

## Synthesis and characterization of MC nylon/modified yttrium hydroxide nanocomposites

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**ABSTRACT:** In this article, monomer casting (MC) nylon is synthesized. MC nylon could replace nonferrous metals in certain applications, including gears, wheels, and other moving parts. However, compared with metals, MC nylon products have poor strength and stiffness, and crack easily, especially at low temperatures. In addition, the dimensional stability of MC nylon is poor, especially in the large casting nylon products, causing significant internal stresses due to shrinkage. Thus, MC nylon cracks easily when cast and molded. The yttrium hydroxide particles are modified by stearic acid and dispersed in the caprolactam. The polymerization time is short due to fast anionic polymerization. Copolymerization with different ratios of yttrium hydroxide particles can be used to prepare the copolymer. The effects of different amounts of yttrium hydroxide on the performance of the monomer casting nylon are studied. The products are characterized using X-ray diffraction, impact, and tensile testing. When the percentage of modified yttrium hydroxide is 0.3 wt %, the composite exhibits the maximum impact strength, thus the 0.3 wt % of modified yttrium hydroxide is the suitable percentage to enhance the impact strength of MC nylon. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43356.

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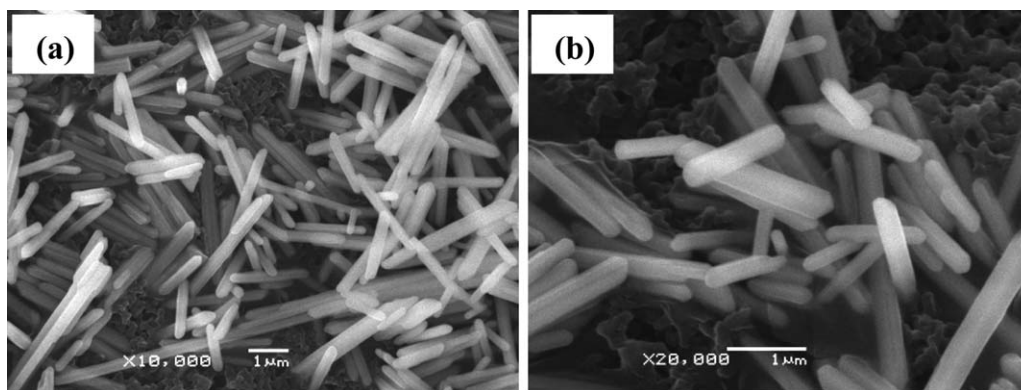
### INTRODUCTION

Monomer casting (MC) nylon with molten raw caprolactam ( $C_6H_{11}NO$ ) is catalyzed by an alkaline substance at atmospheric pressure with added activating agent. It is widely used for the production of gears, bearings and sliding blocks. It is especially suitable for making large products, which cannot be produced by injection molding or compression molding.<sup>1</sup> MC nylon is produced by anionic polymerization techniques to develop various plastics.<sup>2</sup> Base-catalyzed polymerization is used with the caprolactam polymerization directly in the mold so that the polymerization reaction and mold processing are completed at the same time. MC nylon has lower polymerization temperature, higher crystallinity, molecular weight and mechanical strength than ordinary nylon. It is abrasion-resistant, self-lubricating, and has a wide application temperature range, along with other characteristics, allowing it to be used instead of copper, aluminum and other nonferrous metals in certain applications.<sup>3–5</sup> MC nylon is widely used in machinery, petrochemistry and construction.<sup>6</sup>

However, ordinary nylon has high elastic modulus, poor low temperature toughness, low dimensional stability, relatively high

water absorption, and other shortcomings.<sup>7</sup> When the parts are used under high load conditions, the material has poor wear resistance and self-lubrication, thus the wear rate is high.<sup>8</sup> The uses of nylon products are often limited, demanding high impact resistance, antistatic, flame-retardant, and other requirements.

Nanoparticles have been successfully used to reinforce polymer nanocomposites.<sup>9–11</sup> Yttrium hydroxide is in the form of rod-like particles, a couple of microns long and about 400 nm in diameter. The yttrium hydroxide is stable and has alkali properties, and is suitable to modify polymers. Compared with  $SiO_2$  and  $TiO_2$ , the overall  $Y_2(OH)_3$  dissolution reaction is exothermic. Polymer composites with  $SiO_2$  and  $TiO_2$  are more likely to absorb water, opposite to composites with yttrium hydroxide. Therefore, yttrium hydroxide is better suited for certain polymer composite applications where low water absorption is critical. At the same time yttrium hydroxide can enhance the polymer toughness, as demonstrated by several literature reports. Yttrium hydroxide nanoparticles can also be utilized for the MC nylon reinforcement. In this study, yttrium hydroxide was modified by the stearic acid and added to the MC nylon for reinforcement purposes.



**Figure 1.** Scanning electron microscopy images of the unmodified yttrium hydroxide: (a) lower magnification; (b) higher magnification.

## EXPERIMENTAL

### Materials and Methods

Yttrium oxide ( $Y_2O_3$ ) was obtained from the Guoyao Chemical Reagent Co., Ltd., China. The chemicals, including NaOH,  $HNO_3$ , and ethyl alcohol, were all analytical pure grade. Caprolactam was obtained from Unitsika, Japan. Toluene-2,4-diisocyanate was purchased from the Hongxiang Plastic Co., Ltd., China. Toluene and stearic acid were all chemical pure grade. All reagents were used as received.

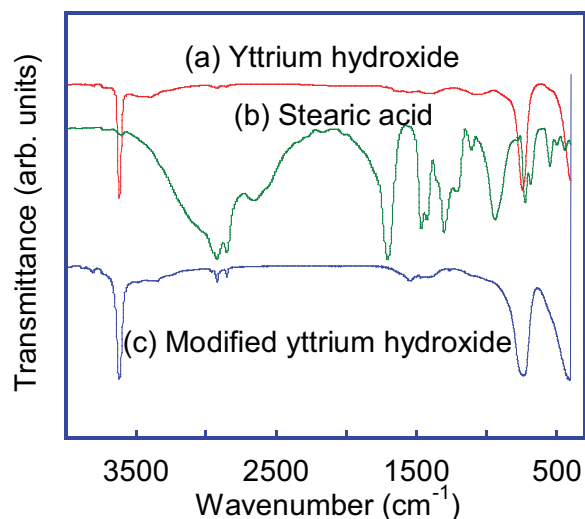
### Modified Yttrium Hydroxide Synthesis

In a typical synthesis, 5.6 g of  $Y_2O_3$  were dissolved in 5 mL of concentrated  $HNO_3$  (16 mol/L) to form 0.25 mol/L  $Y(NO_3)_3$  solution. After that, 2 mL of the  $Y(NO_3)_3$  solution (0.25 mol/L) were poured into the stainless steel beaker and 4 mL of ethyl alcohol and 4 mol/L NaOH were added to the solution to bring the final pH value from 11 to 12. The obtained solution was poured into the 20 mL stainless steel beaker with a screw-on cap, which was filled by 60 to 70% of its volume. The beaker was placed into a vacuum oven at  $140^\circ C$  for 24 h in order to complete the reaction.<sup>12</sup> Finally, the beaker was taken out of the furnace and cooled to room temperature. After opening the beaker, the product was filtered and washed with de-ionized water and ethyl alcohol. The product was washed further to remove the acid and dried at  $100^\circ C$  in a vacuum oven for 8 h. Figure 1 shows scanning electron microscopy (SEM) images of the unmodified yttrium hydroxide. Yttrium hydroxide has a rod-like structure. Yttrium hydroxide nanorods have similar uniform shape and size with the average diameter of about 400 nm and several microns in length. The structure of yttrium hydroxide is stable. A certain amount of stearic acid was dissolved in 100 mL of ethyl alcohol at  $50^\circ C$ , and then dried yttrium hydroxide was added into the solution. After stirring for 30 min, the mixture was heated at  $75^\circ C$  for 10 h. The mixture was washed five times using Soxhlet extractor for 48 h. The powder was dried at  $50^\circ C$  in a vacuum oven for 24 h. Thus, the stearic acid-modified yttrium hydroxide was obtained. Stearic acid reacts with MC nylon, as seen in Figure 2. Stearic acid can reduce the interfacial tension and improve the dispersion of yttrium hydroxide particles in the composite, enhancing its mechanical properties. There are  $2851.92\text{ cm}^{-1}$  and  $2920.89\text{ cm}^{-1}$  C-H bond absorption peaks of stearic acid and a free carboxyl carbonyl stretching vibration at  $1703.59\text{ cm}^{-1}$  in

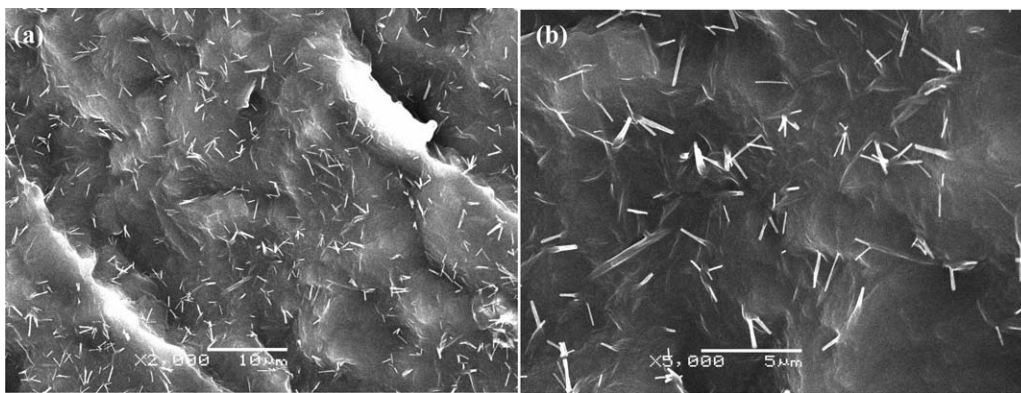
Figure 2. Compared with the yttrium hydroxide (curve a), the characteristic absorption peaks of stearic acid (curve b) appear at  $2850.36\text{ cm}^{-1}$  and  $2918.24\text{ cm}^{-1}$ . Compared with the stearic acid (curve b), a free carboxyl carbonyl stretching vibration peak disappeared at  $1703.59\text{ cm}^{-1}$  in the modified yttrium hydroxide (curve c), and new absorption peaks appeared at  $1467.37\text{ cm}^{-1}$  and  $1546.52\text{ cm}^{-1}$ , corresponding to the C=O symmetric vibration and asymmetric vibration of ester bonds. Thus, stearic acid forms chemical bonds with hydroxyl groups of yttrium hydroxide particles, and the esterification reaction occurs on the yttrium hydroxide surface.

### MC Nylon Nanocomposites Synthesis

First, 140 g of the caprolactam monomer were added into a flask and heated to  $130^\circ C$  to melt it. After reducing the pressure and distillation, the caprolactam monomer was completely melted. Modified yttrium hydroxide with weight fractions of 0 wt %, 0.2 wt %, 0.3 wt %, 0.4 wt %, 0.6 wt %, and 0.8 wt % was added after removing water with a pump. Then, the mixtures were dispersed by stirring for 30 min at  $140^\circ C$ . Sodium hydroxide (0.2 g) was added into the mixture after refluxing for about 1 h. The



**Figure 2.** Fourier transform-infrared spectroscopy (FT-IR) data for: (a) yttrium hydroxide; (b) stearic acid; (c) yttrium hydroxide modified by stearic acid. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 3.** Cross-sectional scanning electron microscopy images of the stearic acid-modified yttrium hydroxide in the MC nylon matrix: (a) lower magnification; (b) higher magnification.

solution has been refluxed for another 30 min while pumping water out. Toluene-2,4-diisocyanate was added as an activator after the solution was poured into the beaker with stirring. Finally, the mixtures were cast into a mold, which was preheated to 180°C. The mold was cooled down to room temperature for 1 day after the polymerization was completed in 1 h. The samples of MC nylon were molded and MC nylon/modified yttrium hydroxide nanocomposites were obtained. Cross-sectional SEM images of the stearic acid-modified yttrium hydroxide in the MC nylon matrix are shown in Figure 3. The nanoparticles are evenly dispersed in the nanocomposite. Due to the small particle size of nanoparticles and large surface energy, there is a thermodynamically unstable state. However, it is not easily dispersed in the nanocomposite matrix, resulting in the loss of characteristics of nanoparticles. This is especially true with a large amount of filler, where agglomeration of the nanoparticles is more severe, and well dispersed nanoparticles are hardly present in the nanocomposite matrix. Inorganic nanoparticles in the nanocomposite have strong cohesion. Strong polar inorganic bonds, small size and surface effects caused nanoparticles non-covalent forces between molecules, as well as polymer and inorganic molecular forces. Therefore, to overcome the self-condensation of the inorganic nanoparticles, stearic acid was used to change the surface properties of the particles in order to make inorganic nanoparticles disperse uniformly in the nanocomposite.

#### XRD Characterization of Modified Yttrium Hydroxide

The characterization of modified yttrium hydroxide was performed by X-ray diffraction (XRD) analysis using Rigaku D/max-2500/PC diffractometer with Cu K $\alpha$  radiation (40 kV, 200 mA). The  $2\theta$  range was 10 to 80° with 0.1°/s scan rate at room temperature.

#### MC Nylon Impact and Tensile Strength Testing

Smooth, pure and unbroken samples were tested at room temperature, following the GB/T 1843-2008 standard.<sup>13</sup> The machine used was GT-7045-MD Izod Charpy Digital Impact Tester (Gotech Testing Machines, Inc., Taiwan) with 5 J energy pendulum bob. Smooth, pure, and unbroken samples were tested at room temperature in tension, according to the GB/T 16420-1996 standard.<sup>14</sup> The tensile test rate was 10 mm/min using the RGL-30A electronic universal testing machine (Shenzhen Rui Geer Instrument Co., China).

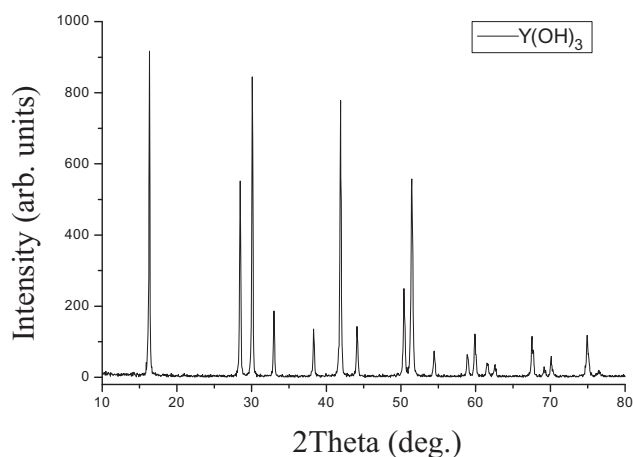
## RESULTS AND DISCUSSION

### Modified Yttrium Hydroxide Characterization

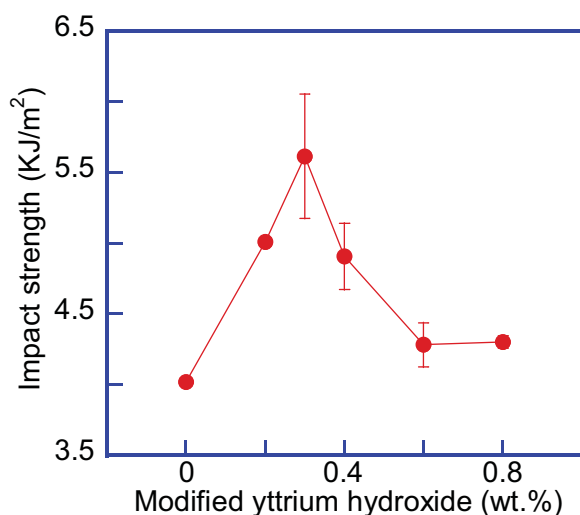
The crystal structure of the modified yttrium hydroxide was characterized by XRD. From the XRD pattern, the sharp reflections at 16.347°, 28.548°, 30.099°, 41.882°, and 51.398° correspond to (100), (110), (101), (201), and (002) planes of the hexagonal Y(OH) $_3$  phase (Figure 4). The lattice parameters,  $a = 0.6258$  nm,  $b = 0.6258$  nm, and  $c = 0.3534$  nm are similar with the literature values of  $a = 0.6268$  nm,  $b = 0.6268$  nm, and  $c = 0.3547$  nm (JCPDS 24-1422). The final product was of high purity and the XRD patterns demonstrated that the modified yttrium hydroxide can be obtained using the presented synthesis method.

### MC Nylon Nanocomposites Impact Strength

The MC nylon nanocomposites impact strength varied significantly with the yttrium hydroxide weight percentage. In the 0 wt % to 0.3 wt % yttrium hydroxide range, the impact strength of the nanocomposites increased rapidly, reaching the maximum value of 5.6 kJ/m $^2$  at 0.3 wt % of yttrium hydroxide (Figure 5). From 0.3 wt % to 0.8 wt % of yttrium hydroxide, the MC nylon nanocomposite impact strength decreased. The force between the MC nylon macromolecules is affected by the increasing percentage of yttrium hydroxide. In the 0.6 wt % to 0.8 wt % yttrium hydroxide weight percentage range, the nanocomposite impact strength tends to be stable. Based on the



**Figure 4.** XRD pattern of the stearic acid-modified yttrium hydroxide.



**Figure 5.** Impact strength of the MC nylon nanocomposites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

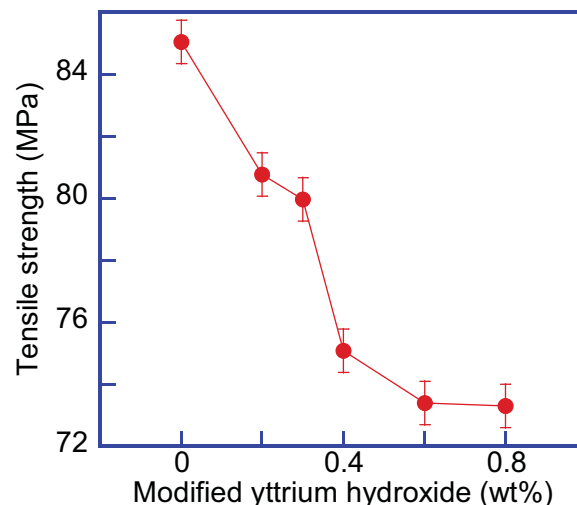
collected data, yttrium hydroxide significantly improves the impact strength of MC nylon. These results indicate that using yttrium hydroxide toughens the MC nylon. However, the weight percentage of yttrium hydroxide toughening effect is reduced when the amount of yttrium hydroxide reaches a certain level, and finally stabilizes. Thus, the optimal value for the yttrium hydroxide weight percentage is about 0.3 wt %, based on the measured nanocomposite impact strength (Figure 5).

#### Tensile Strength of MC Nylon Nanocomposites

With the increase of weight percentage of yttrium hydroxide, MC nylon nanocomposite tensile strength decreased in Figure 6. When the weight percentage of yttrium hydroxide was between 0 wt % and 0.4 wt %, the tensile strength decreased, eventually reaching a minimum plateau in Figure 6. When the weight percentage of yttrium hydroxide was between 0.4 wt % and 0.8 wt %, the nanocomposite tensile strength decreased slightly. There is a tradeoff between strength and ductility, as typically more brittle materials are harder and less ductile. The impact strength is related to the lateral loading, and adding modified yttrium hydroxide can increase molecular weight. On the lateral level, it enhances binding force and forces between the molecules. The tensile strength is related to the axial force. Modified yttrium hydroxide improves the performance on the lateral level, and may influence mechanical performance in other directions. Therefore, more modified yttrium hydroxide makes samples weaker when loaded axially. There were a lot of yttrium hydroxide particles joining with the MC nylon, weakening the bonding forces and resulting in the decreased tensile strength of the MC nylon/yttrium hydroxide nanocomposites. However, compared with other tensile strength tests,<sup>8</sup> the tensile strength of modified  $Y(OH)_3$ /MC nylon composites is higher than of the graphene oxide/MC nylon composites below 0.05 wt %.

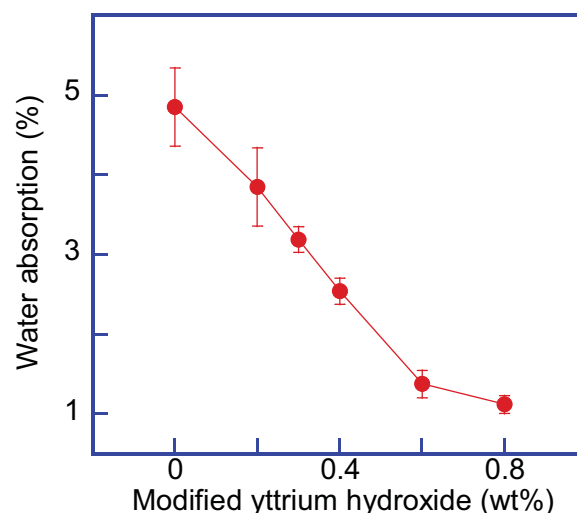
#### MC Nylon Nanocomposites Water Absorption

With the increased weight percentage of yttrium hydroxide, water absorption of nanocomposites showed an overall decrease-



**Figure 6.** Tensile strength of the MC nylon nanocomposites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

ing trend in Figure 7. In the beginning of the increasing percentages of the yttrium hydroxide, water absorption percentage dropped. The nanocomposite water absorption is minimal at 0.8 wt % of yttrium hydroxide (Figure 7). When yttrium hydroxide weight percentage continued to increase, water absorption reached saturation. This is because added yttrium hydroxide changed the number and the size of the voids, along with the mutual arrangement of the particles. Yttrium hydroxide affected the polarity of the main polymer chains, resulting in reduced water absorption at room temperature. Compared with other water absorption tests,<sup>15</sup> the percentage of water absorption in modified  $Y(OH)_3$ /MC nylon nanocomposites can be reduced to nearly 1%, while the highest moisture content in carbon-fiber/MC nylon composites can reach over 4%. These results indicated that modified yttrium hydroxide can also significantly reduce the water absorption of MC nylon.



**Figure 7.** Water absorption of the MC nylon nanocomposites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



## CONCLUSIONS

The effects of modified yttrium hydroxide on toughening of MC nylon were studied. Different percentage ratios of added yttrium hydroxide affect the modified MC nylon toughening. According to a variety of performance tests, the following conclusions can be drawn:

1. X-ray diffraction results demonstrated that the lattice parameters of the yttrium hydroxide did not change significantly with the stearic acid modification.
2. Yttrium hydroxide had a positive effect on the MC nylon toughening. The toughening effect initially increased with the yttrium hydroxide weight percentage, up to 0.3 wt %. Over the 0.3 wt % of yttrium hydroxide, the toughening effect was reduced, and finally leveled off at 0.8 wt %. The optimal weight percentage of yttrium hydroxide is about 0.3 wt %, based on toughening.
3. The tensile strength decreased from 85 MPa to 73.3 MPa with the increasing weight percentage of yttrium hydroxide. It led to the MC nylon/modified yttrium hydroxide nanocomposites weakening because of the excess amount of yttrium hydroxide particles, resulting in the decreased tensile strength of the MC nylon/yttrium hydroxide nanocomposite.
4. Adding modified yttrium hydroxide into MC nylon reduced its water absorption. The water absorption of 1% was minimal at 0.8 wt % yttrium hydroxide weight percentage.

## ACKNOWLEDGMENTS

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