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Effect of CaO Nanoparticles on the Properties of Polyamide 6

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THE number of efforts in order to modify the properties of polymeric fibers by organic or inorganic particles has increased in recent times because of increasing interest of fiber research in hightech fiber applications. In addition to these attempts, the innovation of nanotechnology also leads to the development of nanoparticles for various end uses such as nanocomposite fibers. In this study Calcium oxide nanoparticles (CaO) were introduced into polyamide 6 (PA6) and drawn into filaments through a melt extrusion process. The effect of CaO nanoparticles on the thermal, structural, morphological and tensile properties of polyamide-CaO nanocomposites fibers was investigated by using thermal gravimetric analysis (TGA), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and mechanical properties, respectively.

Dyeing studies underlined the effect of CaO on the dye ability of the fibers which improved the accessibility of the fiber using disperse dye.

The characterization results showed that thermal stability of nanocomposites was notably improved compared to pure polyamide 6.

It is well known with state-of-art technology that incorporation of nanofillers into polymer enhances mainly physical, mechanical and barrier properties. Different synthesis and processing methods have been used to prepare polymer nanocomposites, depending on the type of polymer matrix, type of nanoparticle and the desired final structure. Generally polymer nanocomposites can be prepared using in situ polymerization, melt intercalation or solution mixing. The melt intercalation technique has been reported to be more economical and straightforward than the in situ polymerization technique.

The possibility of direct melt intercalation was first demonstrated by Giannelis *et al.*[1] the melt intercalation method has become a main stream for the preparation of the intercalation polymer nanopcomposites without in situ intercalative polymerization. Since then, extensive research in this field has been carried out globally. At present, development has been widened including polyamide 6 (PA6)[2-6], polypropylene (PP)[7-9] and polyethylene terephthalate (PET) [10-12].

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Polyamides with amide groups –NH-CO- in the main chain are considered to be one of the most important super-engineering materials because of their superior mechanical properties at elevated temperature due to their thermal stability. The two major types of polyamides are polyamide 6 and polyamide 66. Polyamide 6 exhibits polymorphic structures that contained two types of stable crystal form: monoclinic α-form and monoclinic (or pseudohexagonal) γ-form[13], which are very sensitive to the way in which the samples are prepared. Previous studies have also shown that a partially disordered structure of PA6, mesomorphic β-form, could be obtained by cooling the samples rapidly from the melt state, while the α -form crystal of PA6 resulted from slow cooling from the melt state[14]. Polyamide's toughness, low coefficient of friction and good abrasion resistance make it an ideal replacement for a wide variety of applications, replacing metal and rubber. The amide groups of polyamide are very polar, and hydrogen bonds can form between them. Because of these, and because the polyamide backbone is so regular and symmetrical, polyamides are often crystalline, and make very good fibers[15-16]. Mixing and dispersing nanosized particles in polymer matrices provide the resulting materials with a variety of properties which are simply not available for bulk composites with high filler loading.

Among various nanoparticles, calcium oxide nanoparticles have received considerable attention because of their unusual properties and potential applications in diverse fields[17]. Calcium oxide (CaO), in particular, being cheap, and is non-corrosive, economically benign and easy to handle compared to other nanoparticles.

In this study, we have aimed to produce nanocomposite fibers by compounding CaO nanoparticles into PA6 by melt intercalation technique.

Experimental

Materials

PA 6 granule (Ultramide B24 N03) was provided by BASF with relative viscosity (RV) 2.4 in sulfuric acid, melt flow rate (MFR) of 1.6 g / 10 min. density, 1.12 kg m-3, melting point 220 ^{o}C and moisture percentage 5.7%.

Calcium oxide nanoparticle (98%) with particle size less than 160 nm, molecular weight 56.8 g/mol and with density 3.3 g/ml was supplied from Sigma-Aldrich (634182) - Steinheim - Germany.

The disperse dye, namely, Resolin Red GR was supplied by Bayer AG (Leverkusen, Germany).

Methods

Preparation of PA-6 - CaO hybrid nanocomposites via melt intercalation method

Prior to extrusion, nanoparticles of CaO are dried at 110°C in vacuum oven for 24 hr to minimize the effect of moisture, and were kept in sealed desiccators. Polyamide chip was dried at 90°C for 24 hr in a vacuum oven to remove the

absorbed water due to the high moisture absorption capability of polyamides. After drying, PA6/CaO hybrid witrh CaO concentration 0.5% was prepared by melt compounding technique using HAAKE twin screw extruder at a fixed rotational speed of 90 rpm. The temperature profile of barrel was set at 250°C – 255°C – 255°C degree from the hopper to the die. Finally melt strands were cooled in water bath and then pelletized with cutting machine. For comparison, pure PA6 was also extruded in twin screw extruder at the same process condition[18].

PA-6 - CaO fiber production method

In order to prepare nanocomposite fiber, the prepared PA6/CaO was dried at 90°C for 24 hr in a vacuum oven, and in order to be on the safe side, water content of samples was measured according to Karl Fischer method (ASTM E203 – 08). Fiber melt spinning was carried out using a spinning apparatus (HAAKE single screw extruder) consisting of an extruder and a gear pump to control precisely the throughput rate, which was kept at 40 g/min for all polymers. Filaments extruded through a 24-hole spinneret with a diameter of 0.3 mm and at 275°C were taken up by the high-speed winder SW46 of BARMAG Company below the spinneret[9].

Dyeing methods and determination of the color strength (K/S)

PA6 and PA6/CaO yearns were dyed with disperse dye namely Resolin Red by pasting the dye with 1% acetic acid (based on sample weight) and then dissolved in boiling water. The dissolved dye was added to the bath at 60 ºC and the temperature was then raised slowly to 90 ºC. The dyeing was continued for 60 min during which Glauber salt (20% based on sample weight) was added, the samples were rinsed with cold water then soaped and washed with a solution containing 5 g/l Na_2CO_3 and 1 g/l detergent, washed with cold water and then dried. The process was carried out using conventional exhaustion method at dye concentration of 0.2% and Liquor ratio of 1:50. After dyeing, the colour strength (K/S) was followed by measuring the reflectance (R) using a spectrophotometer. This was followed by substituting the measured value of (R) in the following Kubelka-Munk equation[19-20].

$$K/S = [(1-R)^2 / 2R] - [(1-R_t)^2 / 2R_t] = A . C$$

where R is the decimal fraction of the reflectance of the colored; R_t is the decimal fraction of the reflectance of the uncolored sample; K is the adsorption coefficient; S is the scattering coefficient; C is the dye concentration; and, A is the proportionality factor.

Characterization

X-ray diffraction (XRD) measurements were performed using a Philips powder-diffractogram PW 1050 with ADM software and with Ni-filtered Cu-K radiation. The accelerating voltage was 40KV, and the current was 30mA.

The morphology and fracture surface of the polymer and its composite were examined by scanning electron microscope (SEM) analysis using a Zeiss DSM 962 microscope. Colour strength of disperse dye was measured using UV–Vis spectrophotometer (Cary 500, Varian) equipped with a quartz cell having a path length of 1 cm at Ѓ-max 210 nm.

Thermogravimetric analysis (TGA) was determined on a TGA 7 thermogravimetric analyzer (Perkin Elmer) under a nitrogen flow at a heating rate of 10 ℃ min_1. The Fourier transfer infrared (FTIR) spectra were obtained using a Bruker IFS 28 spectrometer 67.

The mechanical properties of the polyamide fibers were measured with a Zwich Zugprufgerat machine (Ulm, Germany) with a force of 10 kN.(ASTM D-3822–07)

Results and Discussion

First: Structure and properties of PA6 and PA6/CaO nanocomposite
   X-Ray Diffraction (XRD)
Figure 1 illustrates the X-ray diffraction pattern of the pure polyamide 6 and nanocomposite with 0.5 CaO nanoparticle content.

From Fig. 1 it is obvious that XRD patterns of both polyamide 6 nanocomposite and the pure polyamide 6 matrix exhibit two α crystalline diffraction peaks. However, besides these two peaks, the nanocomposites exhibit an additional distinct γ crystalline diffraction peak at 2θ value 27.8°.
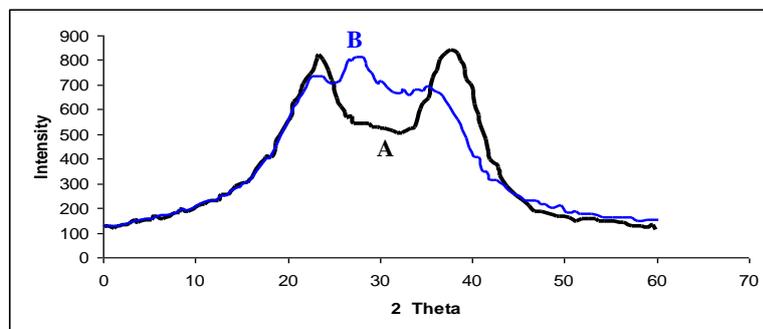

Fig. 1. XRD patterns for A) Pure PA6 and B) PA6/CaO nanocomposite.

Scanning Electron Microscope (SEM)
The surface morphology of the prepared samples was investigated by SEM at X100 um magnification. Figure 2 displays SEM micrographs of pure PA6 and the prepared PA6-CaO nanocomposites. From the figure it is clear that CaO nanoparticle is uniformly distributed in the polymeric matrix of PA6 and a

homogenous dispersion without any CaO agglomeration in the polymer matrix is obtained in the prepared PA6-CaO nanocomposite[21].

A   B
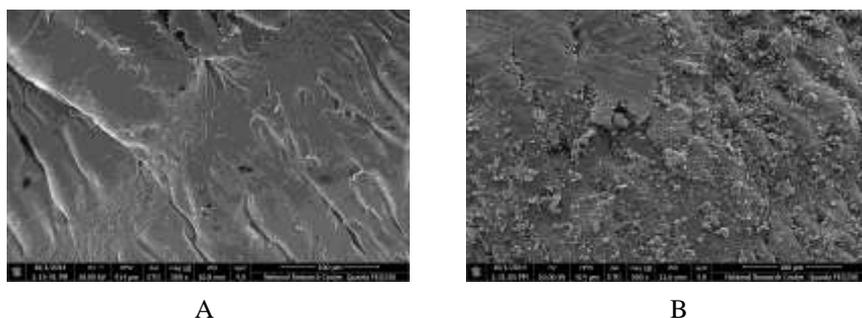
Fig. 2. SEM image for A) Pure PA6 and B) PA6/CaO nanocomposite.

Second: Structure and properties of PA6 and PA6/CaO fiber

Addition of CaO nanoparticles in the production of PA6 fibers is mainly carried out to improve its properties to be satisfied for the end-user application. The desirable properties for the PA6 fibers are its thermal stability, mechanical properties, morphology and dye uptake.

Thermal Gravimetric Analysis (TGA)

The thermal stability of the polymer composites is the most important parameter for their processing and applications, so it is very instructive to characterize the thermal degradation behavior.

The analysis of thermal behavior of Polyamide 6 and its CaO nanocomposite fiber was performed using the Perkin Elmer TGA7 from 50°C to 600°C at a heating rate of 10°C min^{-1} under nitrogen atmosphere and the results are illustrated in Fig. 3 and the detailed data corresponding to the temperature point at which 25% weight loss temperature (T_{25}), 50% weight loss temperature (T_{50}) and 75% weight loss temperature (T_{75}) are listed in Table 1.

From the data, it is clear that all weight loss temperatures for the PA6/CaO nanocomposite fiber are higher than that of pure PA6 fiber which might be attributed to a maximized interaction between the CaO nanoparticle and the polyamide 6 in the fiber structure, due to the availability of a larger surface area of the nanoparticle in case of PA6/CaO nanocomposite fiber[22].

TABLE 1. Degradation temperatures of pure PA6 and PA6/CaO nanocomposites.

Degradation temperature	Pure PA6	PA6/Cao nanocomposite
T_{25}	297	321
T_{50}	370	400
T_{75}	445	472
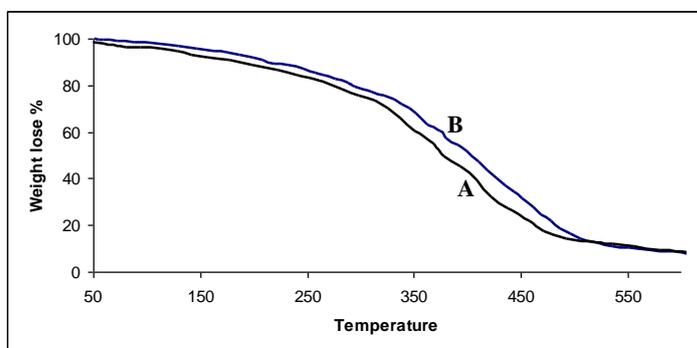
Fig. 3. TGA Thermograms for A) Pure PA6 and B) PA6/CaO nanocomposite.

Mechanical properties

This part of study was carried out to investigate the effect of CaO nanoparticle on the mechanical properties of the polyamide6 fiber. Table 2 shows the mechanical properties expressed as tensile strength (T.S), elongation at break (E) and tenacity (T.N) of pure PA6 fiber and PA6 fiber intercalated with 0.5% CaO nanoparticles.

From the data listed in Table 2, it is clear that, all both tenacity and elongation are decreased when CaO nanoparticles are added to PA6 where incorporating of nanoparticle into the polymer matrix increases the stiffness and makes fibers more brittle. The increase in stiffness is no doubt contributed to the CaO reinforcement[17]. Since the fiber containing nano-CaO is brittle and acquired less elongation.

TABLE 2. Mechanical properties of pure PA6 and PA6/CaO nanocomposites.

Materials	Tensile Strength (T.S) In N/m^2	Elongation at break (%)	Tenacity (T.N) In (gm/denier)
PA6 fiber	110.9	64.7	45.5
PA6/CaO Fiber	174.5	45.8	32.3

FT-IR characterization

An FTIR experiment with polyamide 6 and with functionalized CaO nanoparticles is shown in Fig. 4.

From the figure, it is obvious that, in the PA6/CaO IR figure, the IR absorbance for each of the three basic bonds amide N–H at 3297 cm^{-1}, hydroxyl O–H at 2800–3000 cm^{-1}, and carbonyl C=O at 1637 cm^{-1} has increased significantly , characterized by their sharper and higher peaks. On the other hand, the calcium oxygen bond is formed at 1460 Cm^{-1} which is not seen in the pure PA6 IR figure [23].
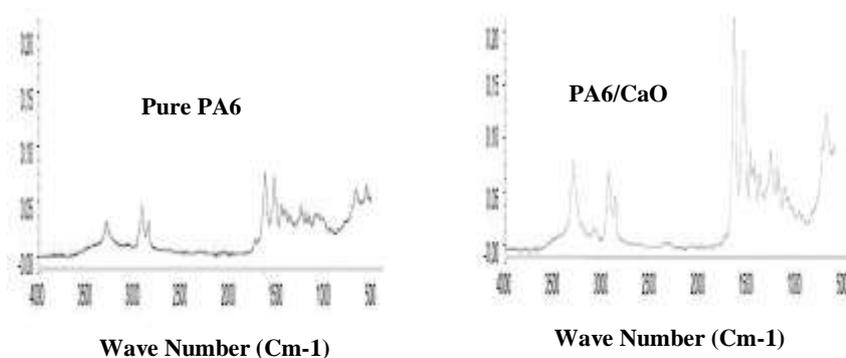
Fig. 4. FT-IR for A) Pure PA6 and B) PA6/CaO nanocomposite.

Scanning Electron Microscope (SEM)

Morphology studied was carried out for pure PA6 fiber and PA6 fiber intercalated with 1% CaO nanoparticle.

From Fig. 5, it is clear that, the pure PA6 fibers are completely smooth while a small aggregate appears in the fiber surface in case of PA6/CaO fibers. It is also evident from the figures that the agglomerates are discontinuous throughout the fiber.

In general it can be noted that fibers are particularly difficult to observe under SEM because of their generally featureless circular shape and transparency [24].

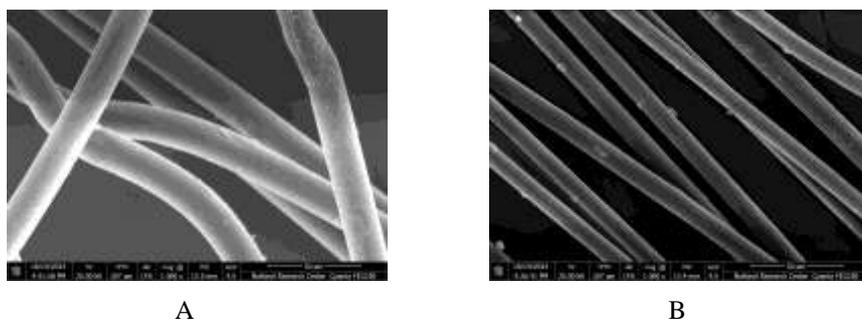A   B

Fig. 5. SEM images for A) Pure PA6 and B) PA6/CaO nanocomposite.

Colour measurement

The dyeing behaviour of a fibre depends on both its physical and chemical structure. As regard to the chemical structure, dyeability is governed by the presence, firstly, of polar groups which interact with water molecules and allow fiber swelling and, secondly, by functional groups that attract dye molecules [21,22].

With regard to the physical structure, the fiber must be accessible to water, dyes and other reagents. It must have a certain permeability, particularly to permit the dye molecules to diffuse into the fiber matrix[15,25].

Pure PA6 fiber and PA6 fiber intercalated with 0.5% CaO nanoparticle were independently dyed with disperse dye. The dying properties expressed as colour strength (K=S) are illustrated in Fig. 6.

From the figure, it is clear that, the presence of CaO nanoparticle in the PA6 fibers improves the K/S value where the low value obtained in the pure PA6 fibers was expected because no sites are available for dye interaction with pure PA6.

The improvement in the K/S in the presence of CaO nanoparticle is due to its high surface area and strong van der Waals forces, as well as hydrophobic and ionic interactions with dyes. The van der Waals forces and hydrophobic interactions were the two major forces for dye sorption onto CaO nanoparticles and is the reason why dye sorption is increased with the presence of nanoparticles [15].
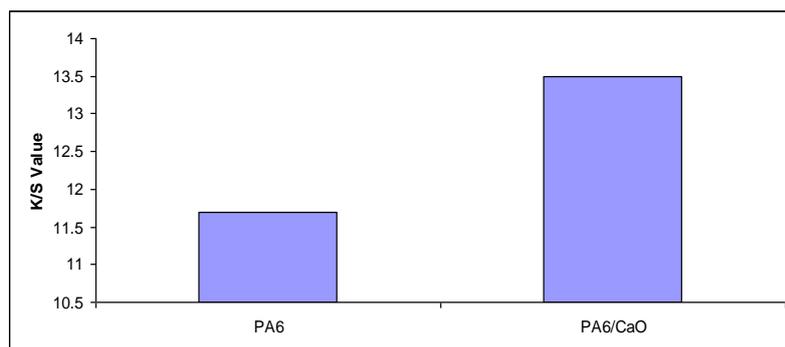
Fig. 6. Effect of disperse dyes on the colour strength of polyamide fibers.

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تأثير جزيئات أكسيد الكالسيوم النانومترية على خصاص البولى أميد 6.

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تلاحظ فى الآونة الأخيرة زيادة الجهود المبذولة من أجل تعديل خصائص الألياف البوليمرية وذلك من خلال استخدام الجزيئات العضوية والغيرعضوية من أجل زيادة التطبيقات التكنولوجية المتطورة للألياف. علاوة على ذلك فأن الإبتكار فى مجال النانوتكنولوجى أدى الى تطوير استخدامات الجزيئات النانوية المتناهية الصغر فى انتاج الألياف البوليمرية النانومترية. تهدف هذه الدراسة الى ادخال جزيئات أكسيد الكالسيوم النانومترية فى ألياف البولى أميد 6 من خلال عملية الذوبان الطارد. وقد تمت دراسة تأثيرجزيئات أكسيد الكالسيوم النانومترية على كل من الخواص الحرارية والمورفولوجية والشد لمتراكبات ألياف البولى أميد 6 مع أكسيد الكالسيوم وذلك بتوصيف الألياف الناتجة باستخدام التحليل الحرارى الوزنى و حيود الأشعة السينية والتحليل الطيفى بالأشعة تحت الحمراء الى جانب الميكروسكوب الإليكترونى الماسح وتعيين الخواص الميكانيكية. كما تمت دراسة تأثير جزيئات أكسيد الكالسيوم النانومترية على صباغة ألياف البولى أميد 6 وأكدت الدراسة تحسين قدرة الألياف على امتصاص صبغة التفرق فى حالة وجود جزيئات أكسيد الكالسيوم النانومترية.

كما أظهرت عملية التوصيف مدى زيادة الثبات الحرارى لمتراكبات البولى أميد 6 مع جزيئات أكسيد الكالسيوم النانومترية مقارنة بالبولى أميد 6 النقى.