

Study on Ester–Amide Exchange Reactions Between Nylon 1010 and Ethylene-Vinyl Acetate Rubber

Xianbo Lu, Hongmei Zhang, Yong Zhang

State Key Laboratory of Metal Matrix composites, School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

Correspondence to: Y. Zhang (E-mail: Yong_zhang@sjtu.edu.cn)

ABSTRACT: Reactive processing is a useful method to improve the compatibility of immiscible polymer blends. Nylon 1010/Ethylene-vinyl acetate rubber (EVM) blends were prepared via melt blending at 240°C and tetrabutyl titanate ($\text{Ti}(\text{OBU})_4$) was used as a catalyst. Ester–amide exchange reactions were proven to take place between Nylon and EVM during the shear processing. Melt flow index, Fourier transform infrared spectroscopy, and proton nuclear magnetic resonance spectra were used to study the reactions. It was demonstrated that tuning the shear rate could control the properties and reaction extent of Nylon 1010/EVM/ $\text{Ti}(\text{OBU})_4$ blends. The results revealed that the reactions were promoted by high shear rate. Tensile strength of the blends increased from 4.5 to 11.4 MPa when the shear rate increased from 20 to 80 rpm. Meanwhile, scanning electron microscopy was adopted to study the morphology of the reactive blends. It was found that the morphology of the blends was changed from sea-island structures to co-continuous structures while increasing the shear rate from 20 to 100 rpm. Dynamic mechanical analysis confirmed that high-shear processing was found to promote the compatibility of the blends. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40064.

KEYWORDS: blends; compatibilization; polyamides; rubber

Received 24 June 2013; accepted 14 October 2013

DOI: 10.1002/app.40064

INTRODUCTION

Immiscible polymer blends have gained wide attention in recent years because of the possibility of combining the advantage features of each component.^{1,2} To prepare the blends with good performance, some specific strategies were adopted to improve the compatibility of the blends.^{3,4} Properties of polymer blends are influenced by several factors, such as size, shape, morphology of the dispersed phase, and interfacial adhesion. The addition of compatibilizer could lower the interfacial tension between different polymer phases and improve the interfacial adhesion. Reactive compatibilization was also commonly used and could be achieved by reactions between functional groups of the components of the blends and formation of a graft or block copolymer in situ during melting processing.^{5,6}

As a reactive compatibilization method, ester–ester and ester–amide exchange reactions have been studied for many years. The reactions for various polymer blends, such as PBS/Polyamide,⁷ EVA/PLA,⁸ PET/PC,^{9–14} PC/PMMA,^{15,16} etc.,^{17–47} were studied, and it was found that some random or graft copolymers were generated by the exchange reactions. The reaction products, which acted as compatibilizer, could effectively improve the compatibility of the blends. However, these studies seldom focused on the influence of processing conditions on the reaction and the effects of the reactions on the

mechanical properties of the blends. In this study, the effect of shear rate on the ester–amide exchange reactions was studied. Moreover, the tensile properties of the blends were improved through tuning the shear rate. Therefore, this research might provide a possible method to regulate the reaction extent and even the mechanical properties for such kinds of polymer blends.

The aim of this study was to have a clear understanding on the ester–amide exchange reactions and their effect on the properties of Nylon/EVM blends. In this work, ester–amide exchange reactions in Nylon/EVM blends were studied in the presence of $\text{Ti}(\text{OBU})_4$ as the catalyst. The amide or terminated amine groups of Nylon 1010 were expected to react with the ester groups of EVM to form graft copolymers at the interface during melt-blending operation. The reactions were characterized by ¹H NMR and Fourier transform infrared spectroscopy (FTIR) analysis. The reaction extent, mechanical properties, and morphology of the blends under different shear rate were studied systematically. Dynamic mechanical analysis (DMA) was used to study the compatibility of the blends.

EXPERIMENTAL

Materials

Nylon 1010 (grade, 09) was produced by Shanghai Salient Chemical Co., Ltd, with the intrinsic viscosity of 83.4 mL/g

Table I. MFI of Nylon 1010/EVM/Ti(OBu)₄ Blends

Nylon 1010/EVM/Ti(OBu) ₄	MFI (g/10 min)
50/50/0 (10 min)	10.9
50/50/1 (10 min)	6.5
50/50/0 (30 min)	14.2
50/50/1 (30 min)	8.4
50/50/0 (60 min)	45.3
50/50/1 (60 min)	19.8

(25°C, 96% H₂SO₄). Ethylene-vinyl acetate rubber (EVM 400, contain 40 wt% vinyl acetate (VA)) was kindly supplied by Lanxess Company (Germany). The Moony viscosity is 20. Tetra-butyl titanate (Ti(OBu)₄), deuterated chloroform (CDCl₃), and trifluoroacetic acid (CF₃COOD) were used as received.

Sample Preparation

Nylon 1010 and EVM was vacuum dried at 80°C for 12 h and 60°C for 4 h, respectively. Blends were prepared by two steps: EVM rubber was compounded with or without catalyst on a two-roll mill for 5 min. Then, Nylon 1010 and EVM were mixed in a Haake rheometer (Haake RC9, Germany) at a set temperature of 240°C and a given rotor speed (20, 50, 65, 80, 100 rpm) for 30 min. Nylon 1010/EVM/catalyst weight ratio was 50/50/1.

The mixed compounds were compression molded on a compression molding machine (Labtech Engineering Co., Ltd., Thailand) at 230°C for 5 min followed by cold pressing for 10 min under 10 MPa to get samples for testing.

Separation

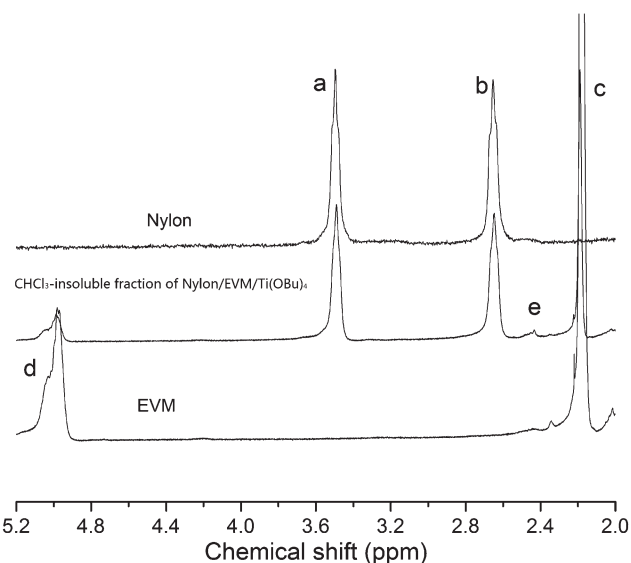
To remove unreacted EVM, 1.0 g of Nylon/EVM/Ti(OBu)₄ blends was added to 20 mL HCOOH/CHCl₃ mixed solution (1:1, v/v) and stirred at room temperature for 24 h. Then, the upper solution (HCOOH) was precipitated using methanol. The suspension was filtered afterward. The CHCl₃-insoluble fraction was then washed with CHCl₃, filtered, and subsequently dried for 24 h. This procedure of washing and drying was repeated until the weight of CHCl₃-insoluble fraction was invariable.

Characterization

To verify the chemical structure changes between CHCl₃-insoluble fraction of the blends and the neat Nylon, the infrared spectra of Nylon 1010, EVM, and CHCl₃-insoluble fraction were obtained using a Nicolet 510P FTIR (USA). The sample was compressed into a thin film for FTIR analysis.

¹H NMR was used to study the reaction mechanism and the reaction extent. Samples were dissolved in a mixture of CDCl₃/CF₃COOD (1:1, v/v) for ¹H NMR measurement using a Bruker 500 MHz spectrometer (Avance AV 500WB, Switzerland) with tetramethylsilane (TMS) as the internal standard.

Melt flow index (MFI) was used to study the effect of blending time and catalyst on the fluidity of the blends. MFI was performed in a Dinateste plastometer (MPCA MFI, Ray-Ran Test Equipment Ltd., UK), according to GB/T 3628-2000, at 230°C with a 2.16 kg load.

**Figure 1.** ¹H NMR spectra of Nylon, EVM, and CHCl₃-insoluble fraction of Nylon/EVM/Ti(OBu)₄ blend (100 rpm, 30 min).

Tensile test was adopted to study the mechanical properties of the blends. Tensile properties were measured using an Instron 4465 test machine (Instron Corp., USA) at a crosshead speed of 20 mm/min according to ASTM D638-2010.

DMA was used to study the compatibility of the blends. Dynamic mechanical behavior of the blends was determined using a DMA 8000 (Perkin-Elmer, USA) in tensile mode at a frequency of 1 Hz and a heating rate of 4°C/min in the temperature range of -60 to 120°C.

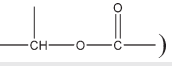
To study the effect of catalyst and the shear rate on the morphology changes of the blends, scanning electron microscope (SEM) was used. Morphology of cryogenically fractured surfaces of the specimen was observed using SEM (HITACHI-S-2150, Japan) with an accelerating voltage of 20 kV. The blends were fractured in liquid nitrogen and etched by CHCl₃ for 8 h to remove EVM phase before observation.

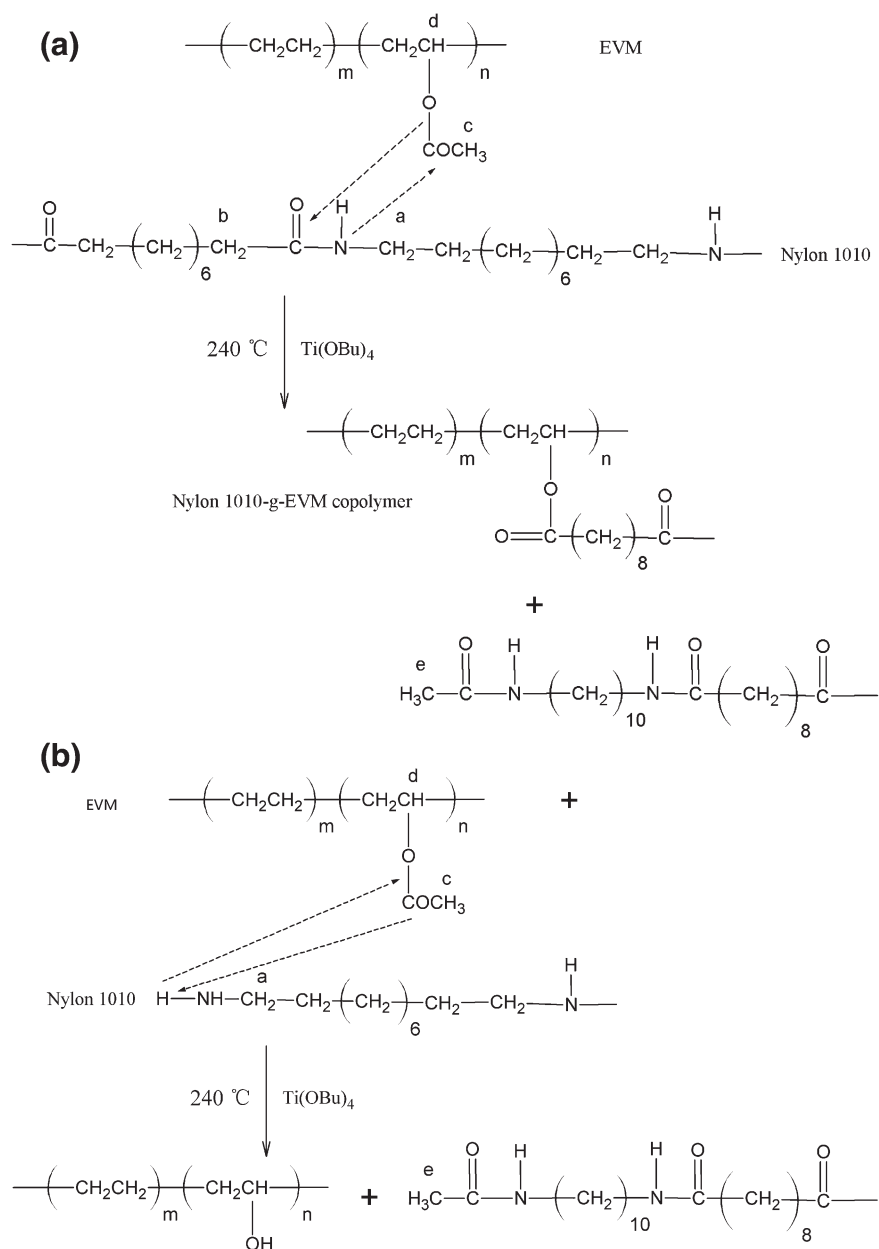
RESULTS AND DISCUSSION

Melt Flow Index

MFI was measured to study the fluidity of the blends at molten state. The effects of blending time and catalyst on the fluidity of

Table II. Assignment of the Characteristic Peaks for Nylon 1010, EVM and the Reaction Products

	Assignment	Chemical shift (ppm)
Nylon 1010	a (-NH-CH ₂ -)	3.50
	b (-CO-CH ₂ -)	2.66
EVM	c (-COO-CH ₃)	2.18
	d (proton in )	4.98
Reaction products	e (CH ₃ -CONH-)	2.43



Scheme 1. (a) Two different mechanisms of melt reaction between Nylon 1010 and EVM at 240°C: ester group attacked amide group. (b) Two different mechanisms of melt reaction between Nylon 1010 and EVM at 240°C: ester group attacked terminated amine group.

the reactive blends were studied and the results are shown in Table I. The MFI values of controlled Nylon 1010 and EVM are 68.3 g/10 min and 4.2 g/10 min, respectively. All these blends were prepared under a shear rate of 50 rpm. As shown in Table I, the MFI values of all the blends were between that of Nylon and EVM. First, MFI values increased with increasing blending time, independent of the catalyst. This might be resulted from the decomposition of the polymers with longer blending time, leading to decreasing molecular weight and therefore higher fluidity of the polymer matrix. Second, MFI values of the blends decreased after adding the catalyst, independent of blending time. For example, MFI of Nylon 1010/EVM (50/50, 10 min) was 10.9 g/10 min. After adding catalyst, the value decreased notably to 6.5 g/10 min. This change was more obvious when

the blending time was increased to 60 min. This means that after adding catalyst, some graft or crosslinking structures might be generated in the blends, which leads to high viscosity and poor fluidity of the blends.

¹H NMR Analysis

¹H NMR was used to analyze the ester–amide exchange reactions in the blends. For comparison, the chemical structures of Nylon and EVM were also analyzed under the same condition. The spectra are shown in Figure 1.

Chemical shifts of the CH₂ groups adjacent to the NH and CO groups in Nylon 1010 were observed around 3.50 ppm (a) and 2.66 ppm (b), respectively.⁴⁸ The peaks at 2.18 ppm (c) and 2.43 ppm (e) corresponded to the methyl protons in the

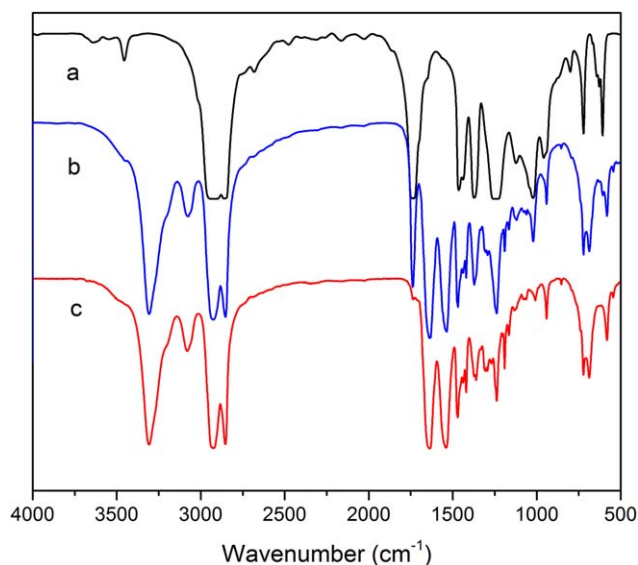


Figure 2. FTIR spectra of (a) EVM, (b) CHCl_3 -insoluble fraction of Nylon/EVM/ $\text{Ti}(\text{O}i\text{Bu})_4$ blend (100 rpm, 30 min) and (c) Nylon 1010. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

molecular chains of EVM and the reaction product ($\text{CH}_3\text{CO-NH-}$), respectively.⁴⁹ Table II lists the assignments of the proton peaks in the spectra.

It has been reported that^{7,8,16} the polyester chain would break at the ester bond site in the presence of catalyst. The proposed exchange reaction mechanism was shown in Scheme 1. The ester–amide exchange reactions occurred between amide groups of Nylon 1010 and the ester carbonyl groups of EVM, leading to the formation of new copolymers comprised of the segments detached from Nylon 1010 and EVM chains. The acetamide terminated Nylon 1010 was generated in the two pathways (Scheme 1) through the reactions between amide or terminated amine groups of Nylon 1010 and the ester groups of EVM. Meanwhile, Nylon-*g*-EVM and alcoholized EVM also were generated by the reactions. The copolymers generated in the reaction might act as a compatibilizer between Nylon 1010 and EVM phase. But unfortunately, compared with the raw materials (Nylon and EVM), the reaction products (Nylon-*g*-EVM and alcoholized EVM) showed no distinguishing peaks in ^1H NMR spectra. The only indicative peak for the exchange reactions appeared at 2.43 ppm assigned to proton of methyl in aceta-

mid terminated Nylon 1010, which was used to evaluate the reaction extent later.

FTIR Analysis

Figure 2 depicts the FTIR spectra of neat Nylon, EVM, and CHCl_3 -insoluble fraction of Nylon/EVM/ $\text{Ti}(\text{O}i\text{Bu})_4$ blend (100 rpm, 30 min). The FTIR spectrum of EVM in Figure 2(a) showed a clear distinguishable stretching vibration peaks at 1738 cm^{-1} corresponding to the C=O of ester group. The other two characteristic stretching vibration peaks were located at 1024 and 1237 cm^{-1} , corresponding to $-\text{COO}-$ and $-\text{O-CH-}$ in $-\text{COOCH-}$ group, respectively. The presence of these two peaks with carbonyl group (1738 cm^{-1}) indicates the presence of ester.^{49–52} In the spectrum of Nylon 1010, the absorption bands in curve c for amide group appeared at 1641 and 1539 cm^{-1} , corresponding to the N–H and C–N of Nylon, respectively.⁵³ CHCl_3 -insoluble fraction of Nylon/EVM/ $\text{Ti}(\text{O}i\text{Bu})_4$ blends not only showed the N–H and C–N peaks of Nylon, but also the peak at 1738 cm^{-1} for C=O of ester group. This suggested that EVM–Nylon 1010 copolymer was generated by exchange reactions, and the copolymer was insoluble in chloroform. The result corroborated the conclusions obtained on the basis of ^1H NMR spectra about the Nylon-*g*-EVM formation in the presence of $\text{Ti}(\text{O}i\text{Bu})_4$ catalyst.

Effect of Catalyst on the Morphology of the Blends

To study the effect of the exchange reaction on the morphology of the blends intuitively, the blends with or without catalyst were prepared for comparison. The blends were etched by chloroform and the EVM phase was removed. The morphology is shown in Figure 3. In Figure 3(a), Nylon/EVM (10 min) blend showed a sea–island structure. The dispersed phases existed in a spherical form as a result of the poor compatibility between Nylon 1010 and EVM. After adding catalyst $\text{Ti}(\text{O}i\text{Bu})_4$, the size of the dispersed phase became smaller evidently. The catalyst could promote the ester–amide exchange reaction, and the reaction product (Nylon-*g*-EVM) might be the main driving force for the morphology evolution. This result revealed that reactive processing might be a useful method to improve the compatibility of the blends. The reactive compatibilization for Nylon/polymer blends have also been studied by other researchers. Valenza et al.⁵⁴ studied the reaction between Nylon 6 and ethylene acrylic acid copolymers (EAA) at different acrylic acid content. They found that the presence of acrylic acid group improved the compatibility between polyethylene and Nylon phases with modifications of blends morphology. And the

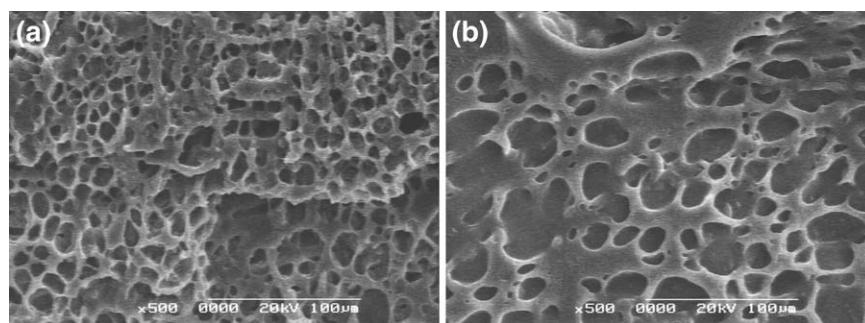


Figure 3. Morphology of (a) Nylon/EVM (10 min) and (b) Nylon/EVM/ $\text{Ti}(\text{O}i\text{Bu})_4$ (10 min).

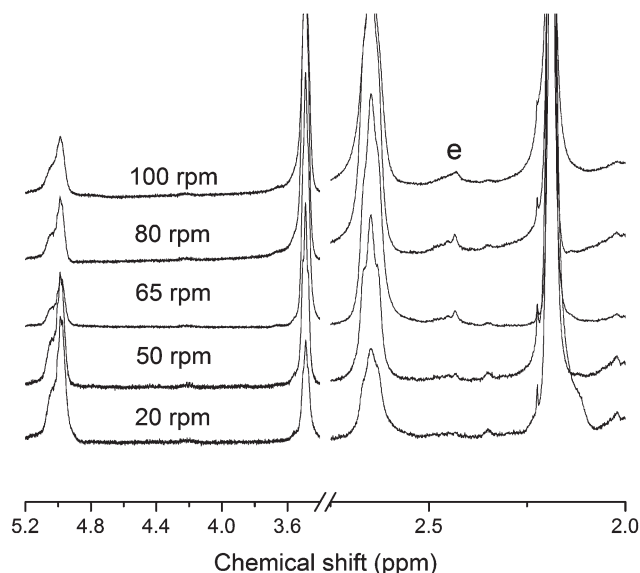


Figure 4. ^1H NMR spectra of Nylon/EVM/Ti(OBu) $_4$ blends with different shear rate.

compatibilizing effect was enhanced with increase in the acrylic acid content in EAA.

Effect of Shear Rate on the Ester–Amide Exchange Reactions

^1H NMR Analysis. ^1H NMR was used to study the effect of shear rate on the reaction extent. Figure 4 shows the ^1H NMR spectra of Nylon/EVM/Ti(OBu) $_4$ blends with different shear rates. Under a shear rate of 20 rpm, the peak at 2.43 ppm for the proton of $\text{CH}_3\text{-CONH-}$ can hardly be observed. This means the reaction extent was very low and difficult to be detected. When the shear rate increased, the methyl protons at 2.43 ppm [Figure 4(e)] appeared in the spectra and became stronger. This means that reaction extent between Nylon and EVM increased during the melting processing. The proton signal intensity ratio between the peak at $\text{CH}_3\text{CO-NH-}$ (2.43 ppm) and -NHCH_2 (-3.50 ppm) ($2I_{2.43}/3I_{3.50}$) was used to evaluate the dependence

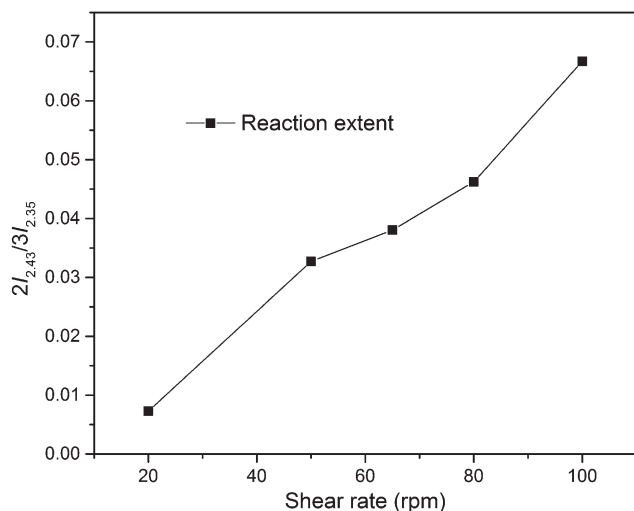


Figure 5. Reaction extents of Nylon/EVM/Ti(OBu) $_4$ blends with different shear rate.

Table III. Mechanical Properties of Nylon/EVM/Ti(OBu) $_4$ Blends with Different Shear Rate

Shear rate (rpm)	Tensile strength (MPa)	Elongation at break (%)
20	4.5 ± 0.3	18 ± 2
50	6.4 ± 0.3	19 ± 1
65	6.5 ± 0.2	22 ± 2
80	11.4 ± 0.4	32 ± 1
100	10.0 ± 0.3	30 ± 3

of the reaction extent with shear rate. After a careful data processing, the integral area ratio ($2I_{2.43}/3I_{3.50}$) (Figure 5) increased with the increasing shear rate, which indicated the increased reaction extent by increasing the shear rate. The result means that the reaction of Nylon 1010/EVM blends was promoted by higher shear rate.

Mechanical Properties. The effect of shear rate on the mechanical properties of the reactive blends was studied and the results were shown in Table III. The blends processed at 80 rpm showed the best tensile properties. It was found that the tensile strength of the Nylon/EVM/Ti(OBu) $_4$ (80 rpm) blend was about 150% higher than that of the same blend prepared under 20 rpm. This might be resulted from the improved miscibility between the two components by high-shear processing. When the shear rate increased to 100 rpm, the decomposition effect of the polymers might be significant, and this led to a decrease in the tensile strength.

Morphology. The morphology plays an important role in the properties of polymer blends. The morphology of the reactive blends with different shear rate is shown in Figure 6. It was found that the morphology of the blends changed from a sea-island structure to a co-continuous structure when the shear rate increased from 20 to 80 rpm. The blends under a shear rate of 20 rpm or 50 rpm showed a sea-island structure. Moreover, when the shear rate increased from 20 to 50 rpm, the size of dispersed phase was decreased. This indicated that the compatibility of the blends was improved. When the shear rate increased to 65 rpm or 80 rpm, the blends changed to co-continuous phase morphology. The domains of EVM phase for high-shear processing (80 rpm) blends became further smaller compared with that of 65 rpm. This indicated that the high-shear processing (80 rpm) refined the morphology efficiently. When the shear rate increased to 100 rpm, the blends changed to a complex structure. The irregular morphology might be resulted from the high-shear processing and the serious decomposition of the polymers matrix.

The morphology of the blends changed from sea-islands to co-continuous phase morphology. This could be explained by two reasons: (1) The refinement effect of high shear rate was benefit for obtaining smaller disperse phase. The agglomeration and partial coalescence of the dispersed droplets caused a change from a disperse morphology to a co-continuous morphology during compression molding.⁵⁵ (2) More reaction products might be generated by high-shear processing as proved by ^1H NMR. The reaction extent increased with higher shear rate,

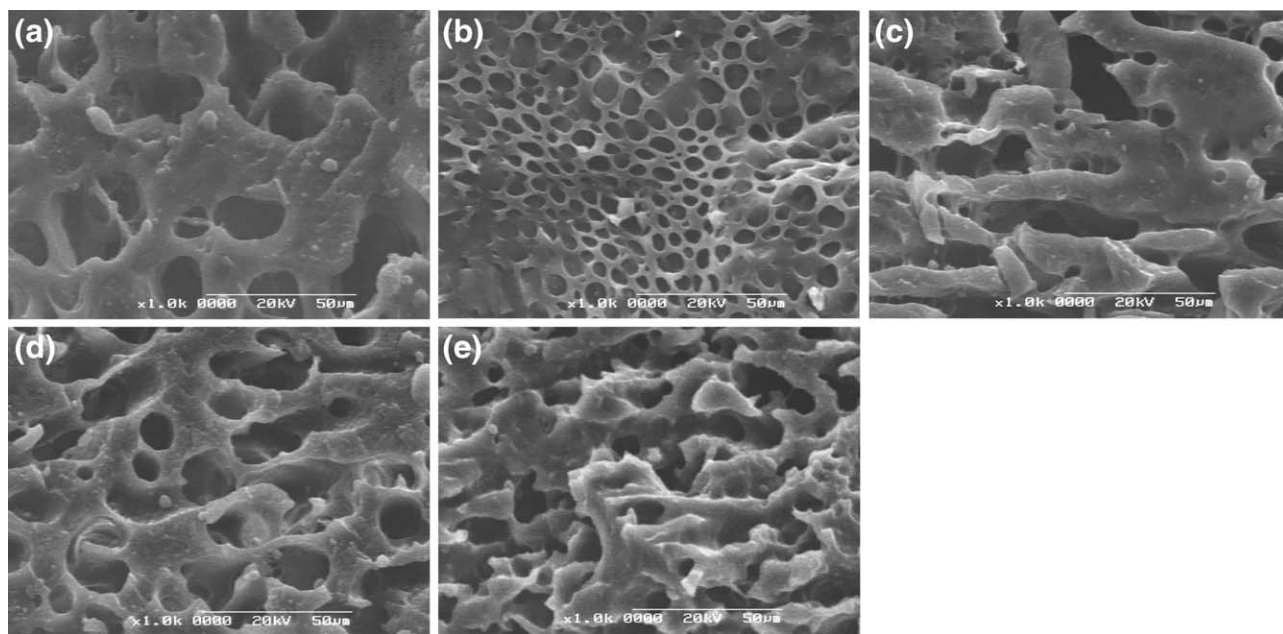


Figure 6. Morphology of the Nylon/EVM/Ti(OBu)₄ with different shear rate (a) 20 rpm; (b) 50 rpm; (c) 65 rpm; (d) 80 rpm; (e) 100 rpm.

resulting in more reaction products staying at the interface and affecting the viscosity ratio. Therefore, the viscosity of the two phases became close to each other, and the co-continuous phase morphology appeared.

To verify the responsibility of the exchange reaction for the co-continuous structure of the blends, the blend without catalyst was prepared under a shear rate of 65 rpm for comparison and the morphology was analyzed by SEM (Figure 7). It can be seen from Figure 7(a), the blend without catalyst showed a complex structure (phase morphology contains sea-island and co-continuous structure). After adding catalyst, as mentioned above, the morphology of the blend changes from partially co-continuous structure to complete co-continuous structure [Figure 7(b)]. The domain size of EVM phase increased obviously compared with Figure 7(a). Excluding the effect of shear rate, it can be concluded that the morphology of the blends was changed after adding catalyst, and exchange reactions played an important role in affecting the morphology development of the blends.

Dynamic Mechanical Properties. The dynamic properties of the Nylon/EVM/Ti(OBu)₄ reactive blends with different shear

rate were investigated by DMA experiments, as shown in Figure 8. The glass transition temperature (T_g) of controlled EVM and Nylon was -31.8 and 60.9°C , respectively. However, T_g of the blends was found to be dependent greatly on shear rate. As shown in Figure 8, T_g of EVM in the low-shear-processed blends (50 rpm) was at -31.5°C , while that of the high-shear-processed blends (80 rpm) was remarkably shifted to about -26.3°C , indicating the improved miscibility between the two components by high-shear processing. The effect of shear rate on the compatibility of the blends has been studied for many years.^{56–61} For example, Shimizu et al.⁶¹ reported the formation of nanostructured PVDF/PA11 blends using high-shear processing. They also found that high-shear processing could improve the miscibility of the blends.

CONCLUSIONS

Nylon 1010/EVM blends were prepared in this study. The ester-amide exchange reactions mechanism and the influence of shear rate on the reaction extent and mechanical properties of the blends were studied. FTIR and ¹H NMR analyses suggested that

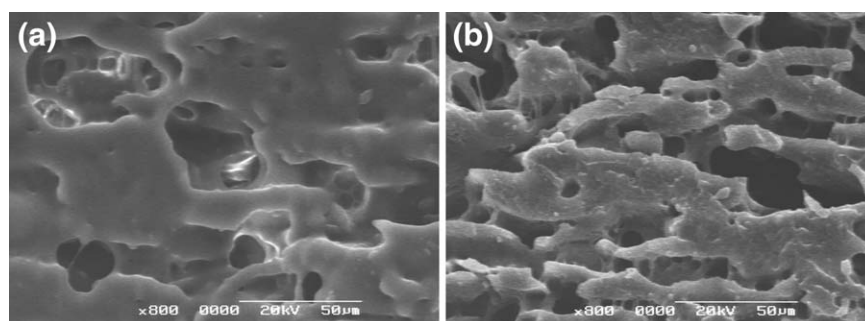


Figure 7. Morphology of the (a) Nylon/EVM and (b) Nylon/EVM/Ti(OBu)₄ blends under a shear rate of 65 rpm.

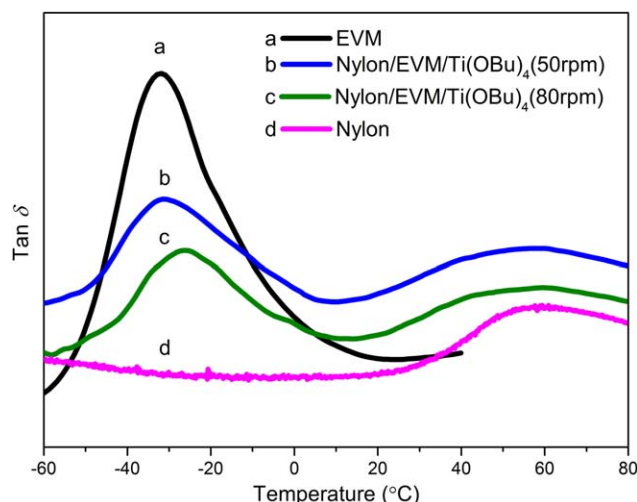


Figure 8. Temperature dependence of the $\tan \delta$ for Nylon, EVM and Nylon/EVM/Ti(OBu)₄ blends with different shear rate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the graft copolymer Nylon 1010-*g*-EVM was generated during the processing. By tuning the shear rate, the reaction extent increased with increasing shear rate and the tensile strength of the reactive blends reached a maximum value of 11.4 MPa when the shear rate was 80 rpm. It was also found that the morphology of the reactive blends changed from sea-island structure to co-continuous structure by increasing the shear rate. DMA showed that the glass transition temperature of the Nylon 1010 and EVM phases got closer to each other after high-shear processing, which confirmed that high-shear processing could promote the compatibility of the Nylon/EVM blends effectively.

ACKNOWLEDGMENTS

This work was supported by research grants from the National Natural Science Foundation of China (51073092).

REFERENCES

- Paul, D. R.; Bucknall, C. B. *Polymer Blends*; Wiley, **1999**.
- DeBolt, M. A. *Morphology and Compatibilization of Multi-component Polymer Blends*; University of Michigan, **2000**.
- Litmanovich, A. D. *Prog Polym Sci*, **2002**, *27*, 915.
- Koning, C. *Prog Polym Sci*, **1998**, *23*, 707.
- Lusinchi, J. M.; Boutevin, B.; Torres, N.; Robin, J. J. *J Appl Polym Sci*, **2001**, *79*, 874.
- Sánchez-Solís, A.; Calderas, F.; Manero, O. *Polymer*, **2001**, *42*, 7335.
- Yao, Z.; Sun, J. M.; Wang, Q.; Cao, K. *Indus Eng Chem Res*, **2012**, *51*, 756.
- Moura, I.; Nogueirab, R.; Bounor-Legarec, V.; Machadoa, A. V. *Mater Chem Phys*, **2012**, *134*, 103.
- Lgnatov, V. N.; Carraro, C.; Tartari, V.; Pippa, R.; Pilati, F.; Berti, C.; Toselli, M.; Fiorini, M. *Polymer*, **1996**, *37*, 5883.
- Aravind, I.; Eichhorn, K. J.; Komber, H.; Jehnichen, D.; Zafeiropoulos, N. E.; Ahn, K. H.; Grohens, Y.; Stamm, M.; Thomas, S. *J Phys Chem B*, **2009**, *113*, 1569.
- Wilkinson, A. N.; Nita, E. M. I.; Clemens, M. L.; Jöbstl, E.; Fairclough, J. P. A. *J Macromol Sci Phys*, **2005**, *44 B*, 1087.
- Al-Jabareen, A.; Illescas, S.; Maspoch, M. L.; Santana, O. O. *J Mater Sci*, **2010**, *45*, 2907.
- Al-Jabareen, A.; Illescas, S.; Maspoch, M. L.; Santana, O. O. *J Mater Sci*, **2010**, *45*, 6623.
- Pereira, P. S. C.; Mendes, L. C.; Ramos, V. D. *Macromol Symposia*, **2010**, *290*, 121.
- Singh, A. K.; Prakash, R.; Pandey, D. *RSC Advances*, **2012**, *2*, 10316.
- Singh, A. K.; Prakash, R.; Pandey, D. *J Phys Chem B*, **2011**, *115*, 1601.
- Pollet, E.; Delcourt, C.; Alexandre, M.; Dubois, P. *Eur Polym J*, **2006**, *42*, 1330.
- Wu, C.; Han, C. D.; Suzuki, Y.; Mizuno, M. *Macromolecules*, **2006**, *39*, 3865.
- Soccio, M.; Lotti, N.; Finelli, L.; Gazzano, M.; Munari, A. *Eur Polym J*, **2008**, *44*, 1722.
- Caligiuri, L.; Stagnaro, P.; Valenti, B.; Canalini, G. *Eur Polym J*, **2009**, *45*, 217.
- Safapour, S.; Seyed-Esfahani, M.; Auriemma, F.; Ruiz de Ballesteros, O.; Vollaro, P.; Di Girolamo, R.; De Rosaand, C.; Khosroshahi, A. *Polymer*, **2010**, *51*, 4340.
- Martinez-Tong, D. E.; Soccio, M.; Sanz, A.; Ezquerro, T. A.; Lotti, N.; Munari, A.; Nogales, A. *Soft Matter*, **2012**, *8*, 2723.
- Lee, S. S.; Kim, J.; Park, M.; Lim, S.; Choe, C. R. *J Polym Sci, Part B: Polym Phys*, **2001**, *39*, 2589.
- Zhou, C.; Ma, J.; Pan, L.; Liang, B. *Eur Polym J*, **2002**, *38*, 1049.
- Yavari, A.; Asadinezhad, A.; Jafari, S. H.; Khonakdar, H. A.; Böhme, F.; Hässler, R. *Eur Polym J*, **2005**, *41*, 2880.
- Yang, H.; He, J.; Liang, B. *J Polym Sci, Part B: Polym Phys*, **2001**, *39*, 2607.
- Wu, D.; Sun, Y.; Lin, D.; Zhou, W.; Zhang, M.; Yuan, L. *Macromol Chem Phys*, **2011**, *212*, 1700.
- Wu, L.; Chen, P.; Zhang, J.; He, J. *Polymer*, **2006**, *47*, 448.
- Wang, F.; Meng, X.; Xu, X.; Wen, B.; Qian, Z.; Gao, X.; Ding, Y.; Zhang, S.; Yang, M. *Polym Degrad Stab*, **2008**, *93*, 1397.
- Wang, C. S.; Lin, C. H. *Polymer*, **2000**, *41*, 4029.
- Oh, T. S. *Polym Eng Sci*, **2004**, *37*, 838.
- Kenwright, A. M.; Peace, S. K.; Richards, R. W.; Bunn, A.; MacDonald, W. A. *Polymer*, **1999**, *40*, 5851.
- Jang, M. O.; Kim, S. B.; Nam, B. U. *Polym Bull*, **2012**, *68*, 287.
- Zhang, Z.; Xie, Y.; Ma, D. *J Polym Sci, Part A: Polym Chem*, **2001**, *39*, 232.
- Na, S. K. *Macromol Res*, **2005**, *13*, 88.
- Dias, M. L.; Silva, A. P. F. *Polym Eng Sci*, **2000**, *40*, 1777.
- Zhang, T.; Zhang, L.; Li, C. *J Macromol Sci, Part B: Phys*, **2011**, *50*, 453.
- Wei, K. *Macromolecules*, **1997**, *30*, 1587.

39. Wilkinson, A. N.; Cole, D.; Tattum, S. B. *Polym Bull*, **1995**, *35*, 751.
40. Tharmapuram, S. R.; Jabarin, S. A. *Adv Polym Technol*, **2003**, *22*, 137.
41. Tattum, S. B.; Cole, D.; Wilkinson, A. N. *J Macromol Sci, Part B*, **2000**, *39*, 459.
42. Andresen, E.; Zachmann, H. G. *Colloid Polym Sci*, **1994**, *272*, 1352.
43. Jacques, B.; Devaux, J.; Legras, R.; Nield, E. *J Polym Sci, Part A: Polym Chem*, **1996**, *34*, 1189.
44. Montaudo, G.; Puglisi, C.; Samperi, F. *Macromolecules*, **1998**, *31*, 650.
45. Su, C. C.; Shih, C. K. *Colloid Polym Sci*, **2005**, *283*, 1278.
46. Kil, S. B.; Park, O. O.; Yoon, K. H. *J Appl Polym Sci*, **1999**, *73*, 2123.
47. Coltelli, M. B.; Aglietto, M.; Ciardelli, F. *Eur Polym J*, **2008**, *44*, 1512.
48. Pillon, L. Z.; Utracki, L. A.; Pillon, D. W. *Polym Eng Sci*, **1987**, *27*, 562.
49. Tang, M.; Hou, J.; Lei, L.; Liu, X.; Guo, S.; Wang, Z.; Chen, K. *Int J Pharm*, **2010**, *400*, 66.
50. Shi, X.; Zhang, J. *Suliao*, **2008**, *37*, 108.
51. Sun, R.; Jin, T.; Lin, M.; Chen, R.; Chu, F.; Wang, C. *Gongcheng Suliao Yingyong*, **2012**, *40*, 22.
52. Cerin, O.; Duquesne, S.; Fontaine, G.; Roos, A.; Bourbigot, S. *Polym Degrad Stab*, **2011**, *96*, 1812.
53. Han, H.; Lin, Z.; Chen, J.; Qian, H. *Gongcheng Suliao Yingyong*, **2012**, *40*, 4.
54. Valenza, A.; Visco, A. M.; Acierno, D. *Polym Test*, **2002**, *21*, 101.
55. Sailer, C. *Macromolecules*, **2007**, *40*, 2019.
56. Patlazhan, S.; Schlatter, G.; Serra, C.; Bouquey, M.; Muller, R. *Polymer*, **2006**, *47*, 6099.
57. Van Puyvelde, P.; Vananroye, A.; Cardinaels, R.; Moldenaers, P. *Polymer*, **2008**, *49*, 5363.
58. Teyssandier, F.; Cassagnau, P.; Gérard, J. F.; Mignard, N.; Mélis, F. *Mater Chem Phys*, **2012**, *133*, 913.
59. Li, Y.; Shimizu, H. *Polym Eng Sci*, **2011**, *51*, 1437.
60. Kapnistos, M.; Vlassopoulos, D.; Anastasiadis, S. H. *Europhys Lett*, **1996**, *34*, 513.
61. Shimizu, H.; Li, Y.; Kaito, A.; Sano, H. *Macromolecules*, **2005**, *38*, 7880.