Synthesis and Characterization of Poly (N-Isopropylacrylamide) Zno Nanocomposites for Textile Applications

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ABSTRACT

High performance polymers exhibiting multifunctional characteristics can be achieved by the introduction of inorganic nanoparticles like ZnO(Zinc oxide) into the functional polymers. In the present work a copolymer epoxy poly(dimethylacrylamide) was synthesized to disperse the ZnO nanoparticles. The aim of the work is to develop a new method/process/material for the dispersion of nanoparticles and evaluation of the performance of these composites. FT-IR studies of the polymer adsorbed ZnO nanoparticles confirmed that the polymer molecules chain were anchored on the surface of the ZnO nanoparticles. The improved interfacial interaction between the particles and polymer enhanced the thermal properties of the composites. The results also show that the newly prepared polymer composite matrix uniformly has the ability to disperse the ZnO nanoparticles well as evidenced by SEM analysis, and the particles almost remain in their original shape and size even after incorporation into the polymer matrix. Nevertheless, it was also found by dynamic light scattering analysis that the mean particle size of the dispersion was increased with increasing ZnO content. The results were consistent with SEM observations. The value of zeta potential results show how the Poly(N–isopropylacrylamide(PNIPAM)) can adsorb onto the ZnO nanoparticles and impart –ve charge to the surface of the nanoparticles.

Keywords: ZnO nanoparticles, epoxy poly(dimethylacrylamide) copolymer, thermal stability, dispersion, pH and humidity responsiveness

1. Introduction

Stimuli –responsive polymers are the polymers which undergo reversible volume change in response to small variation in external stimuli such as temperature, pH and ionic strength. These stimuli responsive polymers are currently being considered as an option in obtaining stimuli response textile materials (Liu and Hu 2005). Poly(N–isopropylacrylamide) PNIPAM is a well-known thermo responsive polymer which shows a coil – globule transition at lower critical solution temperature (LCST) at around 32°C (Schild 1992). This character is particularly useful in textile applications because this falls between body temperature and room temperature.

A multifunctional thermo responsive polymer nanocomposite can be prepared by the combination of inorganic oxide nanoparticles with PNIPAM to form PNIPAM nanocomposites. UV absorbers have been used to protect textile surfaces. Simultaneously, the interest in the application of nanotechnology in the textile industry has increased rapidly and has been the subject of several studies aiming to develop new finishing approaches to improve functional properties. For example, the nanoparticles of zeolites have led to better UV and antimicrobial protection of cotton and polyester fabric (Grancarz and Tarbuk 2000; Grancariz et al.2006; Grancarize et al. 2007). Now Ag has been used to impart antibacterial properties (Lee et al. 2003) nanoTiO₂ is used for UV blocking and self-cleaning properties (Xin et al. 2004; Fei et al.
2006; Qi et al. 2007) and nano ZnO is used for antibacterial and UV blocking properties (Wang et al. 2004; Baglioni et al. 2003; Wang et al. 2005; Vigneshwaran et al. 2006). Imparting functional properties i.e antibacterial and UV protection by using nanoparticles was done earlier by researchers (Ibrahim et al. 2013; 2012; 2010). Inorganic UV blockers are preferable to organic UV blockers (Riva et al. 2006; Scalia et al. 2006) because inorganic absorbers such as zinc oxide are non toxic and chemically stable under exposure to both high temperature and UV radiations. Nanoparticles have large surface area to volume ratio. The proper dispersion and homogeneous distribution of nanoparticles via coating layer yields more effective UV blocking with less material than a coating modified with coarse materials (Yadav et al. 2006). Furthermore these coatings are transparent/colorless which are important for the product appearance. If the employed particles exhibit particle size below 50 nm no light scattering within the coating occurs, guaranteeing transparency. ZnO is widely used in different areas because of its unique photocatalytic, electrical, electronic, optical, dermatological and antibacterial properties (Turkoglu and Yener 1997; Pan et al. 2001; Arnold et al. 2003; Sawai 2003; Xiong et al. 2003; Tang et al. 2006; Sorna et al. 2010).

The aim of the present study is to develop a multifunctional polymer nanocomposite system that could be applied to textiles, providing conditions of effective bonding for obtaining permanent effects.

2. Experimental

2.1. Materials

Zinc nitrate (98% purity) was procured from Acros Organic, New Jersey, USA. Poly(isopropylacrylamide), PNIPAM, with molecular weight of 10205 g/mol was purchased from Sigma Aldrich. Sodium hydroxide and deionised water, of laboratory grade, were obtained from indigenous sources.

2.2 Synthesis of ZnO nanoparticles

Zinc oxide nanoparticles were prepared from zinc nitrate solutions after neutralizing with sodium hydroxide to pH values of 12. Conventional heating experiments were conducted on magnetic stirrer. When the reactions were completed, the solid and solution phases were separated by centrifugation and the solids were washed free of salts with deionized water (3X) and ethanol (2X). Then the white powder obtained was calcined at higher temperature and then grinded manually for uniformity of the powder.

2.3 Preparation of PNIPAM ZnO nanocomposites

Different concentrations of nanoparticles in distilled water are prepared by taking 0.2, 0.4, 0.6, and 0.8 g of ZnO nanoparticles in 100 ml of double distilled water and kept under sonification for 20 minutes. $4 \times 10^3$ g/L of PNIPAM solution was prepared in double distilled water under sonification. Equal volumes of the above solutions are taken and kept under ultra sonification for 12 hours.
2.4 Characterization of ZnO nanoparticles and PNIPAM ZnO nanocomposites

TGA analysis was carried out under N$_2$ on a simultaneous thermal analyzer Mettler Toledo using heating rate of 20°C/min. The particle size and zeta potential was measured by dynamic light scattering using Malvern system at temperature between 25 to 60°C. The X-ray diffraction (XRD) pattern of nanoparticles was analyzed with X-ray diffractometer (Model: Bruker D8 Discover) using Cu K$_\alpha$ radiation at wavelength $\lambda = 0.15406$nm, scan range $2\theta = 20°$– 90°, scanning rate = 0.02 deg/s (applied voltage 40KV, current 20mA). Morphological analysis of the samples was done by Nova Nano SEM 430 and FTIR by ALPHA FT-IR Spectrometer.

Before the coating process, DBD(Dielectric Barrier Discharge) plasma treatment was used in order to try the improvement of the nanocomposite adhesion/reactivity/durability conditions towards the cotton substrate. The atmospheric discharge was performed in a laboratorial prototype which is a patented model “Lisboa” developed by the partnership Softul/University of Minho working with variable power of discharge, velocity and number of passages for 0.5 m electrodes width.

The plasmatic dosage chosen was 2700 W.min.m$^{-2}$, each side of the fabric, in accordance with the results of the hydrophilic character of the fabric evaluated by a wicking test in order to get optimized results of water diffusion and contact in the fabric surface.

For the coating of the cotton fabric with PNIPAM ZnO nanocomposite, the application process was the following:

- The cotton fabric was cut in samples of 70 g each, approximately;
- Then the samples were introduced in the solutions of ZnO - PNIPAM;
- The fabric solutions were homogenized for 30 min in the ultrasound apparel;
- When taking the samples of solution they were passed in foulard with pressure of 4.1 bar and velocity of 2.54 m/min;
- Finally, the samples are air dried.

2.5 Determination of stimuli responsive properties

In order to determine pH-responsiveness of fabric material with incorporated nanocomposites, swelling properties were assessed by a gravimetric method. Fabric samples of dimensions 4X4 cm were immersed in excess of hydrochloric acid solution (pH5) or sodium hydroxide solution (pH 9) until the swelling equilibrium was attained. The weight of the wet sample was determined after removing the surface water by blotting with filter paper. The swelling percentage (AS) was calculated by the following formula.

$$\text{AS} = \frac{W_S - W_D}{W_D} \times 100$$
Where $W_s$ is the weight of sample in swelling equilibrium, $W_D$ is the initial weight of dried sample. In order to determine the influence of humidity on swelling properties of surface modified textile material, a Humidity chamber purchased from Bio Tech India was used. Fabric samples of dimensions 4X4 cm were put in the climatic chamber under conditions of constant temperature and humidity percentage for one hour. For calculating swelling percentage the above equation is used.

3. Results and discussions

3.1 FTIR and XRD of ZnO nanoparticles

Figure 1 shows the FTIR spectrum of the synthesized nano ZnO. The spectrum shows clearly ZnO absorption band near 438 cm$^{-1}$. The peak at 3446 cm$^{-1}$ corresponds to hydroxyl groups (–OH) probably due to atmospheric moisture.

Figure 2 shows the XRD spectrum of the ZnO of the synthesized solid nanopowders. The spectrum shows well defined peaks typical of ZnO in the crystal structure of Zincite. The diffractogram of ZnO sample shows characteristic peaks of crystalline ZnO at 2θ values: 31.8, 34.5, 36.2, 47.6, 56.6, 62.9, 66.4, 67.9, 69.1, 72.9 and 79.9. This indicates the crystallinity of the synthesized solid. Traditionally the broadening of the peaks in the XRD patterns of solid is attributed to particle size effects.

FTIR spectroscopic studies were carried out for PNIPAM and PNIPAM - ZnO nanocomposite which are shown in figure 3. The main characteristic peaks of PNIPAM are at 1080, 1640 and 1540 cm$^{-1}$ attributed to secondary amide C= O stretching and secondary amide N- H stretching of PNIPAM chain (Fu et al. 2007; Suzuki et al.2000; Pan YV, et al . 2001). Characteristic absorption bands are attributed to the asymmetric stretching of C-N-C at 1130–1191 cm$^{-1}$. The characteristic vibrations of –OH on the ZnO surface at 1024 cm$^{-1}$ and 3450 cm$^{-1}$ are also observed. The existence of –OH is important for the modification of ZnO particle surface with PNIPAM.

3.2 Morphology of ZnO nanoparticles and ZnO – PNIPAM nanocomposites

Figure 4 displayed uniform particle morphology and each particle is approximately 80 nm in diameters. The particles are well dispersed. Meanwhile judging from figures 6, 7 & 8 the dimensions of the aggregate particles are significantly larger than values in figure 5 due to the increase in the concentration of nanoparticles which leads to increase in aggregation of the nanoparticles at higher concentration. The ZnO nano particles display uniform particle morphology at lowest concentration.

3.3 Thermal characterization of PNIPAM- ZnO nanocomposite.

Thermal stability of the PNIPAM nanocomposite with different concentration of ZnO is shown in figure.9 Since inorganic species have good thermal stability it is generally believed that the introduction of inorganic composites in to organic materials can improve their thermal stability. Thus the increase in the
thermal stability was attributed to the high thermal stability of ZnO and to the integration between the ZnO nanoparticles and polymer matrix. It is also noted worthy that PNIPAM and the nanocomposites decompose from temperature of 340 - 380 °C and thermal stability of nanocomposites was better than pure PNIPAM which was 300 °C (26).

3.4 Particle size distribution

Figure 10 shows a typical nanoparticles size distribution profile in nanocomposites with 0.2, 0.4, 0.6 and 0.8 % ZnO in PNIPAM. It was found that the nanoparticles have narrow distribution of size. The z-average particle size and polydispersity indexes (PDI) were 716.7 nm (PDI = 0.741), 863.9 nm (PDI = 0.909), 980.2 nm (PDI = 0.946) and 1067 nm (PDI = 0.987) for 0.2%, 0.4 %, and 0.6% and 0.8 % ZnO respectively. Slight increase in polydispersity index for the sample with 0.8 % ZnO was probably due to slight agglomeration of ZnO nanoparticles. It was also found that the mean particle size of the dispersion was increased with increasing ZnO content. The results were consistent with SEM observations.

3.5 Zeta potential analysis

The zeta potential of the nanocomposites with different concentration of ZnO nanoparticles is shown in figure 11. This –ve charge was attributed to PNIPAM. The –ve surface charge of the nanoparticles also illustrate that the PNIPAM was successfully coated on the surface of the ZnO nanoparticle, being the zeta potential often used as an index of the magnitude of electrostatic integration between the nanoparticles and polymer matrix and thus is useful measure to find interaction between PNIPAM and ZnO nanoparticles. The value of zeta potential results how the PNIPAM can adsorb onto the ZnO nanoparticles and impart –ve charge to the surface of the nanoparticles.

3.6 pH dependence of swelling percentage S

In order to determine pH responsiveness of the fabric material with incorporated nanocomposites, swelling properties were assessed by gravimetric method (Table 1) the same trails were run on untreated, DBD treated samples.

The DBD treatment made the fabric hydrophilic and there is slight increase in the swelling properties after DBD treatment. Incorporation of PNIPAM nanocomposites to fabric caused significant changes in swelling behavior. In any case, in terms of difference of swelling between acidic and alkaline pH, the most attractive results obtained with PNIPAM nanocomposites incorporated fabric samples. Swelling increase in acidic as well as alkali media which was expected behavior that could be attributed to the pH responsiveness of PNIPAM. The swelling effect increase after treatment with PNIPAM nanocomposites and the swelling values increases with increase of % of nanoparticles in PNIPAM nanocomposites.

3.7 Moisture Regain with relative Humidity (RH)
As expected, since moisture concentration in air is the driving force for moisture absorption, the moisture regain $R$ always increased with RH increase.

When PNIPAM nanocomposite incorporated to DBD treated fabric, the moisture regain was slightly increased or stayed at similar value as compared with corresponding control samples except for higher values of RH, where noticeable increase was observed.

In general, when dry fabric with incorporated PNIPAM nanocomposite is subjected to an environment containing moisture, both the fibre and the polymeric system absorbs the moisture at rate that depends on a number of physical factors initially the moisture uptake, the competition between the fiber and the polymer nanocomposite is the most important factor. Hence the polymer nanocomposite plays preferential role where the integration with moisture occur. This is also due to low crystallinity of polymer nano composite than the fabric. (Jocić, D. et al 2009)

4. Conclusions

The preparation of nanocomposites in industrial scale is still difficult to achieve. There are many methods for their preparation, but a universal easy and efficient process allowing a perfect distribution of the inorganic particles in a polymer matrix is a challenge. This is mainly due to the difficulties in fulfilling all necessary requirements such as good compatibility and high degree of entanglement between polymer matrix and polymer chains attached to the surface of the inorganic particles. In this work we demonstrated that an excellent surface modification can be achieved by adsorption of copolymers as stabilizers on ZnO surface:

- FT-IR studies confirmed that the polymer molecules chain was anchored on the surface of the ZnO nanoparticles.
- FT-IR measurements showed that the adsorption of polymers on nanoparticles surface derived from the formation of hydrogen bond from the hydrophobic effects of substituents on nitrogen atom. These hydrophobic groups could hinder water molecules replacing the adsorbed polymer molecules and markedly improved the dispersion of ZnO nanoparticles in polymer. The improved interfacial interaction between the particles and polymer enhanced the thermal properties.
- The present study shows that inter phase chemical links between the ZnO and the polymer chain prevent the agglomeration of ZnO nanoparticles making their distribution more homogeneous in polymer as evidenced by SEM analysis.
- It was also found that the mean particle size of the dispersion was increased with increasing ZnO content. The results were consistent with SEM observations. The value of zeta potential results how the PNIPAM can absorb on to the ZnO nano particles and impart – ve charge to the surface of the nano particles.
Incorporation of PNIPAM nanocomposite to the fabric was achieved by the batch method. Swelling behavior and moisture sorption analysis showed the fabric incorporation with PNIPAM nanocomposites present interesting pH and humidity responsiveness. These results prove that the concept of functional finishing of fabric by PNIPAM nanocomposites could lead to the development of a novel material with highly attractive features of responsiveness to the environmental stimuli.

With this new procedure, we have created a tool to obtain a broad range of new inorganic organic hybrid materials in a very easy way for textile applications.
<table>
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<th>Sample</th>
<th>pH 5</th>
<th>pH 9</th>
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<tbody>
<tr>
<td>Control</td>
<td>52.25</td>
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<tr>
<td>Control + PNIPAM</td>
<td>54.28</td>
<td>38.62</td>
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<tr>
<td>Control + DBD</td>
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<td>PNIPAM+DBD</td>
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<td>39.50</td>
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<tr>
<td>PNIPAM+0.2% ZnO</td>
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<tr>
<td>PNIPAM+DBD+0.2% ZnO</td>
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