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Coordination between yttrium ions and amide groups of polyamide 6 and the crystalline behavior of polyamide 6/yttrium composites

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ABSTRACT

Different amounts of yttrium ions were introduced into polyamide 6 (PA6) matrix by solution casting process. Structure, morphology and properties of the obtained PA6/Y³⁺ composite films were investigated by using FT-IR spectroscopy, Raman spectroscopy, scanning electron microscope (SEM), polarized optical microscope (POM) and differential scanning calorimeter (DSC) methods. Yttrium ions show strong coordination ability and their complexation with amide groups of PA6 can be reflected by the appearance of new bands in the amide A and amide I regions in FT-IR and Raman spectra. Furthermore, the FT-IR and Raman spectra of the PA6/ Y^{3+} composite show that the resultant chain conformations of the amide groups in the composite films are twisted from the ideal trans conformation. The DSC results reveal that Y^{3+} ions cause a significant reduction of the melting point of PA6. In addition, the existence of Y^{3+} prevents the crystallization of molten $PA6/Y^{3+}$ composite films during the cooling process. Moreover, the PA6/Y³⁺ composite can convert into γ phase PA6 or α phase PA6 when different solvents are used to remove Y³⁺ ions and induce crystallization of PA6.

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1. Introduction

Polyamide, abbreviated PA, which was first synthesized more than 70 years ago, has been widely used as engineering plastics, fibers and films [1]. As an important structural feature, polyamides possess amide groups. It has been reported that amide groups show considerable ability to coordinate with metal ions, thereby providing a new way to introduce metal complexes into the PA matrix [2–17]. Such a coordination effect is useful to modify the structure and improve the performance of polyamides in various aspects. For instance, Roberts and Jenekhe [2,3] and Kotek et al. [4,5] have demonstrated that polyamides can coordinate with strong Lewis acids such as GaCl₃. As a result, the hydrogen bonds among amide groups are completely disrupted. Ciferri, Ward and their coworkers [6-10] have reported that LiCl and LiBr could drastically reduce the crystallization rate of PA. After drawing and annealing the PA6/lithium halide complex fibers, Young's modulus of the fibers can be improved significantly. Gupta et al. [11] used PA6/GaCl₃ complexes to produce porous fibers by using electrospinning followed by removal of GaCl₃. In our previous work,

interactions between PA6/PA66 and different metal complexes, such as lithium, cooper and rare earths, were investigated by FT-IR spectroscopy, Raman spectroscopy, thermal analysis, X-ray diffraction, extended X-ray absorption fine structure (EXAFS), and near-field scanning optical microscopy (NSOM) [12-17]. The results have shown that the interactions between amide groups and metal complexes can change the hydrogen bonding network, decrease the melting temperature of PA6 and bring about microphase separations.

In recent years, a variety of new materials based on the particular electronic structure and physical and chemical properties of rare earth elements have been developed [18]. We notice that rare earth ions possess three positive charges and multiple coordination sites, and thus rare earth ions exhibit remarkable interactions with the amide groups of PA. In our previous work [15], we found feed-back enhancement mechanism that enhances signals of electronic Raman bands from ⁴I_{9/2} to ⁴I_{11/2} manifold of neodymium complexes by using 1064 nm laser. As a result, an electronic Raman band of Nd³⁺ can be used as a probe to reflect a change in coordination sphere around Nd³⁺. We used the electronic Raman band to study an interaction between Nd³⁺ and PA6 and polyvinylpyrrolidone. Nd³⁺ exhibits considerable ability to coordination with amide group since significant variations could be observed in the

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electronic Raman bands. In another work [16], we carried out a preliminary investigation on PA6 and YCl₃ by using temperature variable FT-IR and thermal analysis. In the melting process, the amide A band at 3294 cm^{-1} in nylon–lanthanide salt systems exhibits a lower wavenumber shift by 60 cm⁻¹ rather than a higher wavenumber shift, and significant wavenumber variations in amide I and II bands are observed.

All the above results have demonstrated that rare earth ions manifest strong coordination ability to amide groups. Based upon the above results, we have introduced an additive containing rare earth elements into the fiber spinning process to produce nylon fibers [19]. It has been found that the additive containing rare earth complexes helps to decrease spinning temperature and improve spinnability of PA6 fibers [20]. As a result, fine denier PA6 fibers were successfully manufactured in a series of pilot plant experiments (denier is a unit of measure for the linear mass density of fibers. If the mass of a fiber whose length is 9000 m is 1.0 g, the linear mass density of the fiber is 1.0 denier). However, the industrial experiments revealed that deep and comprehensive understanding is necessary on variations of physical-chemical properties of PA6 under the influence of rare earth metal ions. Thus, we revisit the PA6 and YCl₃ systems.

The present study further investigates the interactions between PA6 and yttrium chloride and the related phase transition behaviors by using FT-IR, Raman, DSC, polarized optical microscope and SEM methods. The results show that Y³⁺ can coordinate with the amide group of PA6 in a reversible manner. A new finding in the present study is that the coordination brings about remarkable influence on the conformation of the polyamide chain and crystal-line behavior of PA6.

2. Experimental

2.1. Materials

PA6 pellets with a relative viscosity of 2.45 (M_r = 2.65 \times 10⁴ g/mol) were purchased from Baling Petrochemical Co. Ltd (Yueyang, China).

Yttrium oxide (Y_2O_3) with a purity of 99.99% (Shanghai Yuelong Chemical Factory) was used to prepare yttrium chloride by dissolving Y_2O_3 in concentrated HCl.

The aqueous solution of yttrium chloride was carefully heated to remove water and HCl so that yttrium chloride can be crystallized from the solution. To prevent the hydrolysis of Y^{3+} ions during the heating process, HCl was added into to the yttrium chloride solution to keep the pH value of the solution below 5.

PA6 and yttrium chloride were dissolved in formic acid separately, and then mixed together with various proportions to prepare PA6/Y³⁺ solutions. For each solution, the concentration of PA6 always remained as 10 wt%, while the amount of yttrium chloride varied according to different stoichiometric ratios between Y³⁺ ions and amide groups of PA6 ($n_Y:n_{amide} = 0.10:1, 0.14:1, 0.18:1, 0.25:1$). PA6/Y³⁺ composite films were prepared by casting each solution onto a silicon substrate followed by evaporation of the solvent under vacuum at room temperature overnight. These composite films were denoted as PA-Y-1-*x*, where *x* is the stoichiometric ratio of Y³⁺ to amide groups (x = 0.10, 0.14, 0.18, 0.25). For comparison, pure PA6 film (PA-Y-1-0, x = 0) was also obtained by the same method. These films were then kept in a desiccator for 3–5 day before further characterization.

2.2. FT-IR and Raman spectroscopy

FT-IR spectra were measured at a spectral resolution of 4 cm⁻¹ on a Nicolet iN10 MX spectrometer equipped with an attenuated

total reflectance (ATR) accessory. To obtain high signal-to noise ratio, 32 scans were co-added for each spectrum.

Raman measurements were performed under ambient conditions using a Jobin-Yvon HR800 micro-Raman spectrometer and a helium-neon laser (633 nm, 1.96 eV excitation) with the backscattering configuration.

2.3. Thermal analysis

Thermal analysis of the films was performed on a Q100 differential scanning calorimeter of TA Corporation. A nitrogen flux (50 mL min⁻¹) was used as purge gas for the furnace during the experiment. The samples were heated to 260 °C at a heating rate of 10 °C/min and then cooled down to 40 °C at a cooling rate of 10 °C/min.

2.4. Polarized microscope with a hot stage

Polarized optical microscopic observation was used to register crystalline changes in terms of transmitted light during heating on a Leica DMLP polar microscope with a hot stage. PA6 and PA6/Y³⁺ composite films were placed between two glass slides and were heated to 260 °C at a heating rate of 10 °C/min. During the heating process, the micrographs of the sample under the polarized microscope were recorded by using a digital camera. All the parameters of microscope and digital camera were invariant during the heating process. The recorded digital micrographs were converted into black-white mode. Under this mode, each micrograph is a matrix composed of 763×577 pixels and each pixel is characterized by an integer whose value is between 0 and 255 to show how bright the pixel is. The larger the value is, the brighter a pixel is. Therefore, we use the summation of the brightness of all the pixels to characterize the intensity of transmitted light. The calculation was performed by using a program for MATLAB (The Math Works Inc.) written in our lab.

2.5. Scanning electron microscopy (SEM)

The morphology of the films was observed on a scanning electron microscope (JEOL JSM-6700F) at an acceleration voltage of 5.0 kV. The surfaces of the samples were coated with a conductive platinum layer (This thickness of the layer is about 5 nm) before observation.

3. Results and discussion

3.1. FT-IR and Raman studies

Fig. 1 shows FT-IR spectra of a pure PA6 film and PA-Y-1-0.10, PA-Y-0.14, PA-Y-0.18, and PA-Y-1-0.25 films in the 1700-1480 cm⁻¹ region. In the spectrum of pure PA6 film, the amide I and II bands are located at about 1635 and 1540 cm⁻¹, respectively. A new band appears around 1602 cm⁻¹ for the PA6/Y³⁺ composite films. As the content of Y³⁺ increases, the intensity of this new band increases and the band becomes a dominant peak in this region, while the intensities of amide I and II bands decrease significantly. For the PA-Y-1-0.25 film, the amide I and II bands strongly diminish. According to our previous work [16], the 1602 cm⁻ band is assigned to the C=O stretching band of amide groups that are coordinated with Y^{3+} (we denote this band as amide I' band). In comparison with the amide I band of pure PA6, the amide I' band exhibits a significant lower wavenumber shift. Upon the coordination, Y³⁺ ion has a strong electron-withdrawing effect on the oxygen atom of carbonyl group. As a result, the bond strength of the



Fig. 1. FT-IR spectra in the 1700–1480 cm^{-1} region of a pure PA6 film and PA6/Y³⁺ composite films. (a) Pure PA6 film (b) PA-Y-1-0.10 (c) PA-Y-1-0.14 (d) PA-Y-1-0.18 and (e) PA-Y-1-0.25.

carbonyl groups decreases, leading to the lower wavenumber shift of amide I band.

To get a comprehensive understanding on the spectral behavior of amide I band of PA6 upon coordination with Y^{3+} , Raman spectra of PA6/ Y^{3+} composites and pure PA6 were measured and illustrated in Fig. 2. The amide I band for the pure PA6 film can be observed at 1638 cm⁻¹ in the Raman spectrum, quite close to the amide I band at 1635 cm⁻¹ in the corresponding FT-IR spectrum. Different from FT-IR spectra of PA6, the amide II band is absent in the Raman spectra. When Y^{3+} ions are involved, a new Raman band appears around 1586 cm⁻¹. The intensity of the new band increases as the content of Y^{3+} increases. Thus, a plausible assignment of the 1586 cm⁻¹ band is that the band is the amide I' band that is also related to the amide groups that coordinate with Y^{3+} .

However, a large discrepancy on the peak positions of the amide I' band between the FT-IR spectra (1602 cm^{-1}) and the Raman spectra (1586 cm⁻¹) should be explained. The absence of the amide II in the Raman spectra of $PA6/Y^{3+}$ may be one reason, but this is not enough. The 1602 cm⁻¹ band in FT-IR spectra and the 1586 cm⁻¹ band are quite broad, indicating that the amide groups that coordinate with Y³⁺ occur in a variety of states. At least two coordination states of amide groups can be observed in vibrational spectra, one state is represent by an amide I' band at ca. 1605 cm⁻¹ and another state is characterized by an amide I' band at ca. 1585 cm⁻¹. The two coordinating states exhibit different sensitivity in FT-IR and Raman spectra. As a results, the coordinating state of amide group characterized by the 1605 cm⁻¹ exhibits high sensitivity in FT-IR spectra and shows strong band in FT-IR spectrum. On the other hand, the coordinating state of amide group characterized by the 1585 cm⁻¹ exhibits higher sensitivity in Raman spectrum and shows strong band in Raman spectrum. Results of FT-IR and Raman spectra indicate the coordination with Y³⁺ brings about a significant spectral variation on the amide I band of PA6.

Fig. 3 shows the N—H stretching band region of the pure PA film and the PA-Y-1-0.10, PA-Y-0.14, PA-Y-1-0.18 and PA-Y-1-0.25 films. A sharp band at 3294 cm⁻¹ in the spectra can be assigned



Fig. 2. Raman spectra in the 1700–800 cm⁻¹ region of a pure PA6 film and PA6/Y³⁺ composite films. (a) Pure PA6 film (b) PA-Y-1-0.10 (c) PA-Y-1-0.14 (d) PA-Y-1-0.18 and (e) PA-Y-1-0.25.



Fig. 3. FT-IR spectra in the 3600–2800 cm⁻¹ region of a pure PA6 film and PA6/Y³⁺ composite films. (a) Pure PA6 film (b) PA-Y-1-0.10 (c) PA-Y-1-0.14 (d) PA-Y-1-0.18 and (e) PA-Y-1-0.25.

to the N—H stretching mode of the amide group in PAs (amide A). In most cases, the N—H groups of PAs form hydrogen bonds with C=O groups from the vicinal PA chain [12]. The variation in

the amide A band frequency is useful to explore the variation in the hydrogen bonds in PA systems since the peak position of amide A directly reflects the strength of the hydrogen bonds [2,3,21]. The sharp amide A band at 3294 cm^{-1} for the pure PA6 film in Fig. 3a is characteristic of hydrogen-bonded polyamides in a crystalline region [22]. For the PA-Y-1-0.10 and PA-Y-1-0.14 films, the sharp amide A band is still observed around 3294 cm⁻¹. In addition, a broad shoulder at a lower wavenumber side becomes stronger. For the PA-Y-1-0.18 film, the broad shoulder changes into a broad peak, locating at around 3234 cm⁻¹. For the PA-Y-1-0.25 film, the sharp amide A band around 3294 cm^{-1} disappears completely, while the broad peak at 3234 cm^{-1} dominates in the amide A region. We assign the 3234 cm^{-1} band to the N–H stretching mode of amide groups coordinated with Y^{3+} . In comparison with the amide A band of pure PA6 film, the 3234 cm^{-1} band exhibits a 60 cm⁻¹ lower wavenumber shift. The amide A band undergoes a lower wavenumber shift rather than a higher wavenumber shift in the PA6/Y³⁺ composite films, indicating that the hydrogen bonds become stronger as Y³⁺ coordinates with the amide groups. A reasonable explanation for this is that both the hydrogen bonds and the coordinate bonds coexist in this system. In our previous work [12], we proposed a six-member ring model to explain the spectral and thermal behaviors of PA66/lithium salt system. This six-member ring model is still accessible in the PA6/ Y^{3+} system (Scheme 1). The stable six-member ring may favor stronger hydrogen bonds. In our previous work on the PA6/Li⁺ system, the amide A band only underwent a 50 cm^{-1} lower wavenumber shift. That is to say, the PA6/Y³⁺ brought about a larger lower wavenumber shift on the amide A band. This result suggests that the hydrogen bonding in the PA6/ Y^{3+} system is stronger.

As the Y^{3+} ions strongly coordinate with the amide groups of PA6, the chain conformations of PA6, especially for the -CH2-CONH-CH2- segment are also greatly affected. Fig. 4 depicts the CH₂ scissoring vibration region of the FT-IR spectra, where a group of bands can be observed for the pure PA6 film, locating at 1477, 1463, 1438 and 1416 cm^{-1} . Among these bands, the occurrence of the 1438 cm^{-1} band indicates a rotational conformation [23]. The intensity of the 1438 cm⁻¹ peak is relatively low in the spectra of the pure PA6 film. However, when the Y³⁺ ions coordinate with amide groups, the relative intensity of the 1438 cm⁻¹ band increases dramatically and becomes dominant in this region. The above results indicate that a twist of -CH₂-CONH-CH₂- group of PA6 from ideal *trans* conformation occurs upon the coordination between Y^{3+} and the amide groups. To our knowledge, no similar results are reported in the literatures before.

On the other hand, the Raman spectra (Fig. 2) are quite sensitive to the chain conformation. In the C–N–H bending region (1440–1490 cm⁻¹), the pure PA6 film exhibits two shoulder peaks



Scheme 1. Six-member ring model of the Y³⁺ ions and amide groups of PA6.



Fig. 4. FT-IR spectra in the $1500-1150 \text{ cm}^{-1}$ region of a pure PA6 film and PA6/Y³⁺ composite films. (a) Pure PA6 film (b) PA-Y-1-0.10 (c) PA-Y-1-0.14 (d) PA-Y-1-0.18 and (e) PA-Y-1-0.25.

 $(1471 \text{ cm}^{-1}, 1485 \text{ cm}^{-1})$, which are indicative of the *trans* amide groups [24,25]. The intensities of the two shoulder peaks decrease for the PA-Y-1-0.10 and PA-Y-0.14 films and disappear for the PA-Y-1-0.18 and PA-Y-1-0.25 films. In the C-C stretching region, the 1065 cm⁻¹ peak and the 1130 cm⁻¹ peak are usually indicative of an *all-trans* CC backbone conformation while the 1080 cm⁻¹ peak is attributed to the presence of gauche conformation [25,26]. For the pure PA6 film, a strong peak locating at 1130 cm⁻¹ can be observed. As the content of Y^{3+} increases, the intensities of the 1130 and 1065 cm⁻¹ peaks decrease, while the intensity of the 1080 cm⁻¹ gradually increases. For the PA-Y-1-0.18 and PA-Y-1-0.25 films, both the 1065 and 1130 cm^{-1} peaks are too weak to be observed. The above spectral changes show that the coordination between Y³⁺ ions and amide group of PA6 brings about a significant conformational variation. The trans conformations in the pure PA6 film are completely destroyed when the content of Y³⁺ ions is high enough. In addition, preliminary investigation on the second derivative spectra of PA6 and PA6/Y³⁺ composite films was investigated. Significant variations were also observed in the C–H stretching region (please see the Supporting information).

In the 1150–900 cm⁻¹ region of the FT-IR spectra (Fig. 5), information concerning the crystallization behaviors of the PA6/Y³⁺ composite films may be obtained. α crystalline phase can be obtained for the pure PA6 film as indicated by the typical α phase characteristic peaks around 959, 930 and 928 cm⁻¹ in the FT-IR spectra [27,28]. When the content of Y³⁺ is relatively small as in the case of the PA-Y-1-0.10 film, an amorphous peak at 984 cm⁻¹ [29] becomes obvious besides those α phase crystalline bands. As the content of Y³⁺ keeps increasing, the 959 cm⁻¹ band of α phase



Fig. 5. FT-IR spectra in the $1150-900 \text{ cm}^{-1}$ region of a pure PA6 film and PA6/Y³⁺ composite films. (a) Pure PA6 film (b) PA-Y-1-0.10 (c) PA-Y-1-0.14 (d) PA-Y-1-0.18 and (e) PA-Y-1-0.25.



Fig. 6. DSC curves of PA6 and PA6/Y³⁺ composite films during the heating process. (a) Pure PA6 film (b) PA-Y-1-0.10 (c) PA-Y-1-0.14 (d) PA-Y-1-0.18 and (e) PA-Y-1-0.25.

crystalline gradually decreases and becomes a very weak shoulder as can be seen for the PA-Y-1-0.14 and PA-Y-0.18 films. For the PA-Y-1-0.25 film, the characteristic peaks for α phase crystalline cannot be observed any more.

3.2. DSC studies

The melting behaviors of the PA6/Y³⁺ composite films and the pure PA6 film were recorded by using the DSC technique as illustrated in Fig. 6. As for the pure PA6 film, the main melting peak appears around 215.4 °C and the melting peak end at ca. 226 °C (this point is denoted as completely melting point in the following part) in the heating process. The completely melting points for the PA-Y-1-0.10, PA-Y-1-0.14 and PA-Y-1-0.18 films are ca. 208 °C, 206 °C and 202 °C. In addition, the melting peaks become broad and the melting enthalpies decrease as the contents of Y³⁺ increase. Moreover, additional broad peaks around 136 °C and 105 °C appear in the DSC curves of PA-Y-1-0.14 and PA-Y-1-0.18 sample. For



Fig. 7. The transmitted light intensity of the recorded electronic micrographs by polarized optical microscope. (a) Pure PA6 film (b) PA-Y-1-0.10 (c) PA-Y-1-0.14 (d) PA-Y-1-0.18 and (e) PA-Y-1-0.25.

Table 1

The data in the melting process of DSC and polarized optical microscopic (POM) observation experiments.

	Melting point in DSC (°C)	Enthalpy in DSC (J/g)	Completely melting point in DSC (°C)	Ending point in POM (°C)
PA-pure	215.4	77.4	226	228
PA-Y-1-0.10	200.0	59.4	208	208
PA-Y-1-0.14	195.0	27.4	206	206
PA-Y-1-0.18	191.2	14.1	202	200
PA-Y-1-0.25	100.8	68.6	140	115

PA-Y-1-0.25 sample, an endothermic peak at 100.8 °C with a broad background can be observed. The enthalpy is about 68.3 J/g. We suggest that the reason for the large enthalpy of this endothermic peak is as follows: the melting of PA6 crystallites and removal of adsorpted water take place simultaneously.

Fig. 7 shows the variation of the intensity of the transmitted light as a function of temperature. Part of PA6 crystallites were destroyed and changed into isotropic molten upon elevation of the temperature. As a result, the intensities of the transmitted light decrease. When the PA6 crystallites are completely molten, the intensities of the transmitted light reach a minimum value and do not change as the temperature increases further. We denote the lowest temperature at which the intensity of the transmitted light reach minimum as the ending points. For the pure PA6 film, PA6-Y-1-0.10, PA-Y-1-0.14 and PA-Y-1-0.18 samples, the ending points from polarized microscope are roughly the same as the values of completely melting points in the DSC experiments (Table 1). Furthermore, the curves of the intensity of the transmitted light versus temperature demonstrate that intensity of transmitted light of the PA6-Y-1-0.14 starts to decrease at 140 °C and the intensity of transmitted light of the PA-Y-1-0.18 sample starts to decrease at 90 °C. These results confirm the observation of additional DSC peak around 136 °C and 105 °C in the DSC experiment. For the PA-Y-1-0.25 sample, the intensity of transmitted light reaches minimum at 105 °C. The results confirm that the endothermic peak at 100.8 °C is related to the melting of PA6 crystallites.

The PA6 and PA6/ Y^{3+} composite films were cooled down to 40 °C after being heated to 260 °C. A crystallization peak appears

at 181 °C in the cooling process for the pure PA6 film, while no crystallization peaks are observable in the PA6/ Y^{3+} composite films, indicating that Y^{3+} prevents PA6 from undergoing crystallization (Fig. 8). According to the FT-IR and Raman spectra, strong coordination between Y^{3+} and amide group of PA6 plays a labile



Fig. 8. DSC curves of melt PA6 and PA6/ V^{3+} composite films during the cooling process. (a) Pure PA6 film (b) PA-Y-1-0.10 (c) PA-Y-1-0.14 (d) PA-Y-1-0.18 and (e) PA-Y-1-0.25.

cross linking role that binds different PA6 segments together. As a result, the movement of PA6 in the $PA6/Y^{3+}$ melt is constricted. Thus, the crystallization of PA6 is retarded or even prohibited.

3.3. Morphology crystalization studies

The morphology of the PA6/ Y^{3+} composite films was investigated by using SEM (Fig. 9). For the pure PA6 film, a typical spherulite structure with clear boundaries is shown in its SEM image in Fig. 9a. When Y^{3+} ions are involved, some amide groups of PA6 chain participate in the coordination with Y^{3+} ions. Consequently, the chain mobility is hindered due to the labile crosslink by the metal ions and the crystallization of PA6 is depressed to different extent. The boundary among different spherulites becomes vague for the PA-Y-1-0.10 film (Fig. 9b). For the PA-Y-0.14, PA-Y-1-0.18 and PA-Y-1-0.25 films, neither spherulite-like feature nor crystalline lamellar structure can be observed (Fig. 9c–9e). The above results are in good agreement with the FT-IR results.

PA6 usually exhibits peculiar polymorphism phenomenon. For example, PA6 can crystallize into α or γ form in which hydrogen bonding between antiparallel or parallel polymer chains are formed, respectively [29–33]. The introduction of Y³⁺ ions into the PA6 matrix will change the hydrogen bonding structure and the conformation of the polymer chains. Our following experiments demonstrate that the amorphous PA6/Y³⁺ composite is an interesting precursor of crystalline PA6, since the phase transition behaviors of the amorphous PA6/Y³⁺ composite can be controlled by using different solvents, such as water or ethanol, to remove



Fig. 9. SEM images of the pure PA6 film and PA6/Y³⁺ composite films. (a) Pure PA6 film (b) PA-Y-1-0.10 (c) PA-Y-1-0.14 (d) PA-Y-1-0.18 and (e) PA-Y-1-0.25.



Fig. 10. FT-IR spectra in the $1150-900 \text{ cm}^{-1}$ region of (a) the amorphous PA6/Y³⁺ composite film and (b and c) the samples after treatment by water (b) and ethanol (c).

 Y^{3+} ions and induce crystallization of PA6. In our experiments, the amorphous PA-Y-1-0.25 composite film was soaked in water to remove Y^{3+} ions at room temperature. The resultant film shows a strong characteristic peak of γ form at 976 cm⁻¹ in an FT-IR spectrum [34–37] (Fig. 10b), while the characteristic peak of α form did not occur. That is to say, the PA6/Y³⁺ composite film can transform into γ form when Y^{3+} ions are removed by using water. On the other hand, the amorphous PA-Y-1-0.25 composite film re-crystallized into α form rather than γ form when ethanol was adopted to remove Y^{3+} ions (Fig. 10c). Further work is still being performed.

4. Conclusions

In the present work, $PA6/Y^{3+}$ composite films were prepared by the solution casting process. The amide groups of PA6 show a strong coordination interaction with Y³⁺ ions. Upon the coordination between the amide groups of PA6 and Y³⁺, significant spectroscopic variations could be observed for amide I, II, A bands. A 60 cm⁻¹ lower wavenumber shift of the amide A band indicates that stronger hydrogen bonds are formed in the PA6/Y³⁺ composites. The resultant chain conformations of the amide groups in the PA6/Y³⁺ composite films are twisted from the ideal *trans* conformation. The crystallization of the PA6/Y³⁺ composite films during the solution casting process is inhibited due to the labile crosslink effect. When the content of Y³⁺ is high enough, the obtained composite films become amorphous. The amorphous PA6/ Y³⁺ composite is an interesting precursor of crystalline PA6, since it can be converted into γ phase PA6 in water or α phase PA6 in ethanol. Thus, we can use different solvents to remove Y³⁺ ions from the composite films and induce crystallization of pure PA6 in different crystalline forms. In summary, coordination interaction between PA6 and Y³⁺ ions offers a promise way to process PA6 by tailoring its physical and chemical properties.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2012. 04.041.

References

- [1] J. Baiju, M. Furukawa, Polym. Eng. Sci. 49 (2009) 1970.
- [2] M.F. Roberts, S.A. Jenekhe, Macromolecules 24 (1991) 3142.
- [3] M.F. Roberts, S.A. Jenekhe, Chem. Mater. 2 (1990) 224.
- [4] N. Vasanthan, R. Kotek, D.W. Jung, D. Shin, A.E. Tonelli, D.R. Salem, Polymer 45 (2004) 4077.
- [5] M. Afshari, A. Gupta, D. Jung, R. Kotek, A.E. Tonelli, N. Vasanthan, Polymer 49 (2008) 1297.
- [6] A. Ciferri, E. Bianchi, F. Marchese, A. Tealdi, Makromol. Chem. 150 (1971) 265.
- [7] B. Valenti, E. Bianchi, G. Greppi, A. Tealdi, A. Ciferri, J. Phys. Chem. 77 (1973) 389.
- [8] E. Bianchi, A. Ciferri, A. Tealdi, R. Torre, B. Valenti, Macromolecules 7 (1974) 495.
- [9] A. Ciferri, Poly. Eng. Sci. 15 (1975) 191.
- [10] A. Richardson, I.M. Ward, J. Poly. Sci. Part B Poly. Phys. 19 (1981) 1549.
- [11] A. Gupta, C.D. Saquing, M. Afshari, A.E. Tonelli, S.A. Khan, R. Kotek, Macromolecules 42 (2009) 709.
- [12] Y.Z. Xu, W.X. Sun, W.H. Li, X.B. Hu, H.B. Zhou, S.F. Weng, F. Zhang, X.X. Zhang, J.G. Wu, D.F. Xu, G.X. Xu, J. Appl. Poly. Sci. 77 (2000) 2685.
- [13] A.F. Xie, D.L. Tao, Z.B. Zhang, Y.Z. Xu, Y.J. Wu, T.D. Hu, B.Y. Gu, J.G. Wu, G.Z. Yang, D.F. Xu, J. Mol. Struct. 613 (2002) 67–71.
- [14] Y.J. Wu, Y.Z. Xu, D.J. Wang, Y. Zhao, S.F. Weng, D.F. Xu, J.G. Wu, J. Appl. Poly. Sci. 91 (2004) 2869.
- [15] Y.Z. Xu, J.G. Wu, W.X. Sun, D.L. Tao, L.M. Yang, Z.F. Song, S.F. Weng, Z.H. Xu, R.D. Soloway, D.F. Xu, G.X. Xu, Chem. Eur. J. 8 (2002) 5323.
- [16] W.X. Sun, X.B. Hu, Y.Z. Xu, L.W. Qu, Z.L. Yang, D.J. Wang, X.X. Liu, F.X. Guo, S.F. Weng, J.G. Wu, D.F. Xu, Acta Chim. Sin. 58 (2000) 1602.
- [17] H.Z. Li, Y.J. Wu, H. Sato, L. Kong, C.F. Zhang, K. Huang, D.L. Tao, J. Chen, X.X. Liu, Y. Zhao, Y.Z. Xu, J.G. Wu, Y. Ozaki, Macromolecules 42 (2009) 1175.
- [18] P.N. Kumta, S.H. Risbud, J. Mater. Sci. 29 (1994) 1135.
- [19] C.F. Zhang, G.Q. Lai, Y.F. Liu, et al., China Patent, ZL 200710099455.3, 2010.
- [20] K. Huang, J.X. Jiang, C.F. Zhang, et al., China Patent, ZL 200710099454.9, 2010.
- [21] W. Wei, L. Qiu, X.L. Wang, H.P. Chen, C.Y. Lai, F.C. Tsai, P. Zhu, J.T. Yeh, J. Polym.
- Res. 18 (2011) 1841.
- [22] A. Singhal, L. Fina, J. Appl. Spectrosc. 49 (1995) 1073.
- [23] J. Maillo, P. Pages, E. Vallejo, T. Lacorte, J. Gacen, Eur. Polym. J. 41 (2005) 753.
- [24] T. Miyazawa, J. Mol. Spectrosc. 4 (1960) 155.
- [25] J.S. Stephens, D.B. Chase, J.F. Rabolt, Macromolecules 37 (2004) 877.
- [26] K. Song, J.F. Rabolt, Macromolecules 34 (2001) 1650.
- [27] N. Vasanthan, J. Poly. Sci. Part B Poly. Phys. 41 (2003) 2870.
- [28] N.S. Murthy, R.G. Bray, S.T. Correale, R.A.F. Moore, Polymer 36 (1995) 3863.
- [29] H. Arimoto, J. Poly. Sci. Part A Gen. Pap. 2 (1964) 2283.
- [30] D.R. Holmes, C.W. Bunn, D.J. Smith, J. Poly. Sci. 17 (1955) 159.
- [31] H. Arimoto, M. Ishibash, M. Hirai, Y. Chatani, J. Poly. Sci. Part A Gen. Pap. 3 (1965) 317.
- [32] T.D. Fornes, D.R. Paul, Polymer 44 (2003) 3945.
- [33] L. Penel-Pierron, C. Depecker, R. Seguela, J.M. Lefebvre, J. Poly. Sci. Part B Poly. Phys. 39 (2001) 484.
- [34] G. Rotter, H. Ishida, J. Poly. Sci. Part B Poly. Phys. 30 (1992) 489.
- [35] S.Y. Tsou, H.S. Lin, C. Wang, Polymer 52 (2011) 3127.
- [36] V. Miri, O. Persyn, R. Seguela, J.M. Lefebvre, Eur. Polym. J. 47 (2011) 88.
- [37] C.B. Giller, D.B. Chase, J.F. Rabolt, C.M. Snively, Polymer 51 (2010) 4225.