

The Influence of Rare Earth Ions on the Rheological Behavior of Polyamide^{*}

Xin-xin Sang^{a, b}, Jing-nan Zhang^a, Yu-cai Ke^a, Xin-yu Cao^a, Yong-mei Ma^{a**} and Fosong Wang^a

^aKey Laboratory of Green Printing, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

^bUniversity of Chinese Academy of Sciences, Beijing 100049, China

Abstract The polyamide 66 (PA66)/lanthanum acetate blends with small amounts of salt loadings (≤ 1 wt% of PA) have been prepared in a twin-screw extruder. The rheology of PA66 and its blends has been investigated by a rotational rheometer. The results suggested that with the salt loading in excess of 0.2 wt% the typical Newtonian viscosity plateau disappeared and both the low-frequency complex viscosities η^* and storage modulus G' of blends were much higher than those of neat PA66, the storage modulus was higher than the loss modulus at low frequencies ($\tan\delta < 1$), *i.e.*, the melt changed from a viscoelastic liquid for unfilled polymer to a viscoelastic solid ($G' > G''$). While the viscosity followed a strong shear thinning with increasing frequency, the η^* and G' decreased significantly even lower than those of neat PA66 at high frequencies. The combination of dynamic mechanical analysis (DMA) and X-ray photoelectron spectroscopy (XPS) analysis has revealed that coordination effect occurred between lanthanum and carbonyl oxygen atoms in amide groups of the polymer to form pseudo-crosslinked network structure, which makes the glass transition temperatures (T_g) and storage modulus (E') of blends enhanced. The network structure formation-destruction and chains entanglement-disentanglement processes at different frequencies are responsible for the above rheological behaviors of blends.

Keywords: Rheology; PA66-lanthanum acetate blends; Polymer-metal interaction; Coordination; Viscoelastic solid behavior.

INTRODUCTION

Interaction between metal ions and polar groups of polymers provides a new chance to modify the performance of polymers and to develop a variety of functional materials.

Polyamide (PA) is made of repeating units linked by amide bonds and has broad applications in plastics and fibers. The amide group in PA contains two lone electron pairs on oxygen and one lone electron pair on nitrogen. Extensive investigations have shown that the presence of these lone pairs enables the amide group to coordinate with metal ions^[1–5]. Such coordinating sites can act as crosslinking points, which provides significant modification of many properties. In addition, it is a potential way to modify the processing of polyamides.

In earlier works, it has been reported that the addition of inorganic salts, mainly alkali, transition and alkaline earth metal (denoted “non-earth metal” in this work) halides such as lithium, calcium, copper, and magnesium chloride *etc.*, into PA6 strongly depresses the melting temperature^[3, 5–7] and crystallization rates^[5–7], while increases the glass transition temperature^[8–10] and the melt viscosity^[11, 12], *etc.* The enhancement of the

^{*} This work was financially supported by the National Science-Technology Support Plan Projects (No. 2014BAC03B05), the National Natural Science Foundation of China (No. 51373184) and MoST973 Research Program (Nos. 2012CB933801 and 2014CB931803).

^{**} Corresponding author: Yong-mei Ma (马永梅), E-mail: maym@iccas.ac.cn

Received March 23, 2015; Revised June 2, 2015; Accepted June 4, 2015

doi: 10.1007/s10118-015-1699-7

melt viscosity and the decrease of the crystallization rate have been utilized to induce high amorphous orientation through a high draw ratio process, and high modulus fibers and films can be produced after subsequent crystallization^[12, 13]. Additionally, with the help of depression of melting temperature the polymers can be processed well below the conventional processing temperature^[14], which can be applied for processing very high melting or thermally unstable polymers^[15]. Moreover, the enhanced melt viscosity by such additions allowed more convenient for processing low molecular weight polymers^[16]. However, in order to drastically reduce the melting temperature and greatly increase the melt viscosity of PA, customarily it requires a high addition of inorganic salts, above 5 wt% of PA^[5, 7], and it leads the application temperature of materials to reduce. Moreover, to prevent thermal degradation of the polymer during mixing in the melt due to high addition of salt, when a solution mixing method is chosen, an evaporation of residual solvent working procedure is attached still, which makes the process more complex.

Compared with other metals, rare earth elements possess more positive charges and multiple coordination sites^[1]. Studies of the influence of lanthanide on polyamide properties have aroused great interest not only in theory but also in practice. Until now, however, few works have been reported on the rare earth modified PA^[1, 17] and most works were limited to the interaction between rare earth ions and PA.

Since the major forms of processing polymers and their blends frequently occur in the molten state, besides the interest in the detailed mechanism of polymer/salt interaction, the influence of the metal ions on the processibility of polymers must be paid much more attention. The rheological behavior, *i.e.*, the viscosity and elasticity of molten polymers as a function of frequency or temperature, is very important for assessing processibility and optimizing processing operations of polymers. However, only few studies deal with the influence of non-earth metal ions on the melt rheological behavior of polyamide and other polymer systems^[18–21], much less deal with the studies of earth metal ions-polymer complexes.

The rare earth inorganic salt due to the particular electronic structure maybe is a good candidate as an effective aid to improve the processing properties of PA66, *i.e.*, not only the processibility is fine with very small loading but also the application temperature does not reduce. Since the dynamic shear rheological measurement is very useful in investigating the correlation between melt state viscoelastic of polymers and their chain structure. The specific objective of the present work is to investigate the rheological behavior of PA66 with small amount of lanthanum acetate (LaAc₃) by means of DHR2 rotational rheometer. Dynamic mechanical properties (DMA) and X-ray photoelectron spectroscopy (XPS) are used to investigate the interaction between rare earth ions and PA and the effects of that on the glass transition temperature and rheological behavior of blends.

EXPERIMENTAL

Materials

PA66 (EPR2702, $T_m = 260\text{ }^{\circ}\text{C}$) was kindly supplied by China Shenma Engineering Plastics Co. Ltd.

Lanthanum acetate (LaAc₃), industrial-grade, was purchased from China Qufu Lanthanide Chemical Co. Ltd.; the total rare earth oxides TREO were > 99.99%.

Antioxidants, pentaerythritol ester and phosphite ester compounds (mass ratio 1:1) used in this work were commercial grades.

Blend Sample Preparation

PA66 resin granules were dried at 80 °C for 24 h in a blast drying oven, and lanthanum acetate was vacuum dried at 60 °C for 48 h before use. The lanthanide salt content in PA66 blends varied from 0.08 wt% to 10 wt% (the blend containing 10 wt% salt prepared only used as one of the sample for DMA measurements). In order to realize a well dispersion of inorganic salt particles within polymer matrix, especially for lower contents of salt, the preparation of blends was realized *via* a masterbatch process in a twin-screw extruder at screw speed of 250 r·min⁻¹. Firstly, the blend with salt content of 5 wt% was prepared as masterbatch. Then samples containing salt content with or below 1 wt% were obtained by dilution processing of the masterbatch in the same way. The

barrel temperatures were maintained at 260 °C, 260 °C, 260 °C, 265 °C, 265 °C, and 260 °C. The extrudate was subsequently cut into pellets by a pelletiser. Pellets were dried in a vacuum oven at 80 °C for 24 h before use.

PA66 and the blend pellets were melt pressed at 280 °C under a nominal pressure of 5 MPa into a circular disk with a diameter 25 mm and thickness 1 mm for rheological study, and rectangular sheet of a size 2 mm × 12 mm × 25 mm for dynamic mechanical analysis, respectively.

Some pellets were shattered into powder for X-ray photoelectron spectroscopy (XPS) analysis.

Characterization

Rheological measurements

Small amplitude oscillatory rheological measurements were performed on a stress-controlled Rheometer DHR-2 (TA Instrument Ltd., US) using 25 mm parallel plate geometry and a 1 mm sample gap. The dynamic rheological properties were determined at frequencies varied from 0.05 rad·s⁻¹ to 100 rad·s⁻¹, a fixed strain of 5% was used to ensure that measurements were taken well within the linear viscoelastic region of the materials investigated. All measurements were carried out in the nitrogen protection environment at 265 °C. This temperature was higher than the melting temperature of each sample which was chosen to allow adequate duration of the experiments without noticeable degradation as checked by TGA technique (not listed in this paper).

Dynamic mechanical analysis (DMA)

The dynamic mechanical analysis (DMA) was performed with a TA-Q800 instrument operated in a single cantilever mode clamp. Samples were tested over a temperature range from -145 °C to 130 °C at a rate of 3 K·min⁻¹ and a frequency of 1 Hz.

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) data was collected by an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W AlK α radiations. The base pressure was about 3×10^{-13} MPa. The binding energies were corrected by referring to the C 1s peak at 284.8 eV.

RESULTS AND DISCUSSION

Rheological Properties

Figure 1 shows the complex viscosity (η^*) as a function of frequency (ω) for PA66 and PA66/LaAc₃ blends at 265 °C. It can be seen clearly that the neat PA66 and blend sample of 0.08 wt% LaAc₃ exhibit typical Newtonian viscosity plateau behavior, but the apparent viscosity for this blend is higher than that of a neat PA66 over the range of studied frequencies. This behavior indicates that the relaxation of polymer chains in the blend is effectively restrained by the presence of metal ions, even if the addition of salt is very low. However, with the salt loading in excess of 0.2 wt%, the plateau disappears and the low-frequency complex viscosity of blends increases significantly and much higher than that of neat PA66 but lower at high frequencies. Additionally, non-Newtonian behavior flow can be observed obviously for neat PA66 and PA66/LaAc₃ blends. Especially, for blend samples, when the frequency increases, the viscosities exhibit stronger shear-thinning behavior and possess characteristics of pseudoplastic fluid. All these results manifest that the blends are much more sensitive to shearing and can flow more easily when the frequency is enhanced. Similarly, as can be seen from Fig. 2, the low-frequency modulus of blends also increases significantly and much higher than that of neat PA66 but lower at high frequencies especially for the blend samples with high addition of LaAc₃.

The G' curves rise upwards, when the frequency is enhanced, and lead to a pronounced deviation from the terminal behavior which is noticeable at the low frequency end of the curves, implying that very long relaxation times and slow relaxation processes exhibit in polymer melt due to the formation of crosslinking structure of polymer chains.

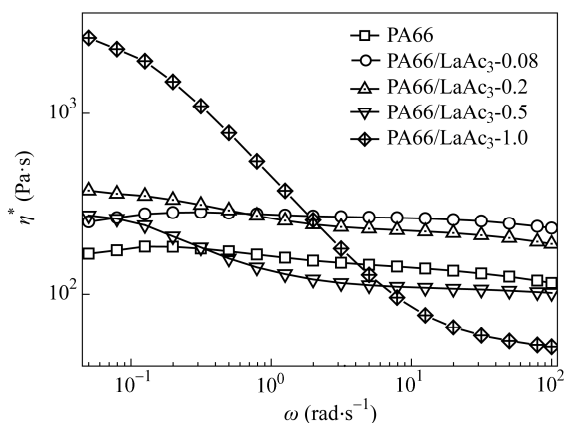


Fig. 1 η^* versus ω of neat PA66 and PA66 filled with different amounts of LaAc₃ (PA66/LaAc₃-X indicates that the weight percentage of LaAc₃ in the PA66/LaAc₃ blends is X wt%)

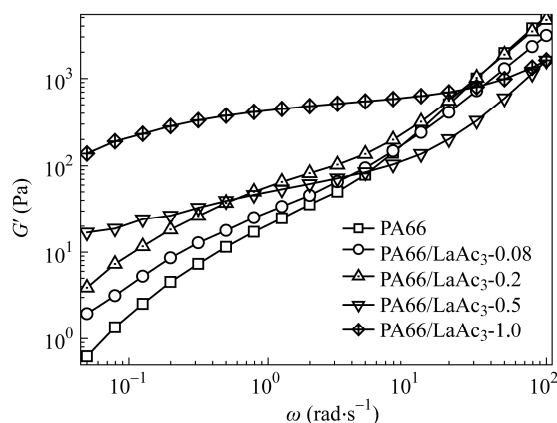


Fig. 2 G' versus ω of neat PA66 and PA66 filled with LaAc₃

In order to evaluate the contribution of the elastic (represented by G') and viscous (by G'') components to the melt, typical storage and loss moduli for PA66 and PA66/LaAc₃ blends are depicted with frequency as shown in Fig. 3. As is well known, in the melt of many polymers the loss modulus is higher than the storage modulus in the lower frequency range and the loss tangent is higher than 1, implying that the melt is of viscous character. With increasing the frequency both the storage modulus and loss modulus gradually increase. It is pointed out that the storage modulus increases more rapidly, and then there will be an intersection. The frequency at which $G' = G''$ and $\tan\delta = 1$ is called the crossover frequency. Above the crossover frequency, the melts of materials start an elastic flow, which is unfavorable for processing. In this work neither PA66 nor the blend samples present their crossover frequency in the higher frequency within the studied frequency range. However, with the salt loading in excess of 0.2 wt% for PA66/LaAc₃ an intersection appears at low frequency as shown in Fig. 3(b); below the intersection point, G' is higher than G'' which shows that the melt of the blend possesses a viscoelastic solid feature ($G' > G''$) at low frequencies.

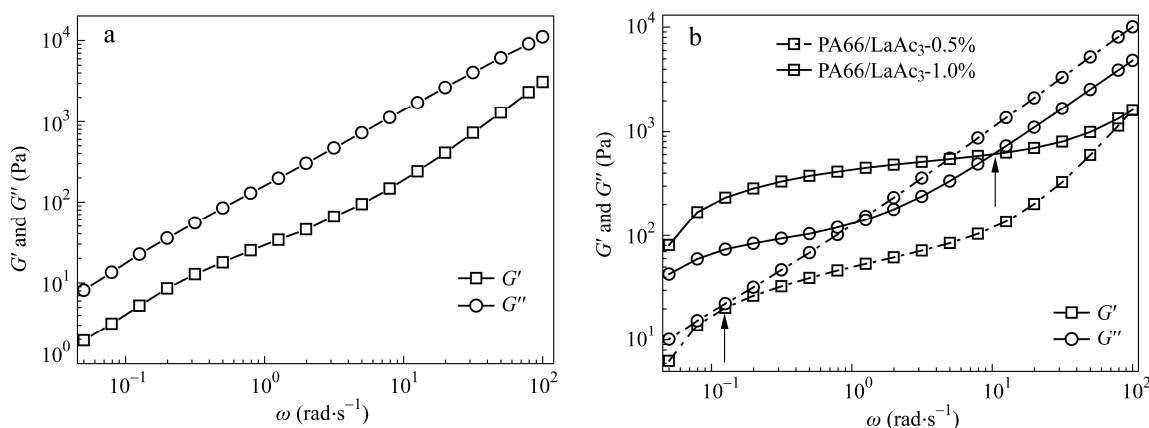


Fig. 3 G' and G'' versus ω of neat PA66 (a) and PA66 filled with 0.5 wt% and 1 wt% LaAc₃ samples (b)

The results are also confirmed by the changes of $\tan\delta (= G''/G')$ as shown in Fig. 4, which means that the more amounts of LaAc₃ introduced into the blend samples, the lower value of $\tan\delta$ to be, particularly the value of $\tan\delta$ that lower than unit occurs below a frequency 0.15 rad·s⁻¹ for 0.5 wt% blend sample and below a frequency 10 rad·s⁻¹ for 1.0 wt% blend sample, indicating that these low-frequency viscoelastic features of the samples exhibit pronounced elastic properties and very long relaxation times.

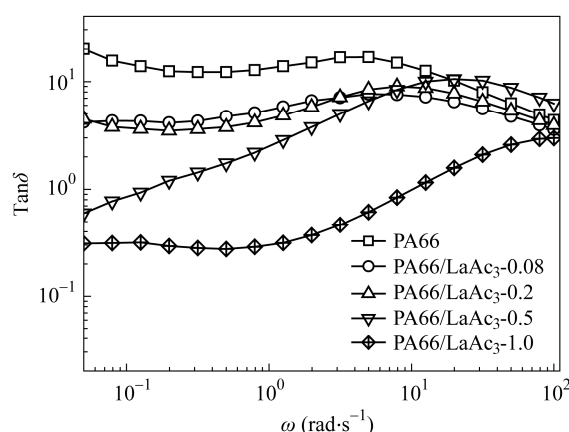


Fig. 4 $\text{Tan} \delta$ versus ω of neat PA66 and PA66 filled with LaAc_3 blends

The above results indicate that when the salt loading is in excess of 0.2 wt% the rheological behavior at low frequency changes from a viscoelastic liquid ($G'' > G'$) for unfilled polymer to a viscoelastic solid ($G' > G''$) for blend samples. It seems like a pseudosolid character that similar to those observed in the many polymer nanocomposites^[22, 23], the difference is that the latter occurs at both low and high frequencies, but the former only at low frequencies. In order to make further discussion of this change in behavior, cross-plots, which are very sensitive to the onset of viscoelastic solid behavior, are depicted by complex viscosity η^* versus complex modulus G^* as shown in Fig. 5. It shows the increments of $|\eta^*|$ at finite values of complex modulus (G^*). With increasing the salt loading, the tendency of cross-plots in the lower complex modulus (G^*) range (that corresponding to the lower frequency range) of blend samples changes greatly, especially the amount of salt more than 0.2 wt%. It indicates that the onset of viscoelastic solid behavior or a percolation threshold that occurs at above 0.2 wt% LaAc_3 in blend systems, beyond the percolation threshold the behaviors of low-frequency viscosity and modulus transit from viscoelastic liquid to viscoelastic solid behavior. This change in behavior towards a viscoelastic solid behavior at low frequency is related to the structural change by addition of salts to this system, *i.e.*, there is a strong interaction between PA66 segments and the lanthanide metal ions, as a result the melt strength and elasticity of blends are enhanced.

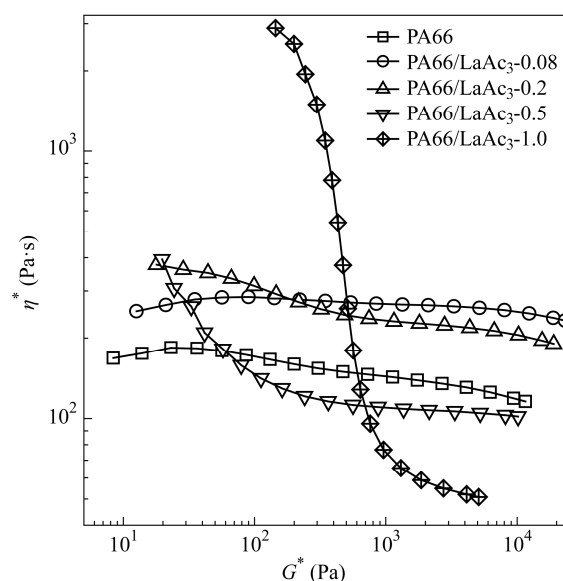


Fig. 5 Complex viscosity η^* versus complex modulus G^* of neat PA66 and PA66 filled with LaAc_3

All of properties mentioned above will be helpful for improving the processability of the PA66 blends with small amount of LaAc_3 . For example, the melt with a sufficiently high viscosity in low frequency range is beneficial to the stability of the membrane bubble during film blowing, which also makes the film more uniform. During the extrusion of large pipes, the draw-down (sag) and deformation phenomenon can be effectively prevented. At the same time, because the melt viscosity drops rapidly as the shear rate increases, it effectively reduces the energy consumption during processing which can greatly improve the production efficiency. Nevertheless, the melting temperatures keep almost no change in our blend systems with small amounts of LaAc_3 (the T_m values are not listed in this paper). Consequently, the addition of lanthanum acetate could effectively improve the processing properties of PA66.

Dynamic Mechanical Properties

The dynamic storage modules as a function of temperature for neat PA66 and blends are shown in Fig. 6. It can be seen that the storage modules of blends is higher than that of PA66 in the wide range of temperature, indicating that the introduction of salts enhances the stiffness of PA66.

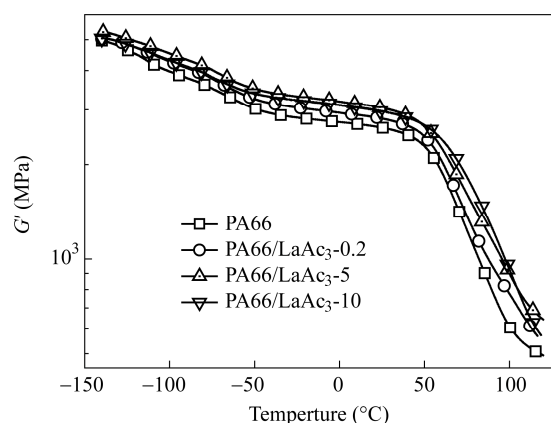


Fig. 6 Temperature dependency of storage modulus of PA66/LaAc₃ blends at 1 Hz

Three different relaxation processes α , β and γ for PA66 are shown in Fig. 7(a): (i) the α relaxation belongs to the glass transition; (ii) the β relaxation is attributed to segmental motion of amide groups not hydrogen bonded to other amides or nearby chains; (iii) the γ relaxation is a result of the crankshaft-like rotation of four or more methylene carbon atom chain between the amide groups^[24].

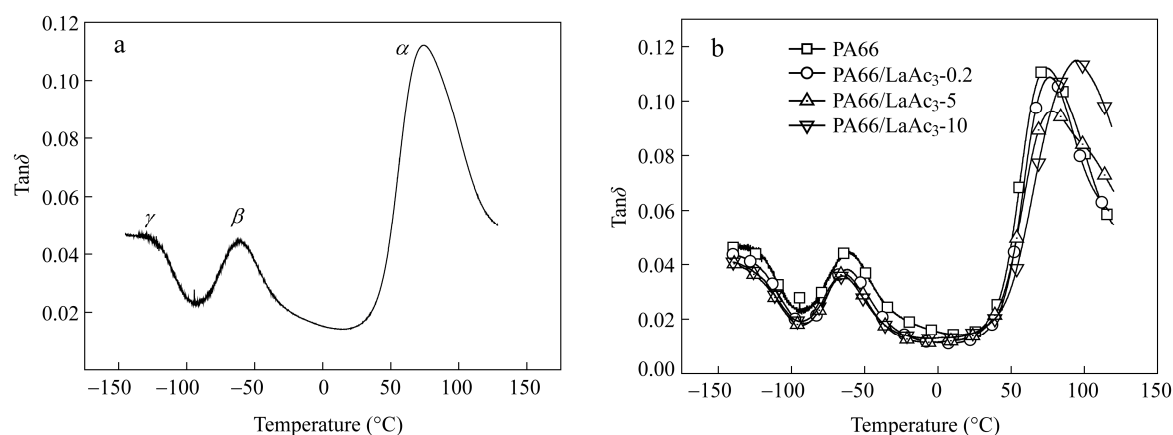


Fig. 7 Temperature dependency of $\tan\delta$ of neat PA66 (a) and PA66/LaAc₃ blends (b) at 1 Hz

It can be seen from Fig. 7(b), the intensity of the β peak decreases with the addition of LaAc_3 . Since the β relaxation is attributed to segmental motion of amide groups not hydrogen bonded to other amides or nearby chains, the decrease in intensity of the β peak with the addition of LaAc_3 indicates that partial segmental motion of amide groups not hydrogen bonded is restricted due to the addition of LaAc_3 . In other words, coordination occurs between the amide groups of PA66 not hydrogen bonded and lanthanide ions leading to the confinement of amide segmental motion.

The values of the glass transition temperatures, T_g , for undoped and doped PA66 samples are listed in Table 1. The result indicates that with increasing the salt loading the glass transition temperature is enhanced owing to the crosslinking effect resulted from the coordination.

Table 1. T_g of PA66/LaAc₃ blends

LaAc ₃ content (wt%)	0	0.2	1	5	10
T_g (°C)	74.3	76.2	76.7	77.8	95.4

Discussion on Interaction Mechanism

It is known that as the metallic ions interact with polymeric groups the chemical state of the metal element and polymer groups may change^[25]. To gain an insight into the electronic characters and the change of chemical state of blend composition before and after mixing, XPS analysis of the La3d5, N1s and O1s binding energy (BE) regions is investigated (Table 2). XPS profiles for PA66, LaAc₃ and their blend are shown in Fig. 8.

Table 2. Binding energy of elements

Sample	N1s	O1s	La3d5
PA66	399.53	531.39	—
LaAc ₃	—	533.05	840.36
PA66/LaAc ₃	399.60	531.89	838.93

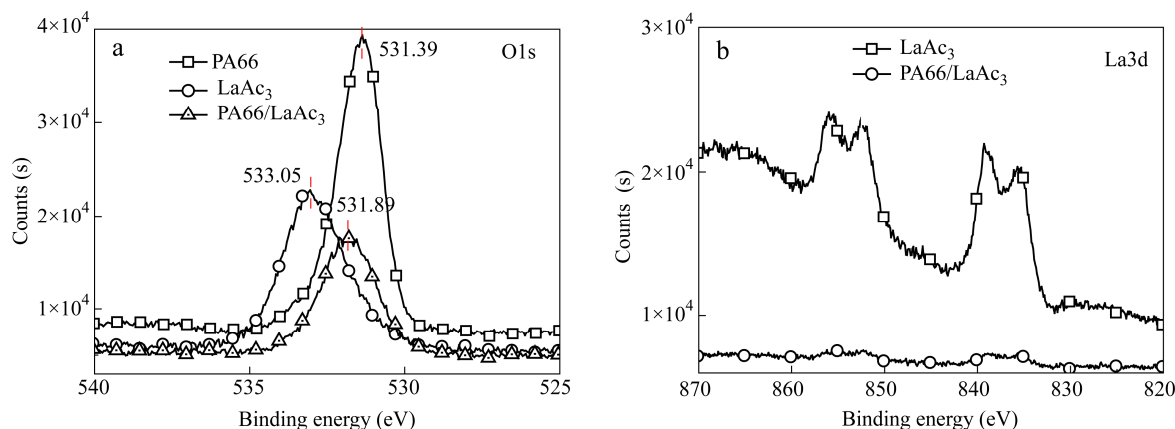


Fig. 8 XPS spectra over the O1s and La3d regions for PA66, LaAc₃ and PA66/LaAc₃

The binding energy value of La3d5 in the blend is 838.93 eV. Compared with LaAc₃, the binding energies of La3d5 in the blend have a decreasing trend because of the interaction between lanthanum ions and amide groups of PA66. In order to identify which is the possible element, the carbonyl oxygen or the nitrogen of amide groups that interacts directly with metal ions, the binding energies of N1s and O1s are analyzed. It can be seen that no change of N1s is observed during blending, while the binding energy of O1s increases. Therefore the coordination occurs between lanthanum and carbonyl oxygen atoms directly in the amide groups of the PA66.

Based on the coordination site discussed above, there are many amide functional groups along the polyamide molecular chains and the amide groups can coordinate with metal ions. Because of the steric effect

and the entanglement state of the polymer chain, the metal ions may coordinate with carbonyl oxygen groups of PA66 from the same molecular chain or from the different molecular chains, therefore the ions play the role of crosslinking points to form a pseudo-crosslinked network structure. The matrix PA66 chains without coordination can be dragged and entangled together with outer chains of crosslinked network, thereby, the networks weaken the mobility of the molecular chains and the free volume of PA66 decreases, consequently the T_g and the storage modulus of blends increase, at the same time they also prevent the melt flow under low frequency shearing due to the increase of the apparent viscosity and storage modulus of the melt. With the increase of metal ion concentration, more coordination chains are formed, once the percolation threshold is reached, extension of network forms through entire of the material. Therefore, viscosities and storage moduli of the melt of the blends at low frequency are much higher than those of neat PA66 which shows that the melt of the blends exhibits a viscoelastic solid ($G' > G''$) feature at low frequencies. As frequency (shear rate) increased, the crosslinked network structures are destroyed and a large amount of chain disentanglements occurs, more pronounced shear-thinning behavior happens. Nevertheless some of the coordination chains are still being saved and those are similar to the branched polymer chains (short or long chain). As well known, branched molecules have small coil dimension or small hydrodynamic volume than linear molecules of the same molecular weight, thus the melt can flow easily past each other under high frequency (shear rate) and results in the decrease of melt viscosity and storage modulus of the systems significantly even lower than those of the neat polymer^[26]. Finally, the power requirement for extrusion is significantly reduced and the rate of production is significantly increased.

CONCLUSIONS

We have reported the influence of adding lanthanum acetate into PA66 on the rheological properties. It can be found that with the salt loading in excess of 0.2 wt% the typical Newtonian viscosity plateau disappears and at low frequencies both the complex viscosity and storage modulus of blends are much higher than those of neat PA66. In addition, the storage modulus is higher than the loss modulus at low frequencies ($\tan\delta < 1$), revealing that the melt flow changes from viscoelastic liquid for unfilled polymer to a viscoelastic solid behavior. When the frequency increases, the viscosities exhibit stronger shear-thinning behavior and both the complex viscosity and storage modulus of blends decrease significantly even lower than those of the neat polymer at high frequencies. Therefore, the addition of small amount of lanthanum acetate could effectively improve the processing properties of PA66. The XPS and DMA analyses have revealed that coordination occurred between lanthanum and carbonyl oxygen atoms in amide groups of PA66. The DMA results also indicate that with increasing the salt loading, the glass transition temperatures and storage modulus of blends are both enhanced owing to the crosslinking effect of the coordination. The network structure formation-destruction and chains entanglement-disentanglement processes, as well as the coordination chains structure (similar to branched polymer chains) of the melt at different frequencies, are responsible for the above rheological behaviors of blends.

REFERENCES

- 1 Clement, O., Rapko, B.M. and Hay, B.P., *Coord. Chem. Rev.*, 1998, 170(1): 203
- 2 Ciferri, A., Bianchi, E., Marchese, F. and Tealdi, A., *Makromol. Chem.*, 1971, 150(1): 265
- 3 Valenti, B., Bianchi, E., Greppi, G., Tealdi, A. and Ciferri, A., *J. Phys. Chem.*, 1973, 77(3): 389
- 4 Wu, Y., Xu, Y., Wang, D., Zhao, Y., Weng, S., Xu, D. and Wu, J., *J. Appl. Polym. Sci.*, 2004, 91(5): 2869
- 5 Siegmann, A. and Baraam, Z., *Int. J. Polym. Mater.*, 1980, 8(4): 243
- 6 Valenti, B., Bianchi, E., Tealdi, A., Russo, S. and Ciferri, A., *Macromolecules*, 1976, 9(1): 117
- 7 Siegmann, A. and Baraam, Z., *J. Appl. Polym. Sci.*, 1980, 25(6): 1137
- 8 Kim, H.G. and Harget, P.J., *J. Appl. Phys.*, 1979, 50(10): 6072

- 9 Mehta, M.J. and Andrews, R.D., Polym. Prep., 1973, 14: 1260
- 10 La Mantia, F.P. and Acierno, D., Colloid Polym. Sci., 1981, 259(7): 693
- 11 Acierno, D., Bianchi, E., Ciferri, A., Decindio, B., Migliaresi, C. and Nicolais L., J. Polym. Sci., Part C: Polym. Symp., 1976, 54: 259
- 12 Acierno, D., La Mantia, F.P., Polizzotti, G., Russo, S. and Titomanlio, G., J. Appl. Polym. Sci., 1980, 25(9): 2001
- 13 Afshari, M., Gupta, A., Jung, D., Kotek, R., Tonelli, A.E. and Vasanthan, N., Polymer, 2008, 49(5): 1297
- 14 Siegmann, A. and Baraam, Z., Macromol. Rapid Commun., 1980, 1(2): 113
- 15 Hansen, J.E., 1971, U.S. Pat., 3,591,565
- 16 Mckelvey, J.M., "Polymer processing", John Wiley and Sons, New York, 1962
- 17 Xie, A., Zhang, Z., Gu, B., Yang, G., Tao, D., Weng, S., Wu, J., Xu, G., Hu, X., Liu, X., Zhao, Y., Xu, Y. and Xu, D., J. Mater. Sci. Lett., 2002, 21(4): 345
- 18 Acierno, D., D'Amico, R., La Mantia, F.P. and Russo, S., Polym. Eng. Sci., 1980, 20(12): 783
- 19 Shenoy, A.V., Saini, D.R. and Nadkarni, V.M., J. Mater. Sci., 1983, 18(7): 2149
- 20 Chao, L.C. and Chang, E.P., J. Appl. Polym. Sci., 1981, 26(2): 603
- 21 Hao, C., Zhao, Y., Zhou, Y., Zhou, L., Xu, Y., Wang, D. and Xu, D., J. Polym. Sci., Part B: Polym. Phys., 2007, 45(13): 1589
- 22 Moghri, M., Garmabi, H. and Molajavadi, V., J. Vinyl Addit. Technol., 2010, 16(3): 195
- 23 As'habi, L., Jafari, S.H., Khonakdar, H.A. and Baghaei, B., J. Polym. Res., 2011, 18(2): 197
- 24 Woodward, A.E., Sauer, J.A., Deeley, C.W. and Kline, D.E., J. Colloid Sci., 1957, 12(4): 363
- 25 Habor, J., Zeits. Chemie., 1976, 11: 422
- 26 Yan, D., Wang, W.J. and Zhu, S., Polymer, 1999, 40(7): 1737