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A Review on Polymer Tio2 Nanocomposites

Satyajeet Chaudhari, Tasnim Shaikh and Priyesh Pandey
Department of Textile Engineering, the Maharaja Sayajirao University of Baroda, Gujarat, India.

Abstract
Nano materials are manufactured through different techniques. The small length scales present in nanoscale systems directly influence the energy band structure and can lead indirectly to changes in the associated atomic structure termed as quantum confinement. Conventional polymer composites usually reinforced by micrometer-scale fillers into polymer matrices involve compromises in properties. Nanoscale filled polymer composites or polymer nanocomposites gave a new way to overcome the limitations of traditional counterparts. Polymer nanocomposites are synthesised through different techniques depend on their nature. Stereoregular polypropylene is produced due to its industrial use. The properties of polypropylene-TiO2 nanocomposite material improved compared to polypropylene in terms of antibacterial, mechanical, UV protection, thermal and hydrophilicity properties.
Keywords: polypropylene, nanocomposite, TiO2, antibacterial, UV, thermal, hydrophilicity.

I. Introduction

The small length scales present in nanoscale systems directly influence the energy band structure and can lead indirectly to changes in the associated atomic structure. Such effects are generally termed as quantum confinement. Two general descriptions that can account for such size-dependent effects in nanoscale systems are: changes to the system total energy and changes to the system structure[1]. As the particle size decreases, its total surface area per unit volume increases. Therefore for the nano size particle, which has less than 100 nm size shows drastic rise (figure 1).

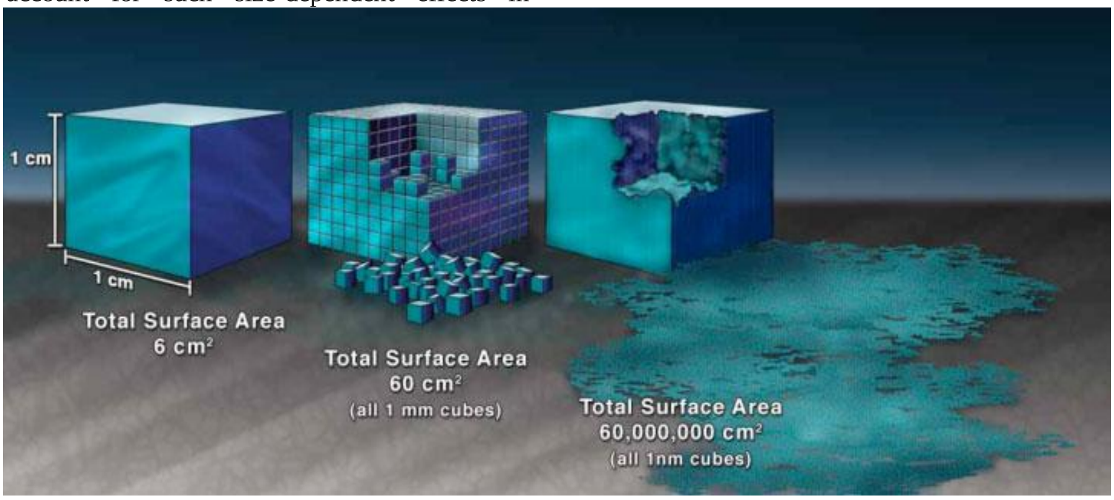

Figure 1: Effect of the increased surface area with nanostructured materials

Courtesy by http://www.nanowerk.com[2].

These nano materials can be applied to the textile in two principal ways. First one is coating of textile surfaces by polymer nanocomposite formulation. This approach confers combined functional properties to textile surfaces and also allows a reduction in the weight content of additives. Nano materials can be applied to fabric surface by spray, transfer printing and padding. Some possibilities of textile functionalization using nano materials are shown in figure 2[3-7].

The second approach is melt spinning of polymer and nano materials to spin yarns or fibres which can be subsequently woven, knitted or used in nonwovens. Many polymer nanocomposites have been manufactured using polyester, polypropylene, polyethylene, nylon as polymers with various nanoparticles like gold, silver, clay, silica, alumina, calcium carbonates and titanium dioxide as fillers. Their various properties have been studied by many researchers[8-13].

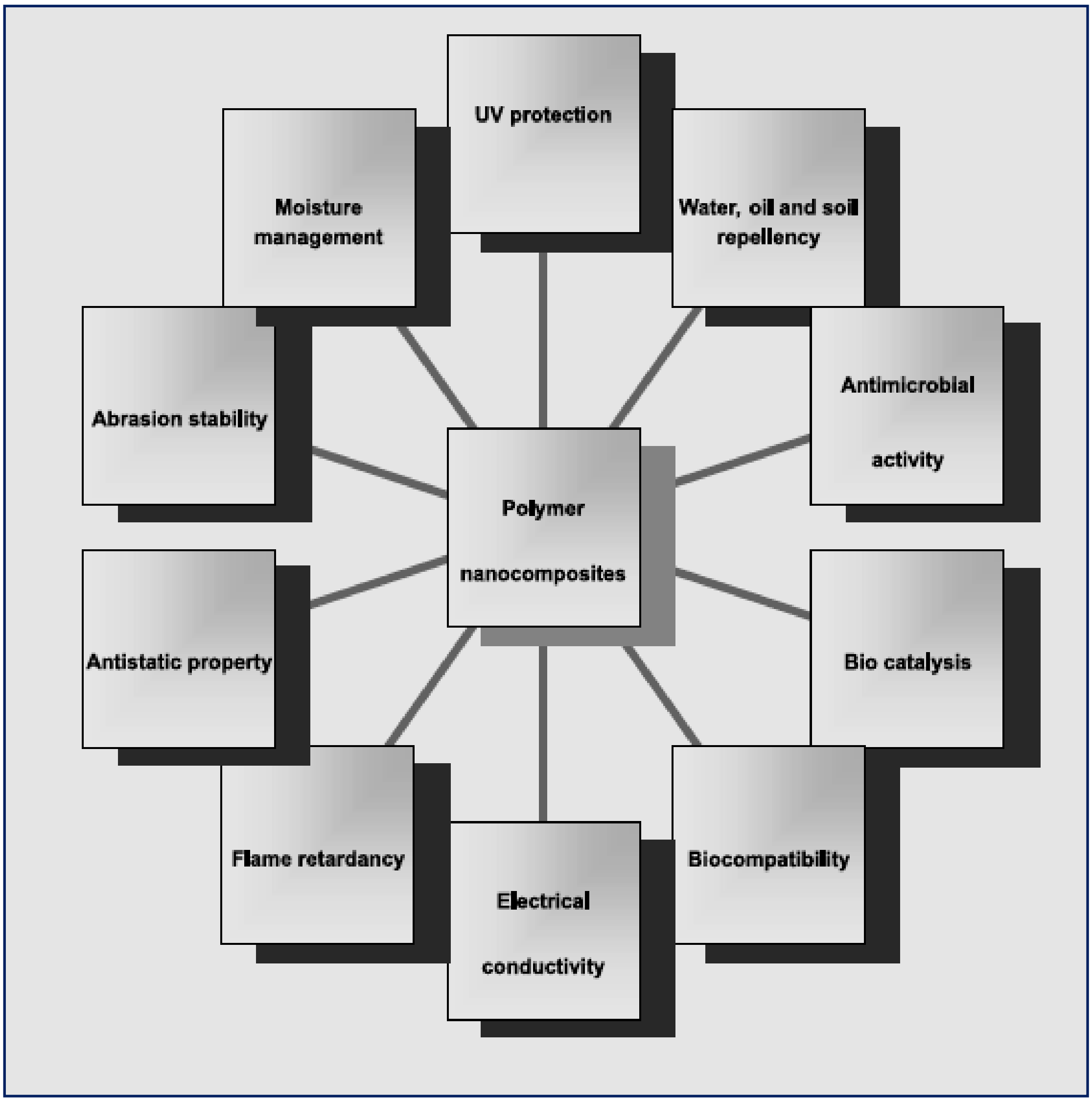

Figure 2: Various functionalizations obtained by using Polymer Nanocomposites.
-Courtesy: Gowri, et al. [14]**,** 2010.

II. Polypropylene

Polypropylene (PP) was the first synthetic stereoregular polymer to achieve industrial importance. It is used mostly for technical end-uses where high tensile strength coupled with low-cost are essential features. The application of polypropylene fibres have been widely in upholstery, floor coverings, hygiene medical, geotextiles, car industry, automotive textiles, various home textiles, wall-coverings, apparel[15]. For apparel sector, textured PP is finding its way into hosiery industry, e.g. in undergarments, swim suits, sportswear, socks etc.

An economic edge in raw material cost and the high efficiency catalysts have made polypropylene a very low-cost fibre-forming plastic material. Numbers of properties are responsible for the widespread usage of polypropylene. The general properties of isotactic polypropylene are shown in Table 1.

Table 1: Properties of Isotactic Polypropylene[16]

Properties	Values
Moisture regain (%)	< 0.1
Melting point (˚C)	160 – 175
Softening point (˚C)	140 -160
Tg (˚C)	40
Density (g/cm3)	0.9
Specific heat (J g-1 ˚C -1)	1.6
Mn	106
Polydispersibility (Mw/Mn)	9 – 11
Heat of combustion (kJ g-1)	44
Heat of fusion (J g-1)	21
Limiting oxygen index (%)	17.4
Decomposition range (˚C)	328 – 410

The configuration of polypropylene consist of methyl groups, arranged systematically around the helix forming three lateral rows about 120˚ apart and thus close packing is possible[17].

Advantages of Polypropylene Fibre

Polypropylene has a density of 0.91 gcm^{-3} which makes it the lightest of all synthetic fibres. It has low moisture regain (0.05%) which means it does not absorbs moisture. So, it means the wet and dry properties of fibre are identical. Also it helps in quick transportation of moisture. It has excellent chemical resistance. Polypropylene fibres are very resistant to most acid and alkalis. It neither support growth of mildew/ fungi nor attacked by insects and pests. It is easy to process and ensures high processing yields and profitability. The thermal conductivity of PP fibre is lower than that of other fibres and may be used in applications as thermal wear[16].

Limitations of Polypropylene Fibre

It has low melting temperature, so requires extra care during ironing. It cannot be dyed after manufacture. PP is normally mass coloured before fibre extrusion. So, major limitation is the lack of wide range of shades. PP has low UV and thermal stability, so requires the addition of expensive UV stabilizers and antioxidants to overcome the problem. PP has poor resilience compared with polyester or nylon. PP under goes creep due to its low Tg. It melts and burns like wax and is flammable; flame retardants may be added to over the problem16.

To overcome these limitations nanocomposite polymer can be the best suitable option. Many researchers had worked in this direction and produced desired nanocomposites with silver, zinc, TiO2, etc. A brief summary of important nano fillers used in the production of polypropylene nanocomposites have been appended below.

III. Nano fillers

TiO2: Titanium dioxide adopts at least 8 structures. Besides its four polymorphs found in nature (i.e. rutile, anatase, brookite, TiO2 (B)), additional high-pressure forms have been synthesized: TiO2 (II) with the α-PbO2 structure, TiO2 (H) with hollandite, baddelleyite with ZrO2, Cotunnite with PdCl218. Among the eight structures, rutile, anatase are mostly manufactured in chemical industry as microcrystalline materials. The two polymorphs are based on interconnected TiO6 octahedra, but their linkages and degree of edge and face sharing differ. Anatase can be regarded to be built-up from octahedrals that are connected by their vertices; in rutile, the edges are connected.

Thermodynamic calculations show that rutile is the most stable phase at all temperatures and pressures below 60 kbar, when TiO2 (II) becomes the favourable phase18. Reverse phase stability is described by particle size experiments due to size effect on surface energy. Anatase is most stable at sizes less than 11 nm, brookite at sizes between 11-35 nm, rutile at sizes greater than 35 nm19.

Silver: The density of silver is 10500 kg m-3, relative atomic mass is 107.868, atomic radius of silver is 2.110 Ao, Covalent radius is 1.36 Ao and Electron affinity is 125.58 kj mol-1 20. Silver nanoparticles have unique optical, electrical, and thermal properties, which can be incorporated into materials that range from photovoltaics to biological and chemical sensors, which include conductive inks, pastes and fillers which utilize silver nanoparticles for their high electrical conductivity, stability, and low sintering temperatures. Other applications of silver nano particles include molecular diagnostics and photonic devices, which take advantage of the novel optical properties. The common application of silver nanoparticles is for antimicrobial coatings to many textiles, keyboards, wound dressings, and biomedical devices. This coatings release a low level of silver ions to provide protection against bacteria21.

Zinc: There are 30 known isotopes of zinc ranging from Zn-54 to Zn-83 . Zinc has five stable isotopes: Zn-64 (48.63%), Zn-66 (27.90%), Zn-67 (4.10%), Zn-68 (18.75%) and Zn-70 (0.6%). Zinc has a melting point of 419.58°C, boiling point of 907°C, specific gravity of 7.133 (25°C), with a valence of 2. Zinc is a lustous blue-white metal. It is brittle at low temperatures, but becomes malleable at 100-150°C. It is a fair electrical conductor. Zinc burns in air at high red heat, evolving white clouds of zinc oxide.

Zinc is used to form numerous alloys, including brass, bronze, nickel silver, soft solder, Geman silver, spring brass, and aluminum solder. Zinc is used to make die castings for use in the electrical, automotive, and hardware industries. The alloy Prestal, consisting of 78% zinc and 22% aluminum, is nearly as strong as steel yet exhibits superplasticity. Zinc is used to galvanize other metals to prevent corrosion. Zinc oxide is used in paints, rubbers, cosmetics, plastics, inks, soap, batteries, pharmaceuticals, and many other products. Zinc is an essential element for humans and other animal nutrition. Zinc-deficient animals require 50% more food to gain the same weight as animals with sufficient zinc. Zinc metal is not considered toxic, but if fresh zinc oxide is inhaled it can cause a disorder referred to as zinc chills or oxide shakes22.

Out of all TiO2 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 in 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 a photocatalyst, as a catalyst support or promoter, as gas sensor, as in electric and electrochromic devices, and so on.

IV. Polypropylene nanocomposites

Various add-on of nano fillers had shown favourable improvements in the performance of the polypropylene nanocomposites. Findings of various researchers while working with different nano fillers in different proportions to produce polypropylene nanocomposites have been briefly summarized here.

Ahmadi et al.23 prepared Ag/ TiO2 nanoparticles doped polypropylene nanocomposite sheet and the antibacterial activities of the nanocomposite was accessed. The bactericidal effect of the nanocomposite was much higher than that of neat PP polymer. About 98% of bacteria were destroyed on the antibacterial PP after 10 minutes while less than 10% of them were killed on neat PP at the same time.

However, Dasterji et al.13 studied antibacterial activity on Ag / TiO2 doped PP nanocomposite continuous filament yarns with various proportions of filler (0, 0.2, 0.35, 0.5, 0.75, 1 % by wt). They found no strict trend of biostatic efficiency with the increase in Ag/ TiO2 content; optimum bacterial activity was shown at 0.75% nano-filled composite yarn.

Metal oxides enhance the mechanical properties of the polymer composites24. Generally tensile properties such as tensile strength, elastic modulus, stress-at-break increase while elongation at break decreases25,26. Altan et al.27 studied tensile properties of PP/ metal oxide nanocomposite with TiO2 nanoparticles, ZnO nanoparticles and these nanoparticles modified with SEBS; and found that TiO2 nanoparticles gave higher yield strength, tensile strength and elastic modulus and also elongation (which was expected to be lower) than ZnO. Madani28 studied mechanical properties of PP film filled with modified TiO2 nanoparticles and found rise in modulus and tensile values of nanocomposite produced by modified and unmodified TiO2 nanoparticles in comparison to unfilled polymer. He observed considerable enhancement in mechanical properties at low loading of modified filler. There was decrease in elongation at break in filled polymer composite.

Similar observation was made by Dastjerdi et al.13 for as-spun, drawn and textured nanocomposite yarns. However, Erdem et al.8 did not find significant change in mechanical properties.

UV protection property of TiO2 doped PP nanocomposite was studied by Erdem et al.8 and El-Dessouky et al.29 Erdem et al.30 found that nanocomposite filaments exhibited excellent UV protection. They observed that adding only a small amount of TiO2 nanoparticles caused sharp decrease in transmittance of UV A and UV B. El-Dessouky et al.29 studied UV in the range of 300 nm to 450 nm and observed that PP transmit all the wavelengths and does not absorb or block any UV. By increasing TiO2 content UV absorbance increases and transmittance decreases. Chiu et al.31 and El-Dessouky et al.29 found that addition of inorganic nanoparticles enhances polymer stability. So, addition of TiO2 nanoparticles make polymer matrix stabilized and TGA decomposition was much slower than pure PP.

Chiu et al.31 and Dastjerdi et al.13 observed reduction in crystallinity in nanocomposite filaments as compared to pure sample; which was attributed to the interference of TiO2 nanoparticles during crystallization as an impurity. However, Erdem et al.8 found enhancement in the degree of crystallinity by addition of TiO2 nanoparticles but it was close to that of neat PP. They suggested the nucleation role of TiO2 nanoparticles in crystallization of PP, resulting in higher crystallinity. Increase in content of TiO2 nanoparticles above certain percentage, caused reduction in crystallinity and was explained by large aggregates prevented crystal growth.

Wei et al.32 studied dynamic contact angle of TiO2/ PP nanocomposite manufactured by two methods: melt compounding and sputter-coating. They observed increase in hydrophilic nature of nanocomposite fibre; however the hydrophilicity was higher in sputter coated nanocomposite. They also concluded that UV irradiation appreciably enhanced hydrophilicity of surface in both cases.

V. Conclusions

There is wide scope of improvement in properties of polymer nanocomposites, due to high surface area to volume ratio of nano materials, high changes in system energy and structure. Polypropylene has limitations in getting desirable properties like antibacterial, mechanical, UV protection, thermal, hydrophilicity, etc. However, it has favourable properties like breathability, handle, fineness, stiffness, low cost, etc. Polypropylene TiO2 nanocomposite has a proficiency to improve different properties without sacrificing the other favourable characteristics. A systematic research in this direction can offer fruitful results and enhances its application areas.

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