, polymer is dry mixed with the reinforcement materials, then heated in a mixer and subject to shear sufficient to form the desired polymer nanocomposites. Melt blending has great advantages over in situ polymerization or polymer solution mixing method. Melt blending is environmentally benign due to the absence of organic solvents. Due to its potential in industrial applications, the melt blending process has become popular.⁴ Also, this method is more economical than others.⁵ Such products bear properties such as antibacterial, high mechanical strength, high UV strength and non-flammability.^{6,7}

Polymers are widely used in nanocomposite production with their excellent properties such as flexible structure, easy production steps, good shaping, and mechanical behaviours.⁷ After some

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investigations about nanocomposites focusing on polymer to be used as matrix phase, there is significant improvement in polymer's quality even if very small amount of nanoparticles is added. Reinforcing nanoparticles are in nanoscale and their area/volume ratio are very high so that interaction between phases are wide.⁸ Polymer matrix nanocomposites are preferred more over metal and ceramic matrix composites.⁹ Polymer nanocomposites are produced by melt fiber spinning. On this method nanoparticles are added into polymer matrix. It is possible to produce composites with more strength and functional properties with the help of polymer matrix nanocomposites.¹⁰

Polypropylene is one of the most important commercial polymer. It is widely used in packaging, automotive, cable production, daily plastic materials etc.¹¹ It has high strength and thermal properties at room temperature. It has high chemical resistance value too.^{12,1} The purpose of using polypropylene (PP) in textile industry is to provide functionality to textile products. It's fiber structure is appeared as wax and flat. Polypropylene fibers are used in production of carpets, fabrics and technical textile products. They are preferred for high strength, low manufacturing cost and chemical resistance.¹² Physical properties of Polypropylene is presented in Table 1.

Fiber is one of the main raw materials of textile industry and it can be obtained from many materials. Cotton fiber is produced from natural sources and the most usage ratio fiber in industry, but alternative fibers have become more popular these days. Polymer based fibers are one of these type fibers and they strengthened with reinforcing materials to obtain functional textile products. Decreasing production problems and developing innovative products are main advantages of fiber matrix polymer nanocomposites.¹⁴

It is important to note that nanoparticles imparts its properties to composite material and then composite gets more functional and stronger with the help of reinforcing material. TiO₂ which shows excellent properties is one of most preferred reinforcing material in nanocomposite applications. It shows

photocatalytic property, high UV strength, hardening etc. For mechanical strength applications when TiO₂ is used, the product's properties improve significantly. ZnO has UV strength property similar to TiO₂. At the same time, flexible structure of ZnO helps to increase elongation at break of composite. Also, ZnO particles improve mechanical behaviour. CuO is metal oxide which shows excellent electrical conductivity and studies about CuO are generally composite's antistatic behaviour. When CuO is added to matrix phase, electrical properties are improved.¹⁵ General properties of nanoparticles are given in Table 2.

Materials and Methods

In this study polypropylene was obtained as granule form. Melt flow index of granule is 20 g/10 min, melting point is 166°C and fiber spinning temperature was 205°C. CuO, TiO₂ and ZnO were used as reinforcing materials and supplied from Sigma-Aldrich. ZnO particles (CAS number: 1314-13-2) are 98% purity and have an average 40 nm particle size. CuO (CAS number: 1317-38-0) has approximately 29 m²/g surface area. Its purity is >96% and 45 nm mean particle size. TiO₂ (CAS number: 12188-41-9) is anatase phase and 35 nm mean particle size. Production process of polypropylene nanocomposites is illustrated in Fig. 1.

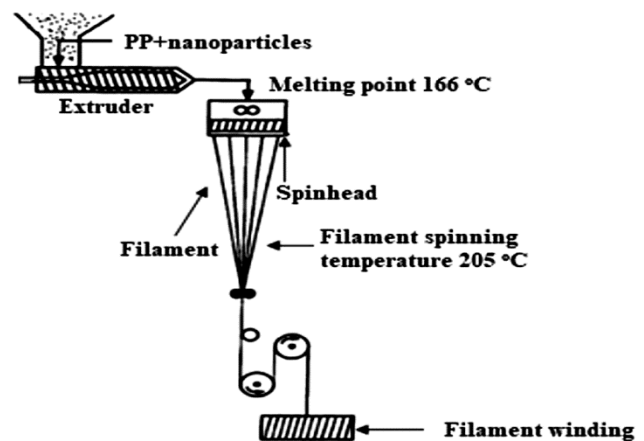


Fig. 1 — Production scheme for polypropylene nanocomposites¹⁶

Table 1 — Physical properties of Polypropylene¹³

Properties	Value
Melting point (°C)	160–175
T _g (°C)	40
Density (gr/cm ³)	0.9
Degradation temperature (°C)	328–410

Table 2 — Some properties of nanoparticles⁸

Parameters	TiO ₂	ZnO	CuO
Melting point (°C)	1843	1975	1975
Molecular weight (g/mol)	79.94	81.39	79.545
Density (g/cm ³)	4.23	5.6	6.31
Dielectric constant	85	8.5	18.1
Size (nm)	35	40	45

Melt fiber spinning was used for obtaining fiber from polypropylene granules within the study. Firstly, 1 mm thick samples were produced by twin screw extruder. During production of composite plate polypropylene granules were fed to extruder at 80 cycle/min speed and with 0.1%, 0.3% and 0.5% weight ratio of reinforcement respectively. These ratios were selected according to some studies. Prasert *et al.* worked on ZnO/PP nanocomposites and reinforcement weight ratio was 0.5%, 1% and 2% wt.¹⁷ All of composite samples were processed for filament spinning after extruder step. Composites were melted for 10 min at 170°C and 60 rpm mixing speed followed by filament spinning. Samples were sent spinhead with pressure, and filament spinning was started at 205°C. Monofilaments were 85 dtex thick. These samples had some codes as presented in Table 3 for characterization.

After production of filaments, characterization of composite samples was done. X-Ray Diffraction Analysis (XRD) was performed for investigation of microstructure of samples. For testing of thermal properties Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) were evaluated successfully. Mechanical properties of samples were performed with elastic modulus and tensile strength. Finally, antistatic properties of composites were determined with electrometer. Mechanical tests were repeated four times and average results were used for stability.

Results and Discussion

XRD analysis was performed for determining crystallinity and microstructure of composite samples since polypropylene fibers generally have crystal structure.¹⁴ It is clear from the XRD analysis (Fig. 2) that polypropylene is semi-crystal in structure. It has six distinctive picks at $2\theta = 15.00^\circ$, 18.00° , 19.00° , 21.00° , 25.00° and 27.00° ranges. When XRD test

results of the nanocomposites are examined it is seen that they are similar to polypropylene XRD graphs. All composites have given picks at 2θ as same as polypropylene. According to graphs reinforcement particles given no effect on polypropylene's characteristic crystal structure and so, nanocomposite's structure remained same as PP structure.

TGA analysis was performed for analyzing thermal properties of nanocomposite samples. Analysis was done with 10 mg of each samples and nitrogen as inert gas. Maximum temperature observed was 500°C. During analysis heating rate remained constant at 15°C. TGA results are illustrated in Fig. 3.

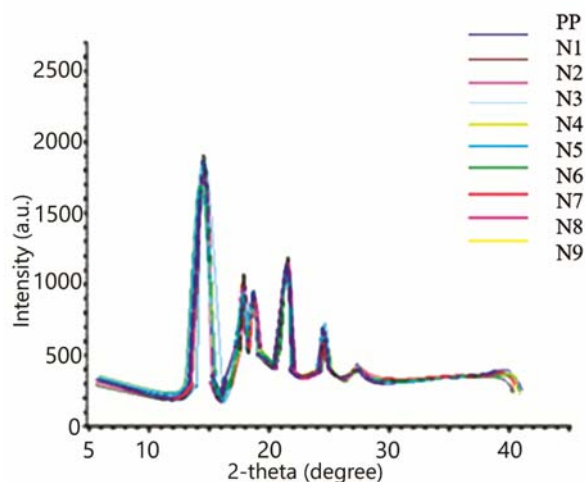


Fig. 2 — XRD results of composite samples

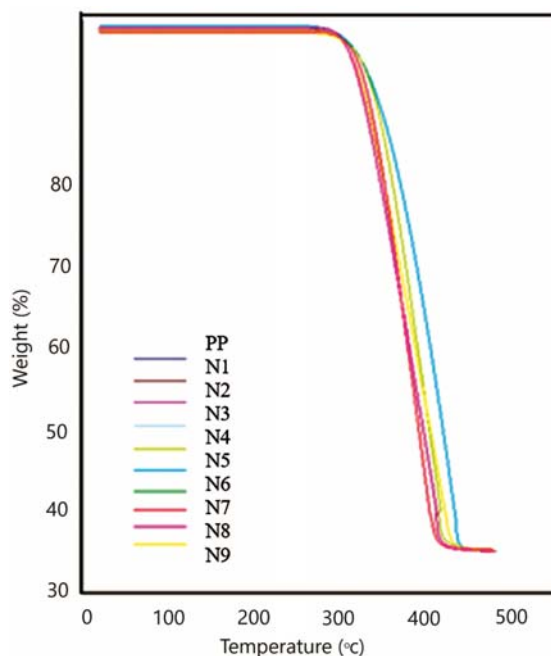


Fig. 3 — TGA results of composite samples

Table 3 — Composite samples and their codes

Sample	Code number
PP/0.1 TiO ₂	N1
PP/0.3 TiO ₂	N2
PP/0.5 TiO ₂	N3
PP/0.1 CuO	N4
PP/0.3 CuO	N5
PP/0.5 CuO	N6
PP/0.1 ZnO	N7
PP/0.3 ZnO	N8
PP/0.5 ZnO	N9

The results of analysis have given that the graphics of samples and virgin polypropylene were remained same. All of samples and polypropylene curves overlapped indicating that degradation temperature of samples and virgin polypropylene gave the same value. It is clear that the reinforcing materials did not affected degradation temperature of virgin polypropylene. This is because of low weight ratio of reinforcement materials. Compared with literatures about same matter, it was clearly seen that nanoparticle reinforcement is not affected polymer's degradation temperature. The test results obtained from the studies are assisted with literature. Kumar *et al.* studied on injection moulded PP/TiO₂ composites and found that TiO₂ increased degradation temperature of original PP. This was because weight ratio of TiO₂ was 5%, 10%, 15%, 20%. These ratios provided better interfacial interactions.^{18,4}

Analysis on endothermic cycles melting point of polypropylene and composite samples were examined by DSC test. As seen in Fig. 4, melting point of virgin polypropylene is read as 166°C. When melting point of composite samples was investigated there was no change from polypropylene's melting point. All of samples' melting point was read as 166°C. Exothermic cycle of samples was given that reinforcing nanoparticles caused decreasing percentage crystallinity in virgin polypropylene. For homogeneous dispersing of reinforcing particles, it was appropriate to decrease the percentage of crystallinity of polypropylene. The results of DSC curves are given in Table 4.

Erem *et al.* studied with virgin PP and TiO₂ reinforcement and applied DSC analysis on composite

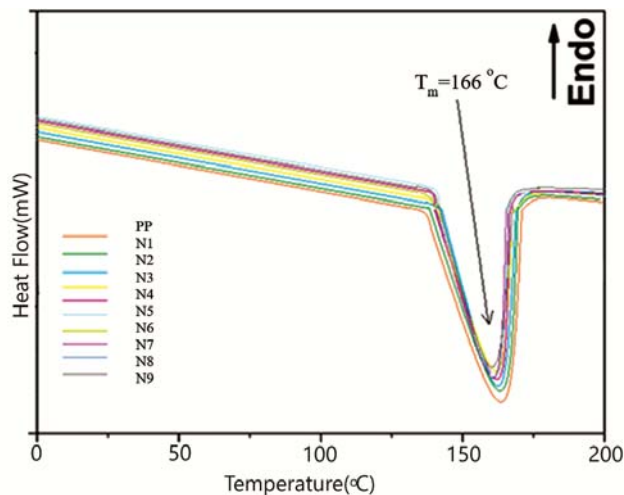


Fig. 4 — DSC results of composite samples.

samples. According to the results, TiO₂ increased heat conduction and cristallinity temperature of samples changed significantly. Altan *et al.* studied PP also and they reported that nanoparticles decreased cristallization temperature of samples from DSC curves. Our results are suitable for literture.^{13,19}

According to results of mechanical strength tests of samples as presented in Table 5; elasticity, elongation at break, and tensile strength of virgin polypropylene increased. TiO₂ and ZnO particles contributed to improve mechanical properties of composites significantly. 0.5% TiO₂ reinforced N3 coded composite sample's tensile strength value is more than 5% of virgin polypropylene. Wanga *et al.* performed tensile strength test on TiO₂/PP composites and results showed that TiO₂ filled samples gave better mechanical properties.²⁰ The peak was achieved with CuO reinforced composite. N4, N5 and N6 coded samples had more than 7.5% value of polypropylene's tensile strength. Tensile strength of the composite is important for industrial applications.²¹ CuO reinforcement provided significant mechanical strength to composites. Elongation at break test showed that ZnO particle provided most significant increase. ZnO is more flexible structure than TiO₂ and CuO so that it can

Table 4 — Phase change characteristic of samples and virgin PP

Samples	T_{m-o} (°C)	T_{m-p} (°C)	χ (%)
PP	166	121	46
N1	166	121	44
N2	166.1	122	44
N3	166.1	122	43
N4	166.1	122	44
N5	166.2	123	44
N6	166.2	123	44
N7	166.2	123	44
N8	166.2	124	124
N9	166.3	124	124

Table 5 — Mechanical experiment results of composite samples

Samples	Tensile strength (MPa)	Elongation at break (%)	Elastic modulus(MPa)
PP	44.6	15.17	790
N1	44.86	15.03	978
N2	45.24	14.96	1130
N3	46.93	14.39	1320
N4	44.12	15.03	853
N5	46.07	14.83	912
N6	47.98	14.66	1123
N7	45.67	15.94	993
N8	46.38	16.24	1215
N9	47.24	16.82	1400

Table 6 — Resistance measurements of composite samples

Sample	Electrical resistance, R_s (ohm)
PP	3.6×10^{14}
N1	1.02×10^{14}
N2	6.74×10^{13}
N3	2.12×10^{13}
N4	9.78×10^{13}
N5	3.72×10^{13}
N6	7.84×10^{12}
N7	1.96×10^{14}
N8	7.42×10^{13}
N9	1.24×10^{13}

give flexibility to nanocomposites and increased their elongation at break. Oppositely, TiO_2 and CuO are tough and hard structure and their composites get hardly when TiO_2 and CuO reinforced was increasing in matrix surface, composites became more fragile.

Elastic modulus of composites achieved maximum value with 0, 5% ZnO reinforced N9 coded composite sample. It was slow rising on elastic modulus with CuO and TiO_2 composites. The reason for this was thought that CuO and TiO_2 have high hardness values.

The reason of significant improvement of mechanical properties in composites is that nanoparticles get dispersed homogeneously on matrix surface and interactive interface between matrix and reinforcements. Mechanical properties of matrix phase have big impact on the composite's performance.

Electrical resistance of composites is given in Table 6. After increase in electrical resistance of composites, increased antistatic properties were observed. Resistance values of samples were measured by Keithley 6517-B model electrometer. Electrical resistance of all composites decreased. Polymers are nonconductive materials and their surface resistance are high. Polypropylene's resistance was measured as 10^{14} ohm. When composite sample's resistances are compared, significant decrease in CuO reinforced composites is observed. Copper is a metal with high electrical conductivity. Even it added too low weight ratio. Conductivity of composites increased. In ZnO and TiO_2 composites electrical properties improved slowly. Both of reinforced particles gave same effect to composite samples.

Conclusions

When composite sample's thermal properties were examined, it was seen that polypropylene properties has not changed with addition of reinforcement

particles. The nanocomposites have shown improved mechanical properties than virgin polypropylene. From overall results, composite materials with TiO_2 can be considered as the best. Especially, filaments that need mechanical resistance, TiO_2 particles can be used as successful PP/ TiO_2 composites. However, from the view point of ease of application and production, accessibility of raw materials, N3 coded nanocomposite could be considered as most suitable. Future scope of this study is to understand microstructure details. For this, Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM) analysis will be performed.

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