

Effects of Blending Time and Catalyst on the Properties of Nylon 1010/Acrylate Rubber Blends

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ABSTRACT: Nylon 1010 and acrylate rubber (ACM) were prepared by melt blending. The effects of blending time and catalyst on the properties of the blends were studied. It was found that ester-amide exchange reactions between the Nylon 1010 and ACM occurred during melt processing. Long blending time and Tetrabutyl titanate ($\text{Ti}(\text{OBU})_4$) as a catalyst could promote the reactions, and grafted copolymer Nylon-g-ACM was *in situ* generated as a compatibilizer during processing procedure. The tensile strength of the blends increased from about 12.0–15.0 MPa when the blending time increased from 10 to 30 min. The presence of $\text{Ti}(\text{OBU})_4$ led to the decrease in melt flow index (MFI), independent of the blending time (30 or 60 min). Glass transition temperature and heat of fusion of the blends increased after addition of the catalyst. Rheological behavior analysis provided evidence of formation of Nylon-g-ACM graft copolymer. Scanning electron microscopy (SEM) showed that the compatibility of the blends was improved by longer blending time and the addition of catalyst. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 4587–4597, 2013

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INTRODUCTION

Reactive processing of two or more polymers to prepare new kinds of technologically useful blends has received wide attention.^{1,2} It is an effective method to improve the compatibility of immiscible polymer blends and thus to control the properties and the morphology. Reactive compatibilization can be carried out through three methods: (1) The components of the blends with functional groups can react with each other and form a graft copolymer or block copolymer *in situ* at the interphase in the melt processing^{3,4}; (2) adding a certain kind of polymer which can form covalent or ionic bonds with the component of the blends to improve the miscibility^{5–7}; (3) adding catalysts to promote reactions between the components to generate copolymers with crosslinking structure *in situ* during the melt processing, such as ester-ester and ester-amide exchange reactions.^{8,9}

Ester exchange reactions, as a useful reactive compatibilization method, have been studied.^{10–12} Some kinetic studies reported that the reactivity of the polymers in molten condition is the same as in solution.^{13,14} Reactions depended on the location of the reactive groups.¹⁵ An end-functional group reacts faster with another end-functional group than with a mid-functional one. Cassagnau et al.¹⁶ and Pesneau et al.¹⁷ found the ester exchange reaction in the melt processing only happened at tem-

perature higher than 250°C without a catalyst or lower temperature from 100°C in the presence of catalyst. Blending time and catalyst content greatly affected the mechanical and the thermal properties of the blends.¹⁸

Polyamide is a kind of important engineering plastics. It has high stiffness and good resistance to hydrocarbon solvents. It is well known that at high temperatures, amide-amide or ester-amide exchange reactions would occur in polyamide/polyamide blends^{19–23} and polyester/polyamide blends, respectively.^{24,25} Polyamide/polyacrylate alloys have been studied, and their physical properties depended on the acrylate content. Ren et al.²⁶ reported the addition of acrylate rubber (ACM) promoted α crystal formation, while restricted the γ crystal formation of PA 6 (Polyamide 6), and the crystal transformation occurred from γ to α with the addition of ACM into PA 6. Jha et al.^{27,28} studied the influence of dynamic vulcanization and phase interaction on the swelling behavior of thermoplastic elastomers of Nylon-6 and ACM in various solvents and oil. They found that swelling of the dispersed ACM particles in Nylon-6 matrix was greatly constrained compared to the free swelling of crosslinked ACM rubber. Addition of fillers reduced the processability of the blends, but improved the extensibility and damping characteristics as well as the tension set properties of the blends.²⁹ Dong et al.³⁰ found that ACM particles and clay platelets could

Table I. Properties of Polymer Materials

Material	Brand	Supplier	Properties
Nylon 1010	09	Shanghai Salient Chemical, China	Intrinsic viscosity = 83.4 mL/g (25°C, 96% H ₂ SO ₄).
ACM	AR801	TOPHE Company, Japan	Density = 1.08 g/cm ³ ; moony viscosity = 54 (ML 1+4, 100°C); copolymerization unit: ethyl acrylate (EA), cure site monomer: active chlorine, the content less than 5 wt %.

help each other to disperse or exfoliate in Nylon-6/clay/ACM nanocomposite. Ding et al.³¹ reported the effect of ultrafine, fully vulcanized powdered ACM (UFAPR) on the mechanical properties and crystallization behavior of Nylon 6. With the addition of a little UFAPR, crystallization rate of Nylon 6 could increase, and the crystal size distribution of the crystal grain became narrowed. However, very little has been reported on the ester-amide exchange reactions in these polyamide/ACM blend,³² especially the influence of blending time and catalyst on the reactions.

The aim of this study was to have a clear understanding on the ester-exchange reactions and their effect on the properties of the blend. In this articles, Nylon 1010/ACM blends were prepared through reactive processing. The amide or amine end groups of Nylon 1010 were expected to react with the ester groups of ACM to form graft copolymers at the interface during melt-blending operation. The reactions were characterized by ¹H NMR analysis and the reaction mechanism was discussed. The influence of blending time and catalyst amount on the interfacial reactions, and the properties were studied.

EXPERIMENTAL

Materials

Nylon 1010 and ACM were commercially available, their specification is listed in Table I. Tetrabutyl titanate (Ti(OBu)₄), chloroform (CHCl₃) and deuterated chloroform (CDCl₃), and trifluoroacetic acid (CF₃COOD) were purchased from Sino-pharm Chemical Reagent Co.

Sample Preparation

Blends were prepared by two steps: Nylon 1010 and ACM were vacuum dried at 80°C for 12 h and 60°C for 4 h, respectively. ACM rubber was masticated on a two-roll mill for 2 min and then compounded with or without catalyst for another 4 min. Then Nylon 1010 and ACM were mixed in a Haake rheometer at a rotor speed of 50 rpm and a set temperature of 240°C for given time (10, 30, and 60 min). Nylon 1010/ACM/catalyst weight ratio was 50/50/1. Based on the stoichiometry of the possible reactions between Nylon and ACM, the weight ratio 50 : 50 was selected. The reaction extent in a short time might be very low and the effect of the exchange reaction on the properties of the blends would be limited. Therefore, 10, 30, and 60 min were set as mixing time which has a wide time span.

The mixed compounds were then compression-molded at 230°C for 5 min followed by cold pressing for 10 min under 10 MPa to get samples for testing.

Separation

To remove the unreacted ACM component of the ACM/Nylon (50/50) blend, 1.0 g blend was added to 20 mL CHCl₃ (a good solvent for ACM) and stirred at room temperature for 72 h. Then, the suspension was filtered. The insoluble fraction was then washed with CHCl₃ for three times, and subsequently dried for 24 h. The procedure of washing and drying was repeated for several times until the weight of the insoluble fraction was invariable.

Characterization

FTIR Analysis. The infrared spectra of Nylon 1010, ACM, and the insoluble substances in chloroform were obtained using a Nicolet 510P Fourier transform infrared spectroscopy (FTIR). A sample was first compressed into a film with a diameter of 10 mm and used for FTIR analysis.

¹H NMR Analysis. The CHCl₃-insoluble fraction was dissolved in a mixture of CDCl₃/CF₃COOD (1 : 1, v/v) to get a solution 15 wt % for ¹H NMR measurement using a Bruker 500 MHz spectrometer (Avance AV 500WB) with tetramethylsilane (TMS) as the internal standard.

Mechanical Testing. The tensile properties were measured using an Instron 4465 test machine at a crosshead speed of 20 mm/min according to ASTM D638. The notched impact strength of the specimens was measured according to the ASTM D256.

Melt Flow Index. MFI was performed using a Dinateste plastometer, according to GB/T 3682–2000, at 230°C with a 2.16 kg load.

TGA and DSC Analysis. DSC analysis was performed on a TA Instruments differential scanning calorimeter (TQ 2000). A sample was heated from 40 to 240°C at a heating rate of 20°C/min, and cooled down to –60°C at 20°C/min as the first run. Then, the sample was reheated from –60 to 240°C at a heating rate of 20°C/min.

For TGA measurement, a sample was heated from 20 to 700°C at a heating rate of 20°C/min, using a TQ 5000 thermobalance

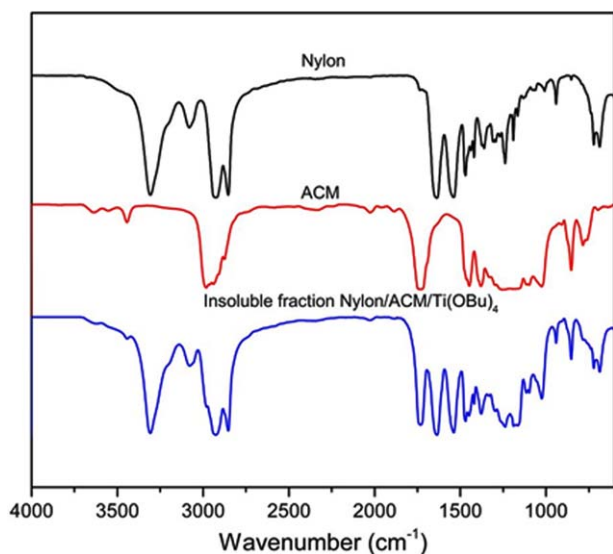


Figure 1. FTIR spectra of Nylon, ACM, insoluble fraction of Nylon/ACM/Ti(OBu)₄ (10 min) blend. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(TA Instruments) under a nitrogen flow atmosphere (50 mL/min).

Initial decomposition temperature (IDT) was determined at the temperature corresponding to 5% weight loss. The temperature with maximum rate of weight loss (T_{max}) was decided according to the peak shown in the differential thermogravimetric (DTG) thermogram.

Rheological Measurements. Oscillatory rheological measurement was carried out in a Gemini 200 HR rheometer (Bohlin Instruments, UK) at 210°C using a parallel plate geometry. The gap and diameter of the plates were 1 and 25 mm, respectively. A frequency sweep from 0.01 to 100 rad/s under constant strain was performed for each sample.

Morphology Analysis. Morphology of cryogenically fractured surfaces of specimens was observed using scanning electron microscope (SEM, HITACHI-S-2150, Japan) with an accelerating voltage of 15 kV. The fractured surfaces were etched with CHCl₃ for 8 h to remove the ACM phase before observation.

RESULTS AND DISCUSSION

FTIR Analysis

Figure 1 shows the FTIR spectra of Nylon, ACM, insoluble substances of the Nylon/ACM/Ti(OBu)₄ (10 min) blend. The FTIR spectrum of ACM shows a clear distinguishable stretching vibration peak at 1731.9 cm⁻¹ corresponding to the carbonyl group.³³ The stretching vibration peaks located at 1025.8 and 1255.6 cm⁻¹ can be attributed to —COO— and —O—CH— in —COOCH— group, respectively. In the spectrum of Nylon, the absorption bands for amide group appear at 1637.3 cm⁻¹ (C=O) and 1540.4 cm⁻¹ (N—H). The spectrum of insoluble substances of the nylon/ACM/Ti(OBu)₄ (10 min) blend has peaks from both ester and amide groups which might be resulted from the chemical interaction between Nylon and ACM.

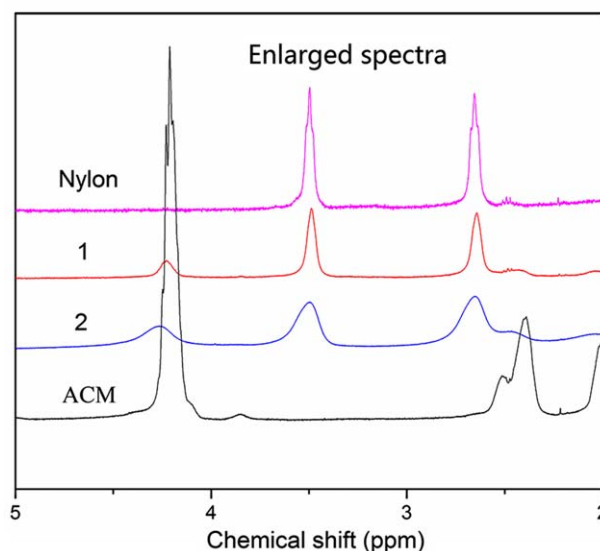
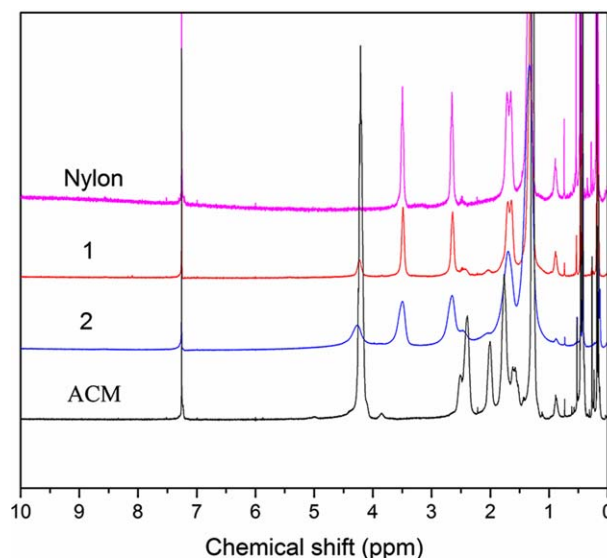


Figure 2. ¹H NMR spectra of Nylon 1010, ACM, (1) insoluble fraction of Nylon 1010/ACM (50/50, 10 min) and (2) insoluble fraction of the blend Nylon 1010/ACM/Ti(OBu)₄ (50/50/1, 10 min). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

¹H NMR Analysis

To further study the mechanism of possible exchange reaction between nylon and acrylate phases, ¹H NMR studies were carried out on Nylon 1010, acrylate rubber, CHCl₃-insoluble fraction of the nylon 1010/ACM blend with and without Ti(OBu)₄ as catalyst. The spectra are shown in Figure 2.

The assignment of the characteristic peaks of Nylon 1010 and ACM are listed in Table II according to the references.^{34–36} For the Nylon 1010/ACM (50/50, 10 min) and Nylon 1010/ACM/Ti(OBu)₄ (50/50/1, 10 min), after carefully treatment with CHCl₃, there should be no free ACM molecules left in the insoluble fraction. The peaks at 4.212 and 2.391 ppm corresponded to the —COO—CH₂—CH₃ proton and the proton of methyl on acrylate group of ACM structure. The peaks at 3.854 and 3.497 ppm corresponded to the proton of methylene on curing site of ACM and —NH—CH₂— of Nylon, respectively. It can be

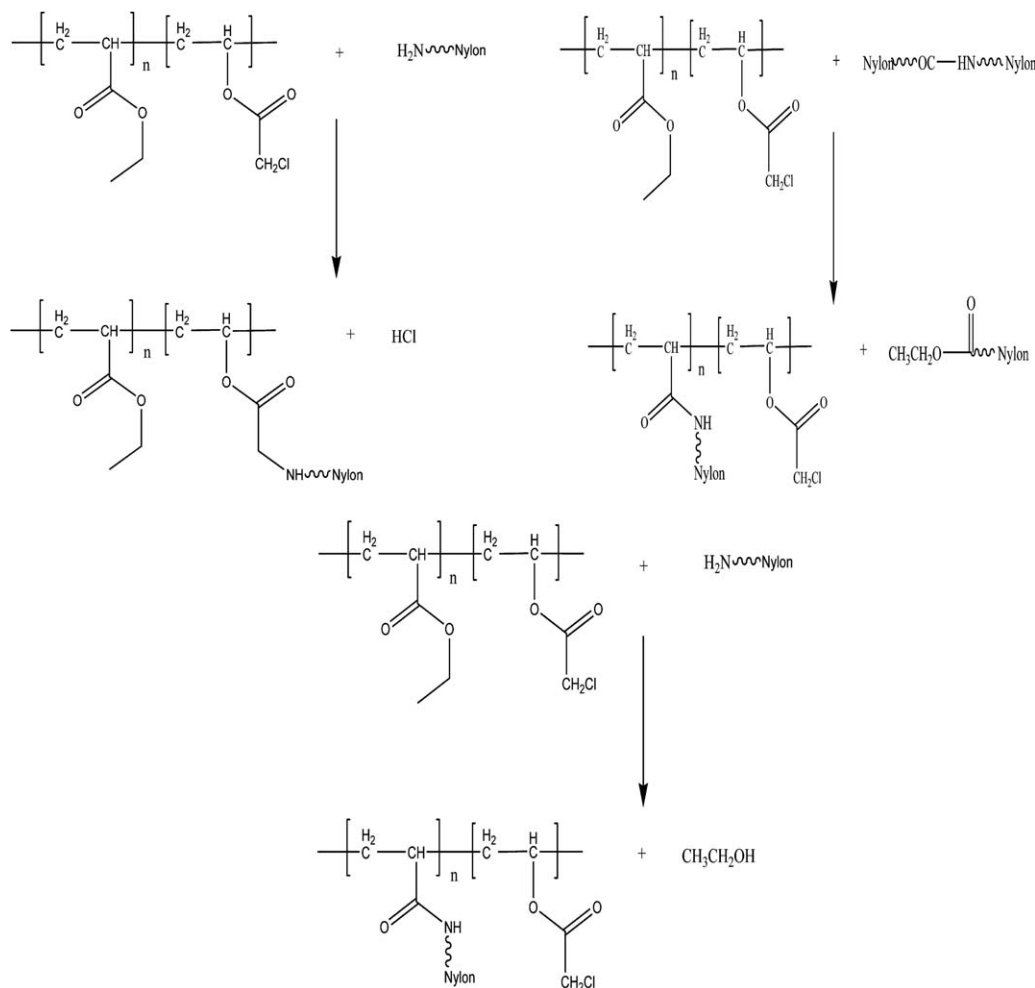
Table II. Assignment of the Characteristic Peaks of Nylon 1010 and ACM

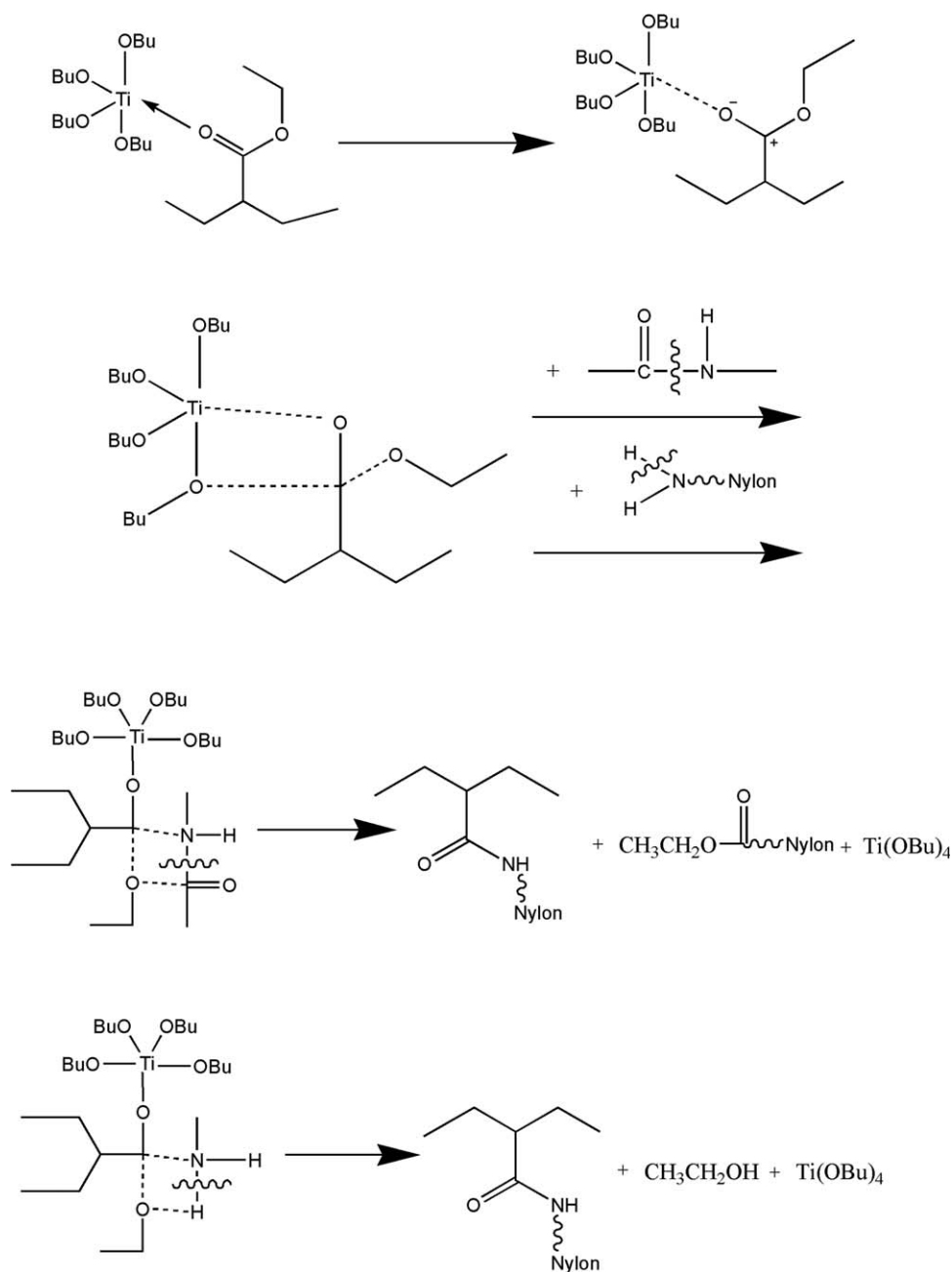
Assignment		Chemical shift (ppm)
Nylon 1010	—NH—CH ₂ —	3.50
	—CO—CH ₂ —	2.65
ACM	—COO—CH ₂ —CH ₃	4.21
	Proton of methenyl On curing site	3.85
	Proton of methenyl on acrylate group	2.39

observed from Figure 1 that the peaks at 4.212 and 2.391 ppm ascribed to ACM appeared in the curves of the blends both with and without catalyst. This means that some reactions between Nylon1010 and ACM occurred during the melting processing, leading to the chemical connecting of ACM onto Nylon 1010.

Taking the peak at 3.497 ppm from Nylon 1010 as a reference peak, the integral area ratio between the two peaks at 4.212 and 3.497 ppm can be used as an indication for the reaction extent.

The ratio is 0.29 and 0.78 for Nylon 1010/ACM (50/50, 10 min) and Nylon 1010/ACM/Ti(OBu)₄ (50/50/1, 10 min), respectively, indicating that the extent of reaction increased by the addition of catalyst. The reaction between —CH₂Cl and —NH₂ is well known in the curing of polyacrylate rubber as shown in Scheme 1(1). The proton signal intensity ratio between the peak at 3.854 and 3.497 ppm can be used as an indication for the extent of this reaction. The ratio is 0.00703 and 0.00705 for Nylon 1010/ACM (50/50, 10 min) and Nylon 1010/ACM/Ti(OBu)₄ (50/50/1, 10 min), respectively. The calculated values are very small because the cure site monomer (active chlorine) contents of ACM are very low. Considering the error of measurement, it is difficult to conclude the effects of catalyst on this reaction. It has been reported that, the polyester chain would break at the ester bond site in the presence of catalyst.^{2,10,11} Then, CH₃CH₂CO— would attack secondary amine group (—NHCH₂—) or the terminated —NH₂ of Nylon 1010 and the ester-amide exchange could occur as shown in Scheme 1(2) and (3).^{11,37} It shows that the ester-amide exchange reactions between amide groups of Nylon 1010 and the ester carbonyl groups of ACM, leading to the formation of new copolymers comprised of the segments detached from Nylon 1010 and ACM chains. The acetamide terminated Nylon 1010

**Scheme 1.** Mechanism of melt reaction between Nylon 1010 and ACM at 240°C.



Scheme 2. The catalytic mechanism of the catalyst $\text{Ti}(\text{OBu})_4$ for the ester-exchange reactions between Nylon and ACM.

generated in the reaction [Scheme 1(2)] was one of the products through the reaction between amide of Nylon 1010 and the ester group of ACM. At the same time, the product Nylon-g-ACM was generated by the reaction [Scheme 1(3)] between terminated $-\text{NH}_2$ of Nylon 1010 and the ester group of ACM.

The catalytic mechanism of the catalyst $\text{Ti}(\text{OBu})_4$ for the ester-exchange reactions between Nylon and ACM is shown in Scheme 2. Firstly, metal-oxygen bond was formed between ACM and $\text{Ti}(\text{OBu})_4$ due to the coordination effect and ACM chain was functionalized by $\text{Ti}(\text{OBu})_4$. By the effect of electron transfer and carbocation (C^+) was formed. Then, the nitrogen anion (N^-) in the amide or amine groups of Nylon would

attack the C^+ .^{38,39} As a result, the ester-exchange reactions took place and the Nylon-g-ACM was generated.

Mechanical Properties and Melt Flow Index

The ACM content significantly affects the notched Izod impact strength of Nylon 1010/ACM blends (Figure 3). Nylon 1010 has low impact strength of 5.9 kJ/m^2 . The addition of ACM has slight effect on the impact strength when the ACM content is lower than 30 wt %. When the ACM content is higher than 30 wt %, the impact strength of the blends increases significantly.

Table III gives the mechanical properties and melt flow index (MFI) of Nylon 1010/ACM blends with or without catalyst with

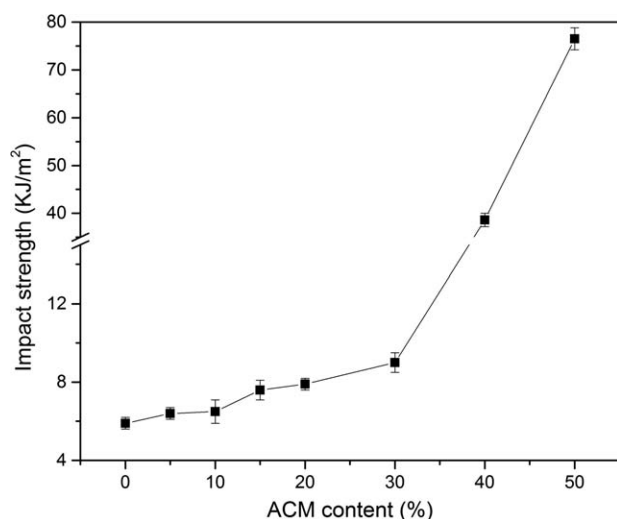


Figure 3. Effect of ACM content on the notched impact strength of Nylon 1010/ACM blends.

different blending time. Compared to the blends without catalyst, the introduction of the catalyst has slight effect on tensile strength and elongation at break. This phenomenon was same as reported by Lei et al.⁴⁰ The tensile strength shows a slight decrease after adding the catalyst. The catalyst $Ti(OBu)_4$ might promote the reactions and improve the compatibility of blends, but also accelerate degradation of the blends as well. That is an explanation for the change in the tensile strength. When the blending time reached 30 min, the tensile strength increased to 15.3 MPa, but no further improvement with further increasing time. There should be more copolymers produced at the interface as compatibilizers for the blend, but their effect on the properties was limited partially because of the degradation effect.

MFI of Nylon 1010/ACM (50/50, 10 min) blend increased slightly after adding the catalyst. But when the blending time increased to 30 or 60 min, MFI of Nylon 1010/ACM (50/50) blend decreased obviously after adding the catalyst. A lower MFI value means a poor flowability, which might be due to the presence of copolymers and some interactions between the components in the molten state.

Reactions taking place in the reactive processing of the blends might proceed in two steps. First, the grafted copolymers

formed and the lengths of some Nylon chains become shorter, which leads to better flowability and higher MFI values. Secondly, with longer blending time or the addition of catalyst, the reaction extent would be enhanced, leading to longer branched copolymer or even crosslinked polymers resulting in lower MFI values.

In this system, decomposition and crosslinking are two opposite factors to affect MFI of the blends. The decomposition of polymers increased MFI value while the crosslinking reactions decreased MFI value. For Nylon 1010/ACM (50/50, 10 min), the addition of the catalyst accelerated the generation of the grafted copolymer and the decomposition of the polymer matrix occurred at the same time. However, few crosslinking and longer branching chains were formed because of the short blending time. As a result, MFI was almost unchanged and independent of the catalyst. While for Nylon 1010/ACM (50/50, 30 min) and Nylon 1010/ACM (50/50, 60 min) with longer reaction time, the addition of catalyst enhanced the reaction extent, leading to longer branching chains and more crosslink in the blends. Compared to the decomposition, crosslinking might play a more important role to determine the flowability of the blends and result in lower MFI values.

Thermal Properties

Thermal behavior of Nylon 1010 and Nylon 1010/ACM blends were studied using DSC. Double melting peaks appeared in the curves of Nylon 1010 and Nylon 1010/ACM blends and the data were shown in Table IV. Double melting peaks are a common phenomenon which occurs during the melting process of Nylon 1010, resulted from the melt recrystallization.^{41,42} It was reported that the lower temperature peak corresponds to the crystal melting at different crystallizing temperatures, and the higher temperature peak corresponds to the melting of the recrystallized polymer.

The two melting temperatures (T_{m1} and T_{m2}) of all blends decreased with increasing the blending time, no matter the addition of the catalyst. This is associated with grafted polymers produced by the addition of ACM in the blends. First, the grafted polymers can increase intermolecular distance and decrease intermolecular force.²⁶ Second, the molecular weight of the Nylon1010 decreases with increasing the blending time during the ester-amide exchange reaction due to decomposition of

Table III. Effects of Blending Time and Catalyst on the Mechanical Properties and Melt Flow Index of Nylon 1010/ACM Blends

Original weight ratio Nylon 1010/ACM/ $Ti(OBu)_4$ (time, min)	Tensile strength (MPa)	Elongation at break (%)	Hardness (Shore D)	Hardness (Shore A)	MFI (g/10 min)
Nylon 1010	47.8 ± 1.1	91 ± 26	84	-	68.3
ACM	1.5 ± 0.1	2119 ± 60	-	20	-
50/50/0(10)	11.6 ± 1.2	42 ± 7	56	89	3.3
50/50/1(10)	11.8 ± 1.6	55 ± 12	57	90	3.8
50/50/0(30)	15.3 ± 0.8	66 ± 14	57	90	6.4
50/50/1(30)	14.8 ± 1.1	42 ± 13	57	-	3.9
50/50/0(60)	15.1 ± 1.1	60 ± 10	58	-	2.9
50/50/1(60)	14.4 ± 1.4	53 ± 19	58	-	0.9

Table IV. Thermal Properties of Nylon 1010/ACM and Nylon 1010/ACM/Ti(OBu)₄ Blends

Original weight ratio Nylon 1010/ ACM/Ti(OBu) ₄ (time, min)	T_g (°C)	T_c (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔT_m (°C)	ΔH_m (J/g)	ΔH_c (J/g)	X_c (%)
Nylon 1010	43.9	172.8	190.5	201.7	11.2	73.9	69.5	30.3
50/50/0(10)	43.3	174.2	188.0	198.0	10.0	68.2	63.4	28.0
50/50/1(10)	45.1	174.7	188.9	198.7	9.8	70.4	67.6	28.8
50/50/0(30)	47.8	170.0	186.4	196.8	10.4	73.8	63.6	30.2
50/50/1(30)	48.3	172.2	187.6	197.9	10.3	80.4	66.8	33.0
50/50/0(60)	45.5	167.5	184.5	194.7	10.2	78.0	64.5	32.0
50/50/1(60)	45.2	170.1	185.1	195.2	9.9	80.2	68.1	32.8

Note: T_g is the glass transition temperature of Nylon 1010; T_c and T_m are the crystallization and melting temperatures, respectively; ΔT_m is the difference of two melting temperatures, $T_{m2}-T_{m1}$; and ΔH_m is the heat of fusion and ΔH_c is the crystallization enthalpy.

the amide bond. Finally, the graft polymers between the interface of Nylon 1010 and ACM results in restricted movement of the chains in the blends, and impart perfect crystals of Nylon 1010. Longer blending time led to high amounts of the graft polymers. The existence of catalyst decreased ΔT_m . This also

means the melting of Nylon 1010 became easier after the catalyst was added.

For the blends with longer blending time and addition of catalyst, the lower temperature melting peak intensity decreased, implying that the melting of crystallized polymer becomes easier. This is probably due to the fact that polymer chains bonded between two phases might have led to some inferior crystals.

Accordingly, the crystallization temperature of 50/50 or 50/50/1 blends decreases with increasing blending time (Table IV). In Figure 4(1, 2), a similar conclusion can be drawn with the crystallization temperature of Nylon 1010/ACM blends. As mentioned above, only lower temperature chain mobility will be hindered and the polymer can crystallize. The graft copolymers may bring a negative effect on crystallization in the blends with catalyst, which decreased the crystallization temperature.

As the catalyst introduced into the blends, T_g of Nylon 1010 increased notably in the blends (Nylon 1010/ACM/Ti(OBu)₄ (50/50/1, 10 min) and (50/50/1, 30 min)), this might be due to the addition of ACM, which restrain the movement of Nylon1010 chain. In the Nylon/ACM blends, the ester-amide exchange reactions stayed at the interface of the two phases, and the Nylon 1010-g-ACM also restrained the movement of Nylon 1010. But for the Nylon 1010/ACM/Ti(OBu)₄ (50/50/1, 60 min) blend, T_g of Nylon 1010 decreased. More flexible ACM molecule chains connected onto Nylon chains with longer blending time, which might enlarge the space of Nylon chains and decrease the intermolecular interaction. As a result, T_g decreased with this “internal plasticization” effect.

Thermal Degradation Behavior of NYLON 1010/ACM Blends

Figure 5 shows the TGA thermograms of Nylon, ACM, Nylon 1010/ACM blends (30 min). The data are summarized in Table V. The blends show two stages of decomposition, and therefore two T_{max} at DTG curves. Compared with pure Nylon 1010 and ACM, the two T_{max} values of the blends became higher with longer blending time. This indicates that some chemical interaction occurred between the two polymers during processing, which stabilized the rubber phase in the blends. The IDT of the blends decreased after adding catalyst although the T_{max} increased slightly, indicating that some degradation occurred in the two polymers caused by the catalyst during processing.^{43,44}

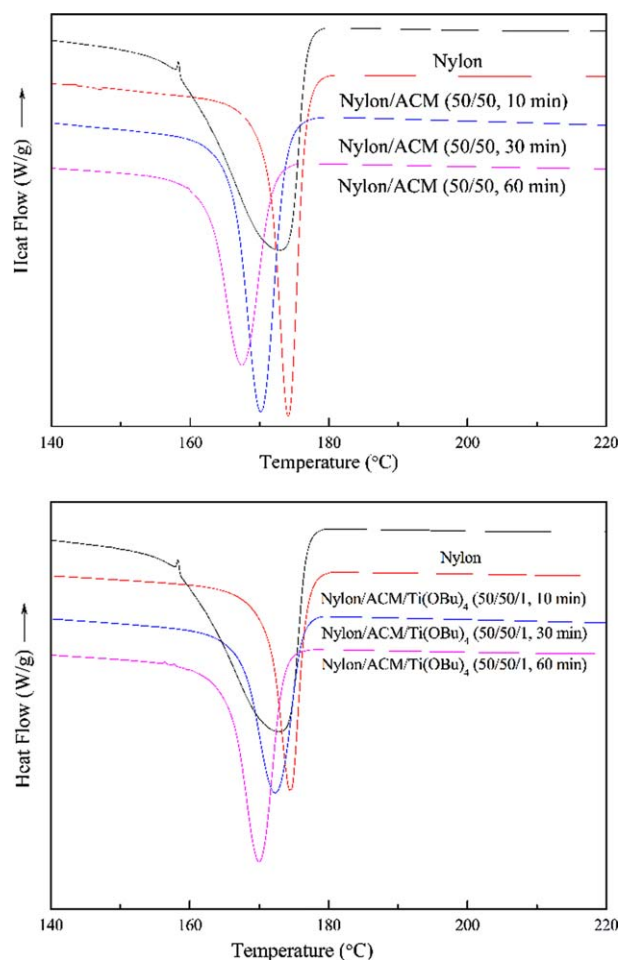


Figure 4. DSC cooling curves of (1) Nylon1010 and Nylon1010/ACM blends with different blending time and (2) Nylon1010 and Nylon1010/ACM/Ti(OBu)₄ blends with different blending time. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

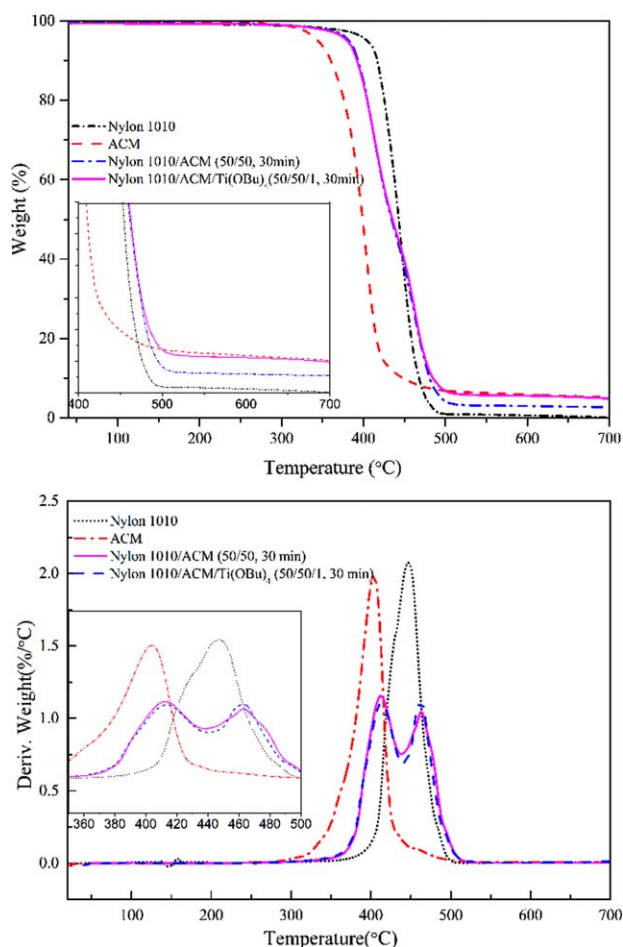


Figure 5. TGA (1) and DTG (2) curves of Nylon 1010, ACM and Nylon 1010/ACM blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Char yield of the blends at 700°C increased after adding catalyst, which might be resulted from high residue of the catalyst itself.

Rheological Measurements

Oscillatory rheological measurements were carried out to get information on the structure of the copolymers being formed.

Table V. TGA Data of Nylon 1010/ACM Blends

Sample	IDT (°C)	T_{max1} (°C)	T_{max2} (°C)	Char yield at 700°C (%)
Nylon 1010	405	-	445	0.56
ACM	345	404	-	5.59
50/50/0(10)	384	413	463	3.26
50/50/1(10)	378	410	463	4.57
50/50/0(30)	383	413	463	3.17
50/50/1(30)	380	413	463	5.57
50/50/0(60)	384	417	471	3.21
50/50/1(60)	383	418	469	4.77

IDT: initiation decomposition temperature; T_{max} : the temperature of the maximum rate of weight loss.

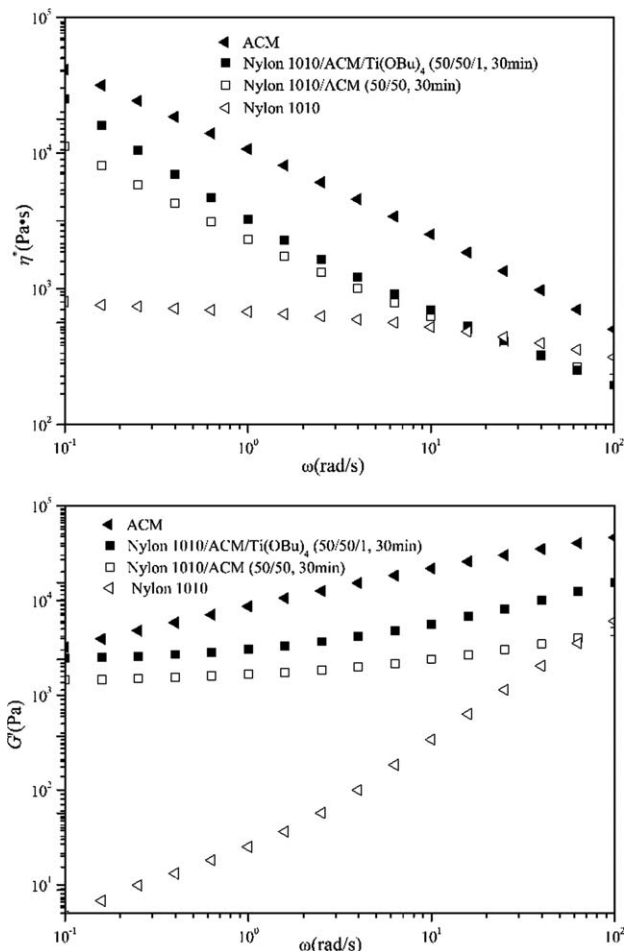


Figure 6. Rheological behaviors of the polymers and blends (1) complex viscosity and (2) storage modulus.

The complex viscosity and storage modulus versus the frequency are shown in Figure 6.

It can be seen from Figure 6(1), all the materials shows a non-Newtonian behavior, but there are still some differences. The complex viscosities of the blends are lower than ACM and higher than pure Nylon 1010 especially when the frequency is lower than 10 rad/s. Nylon 1010/ACM (50/50, 30 min) has a lower complex viscosity at low frequency (below 10 rad/s) than Nylon 1010/ACM/Ti(OBu)₄ (50/50/1, 30 min). It means that with the addition of catalyst, the entanglements or the formation of crosslinked copolymers increases due to longer grafting chains, and therefore the complex viscosity at low frequencies shifts to higher values. These results corroborate that graft polymer formation occurred during melt mixing when the catalyst added and correlated with ¹H NMR and MFI. A similar result for storage modulus can be seen from Figure 6(2) as for complex viscosity. Nylon 1010/ACM/Ti(OBu)₄ (50/50/1, 30 min) presents higher storage modulus than Nylon 1010/ACM (50/50/0, 30 min), due to the similar reasons as explained above.

To prove the rheological experiments, a power law model $\eta = K\dot{\gamma}^{n-1}$ is used to emulate the shear-thinning behavior of non-Newtonian fluids according to Cox-Merz rule.⁴⁵ In this

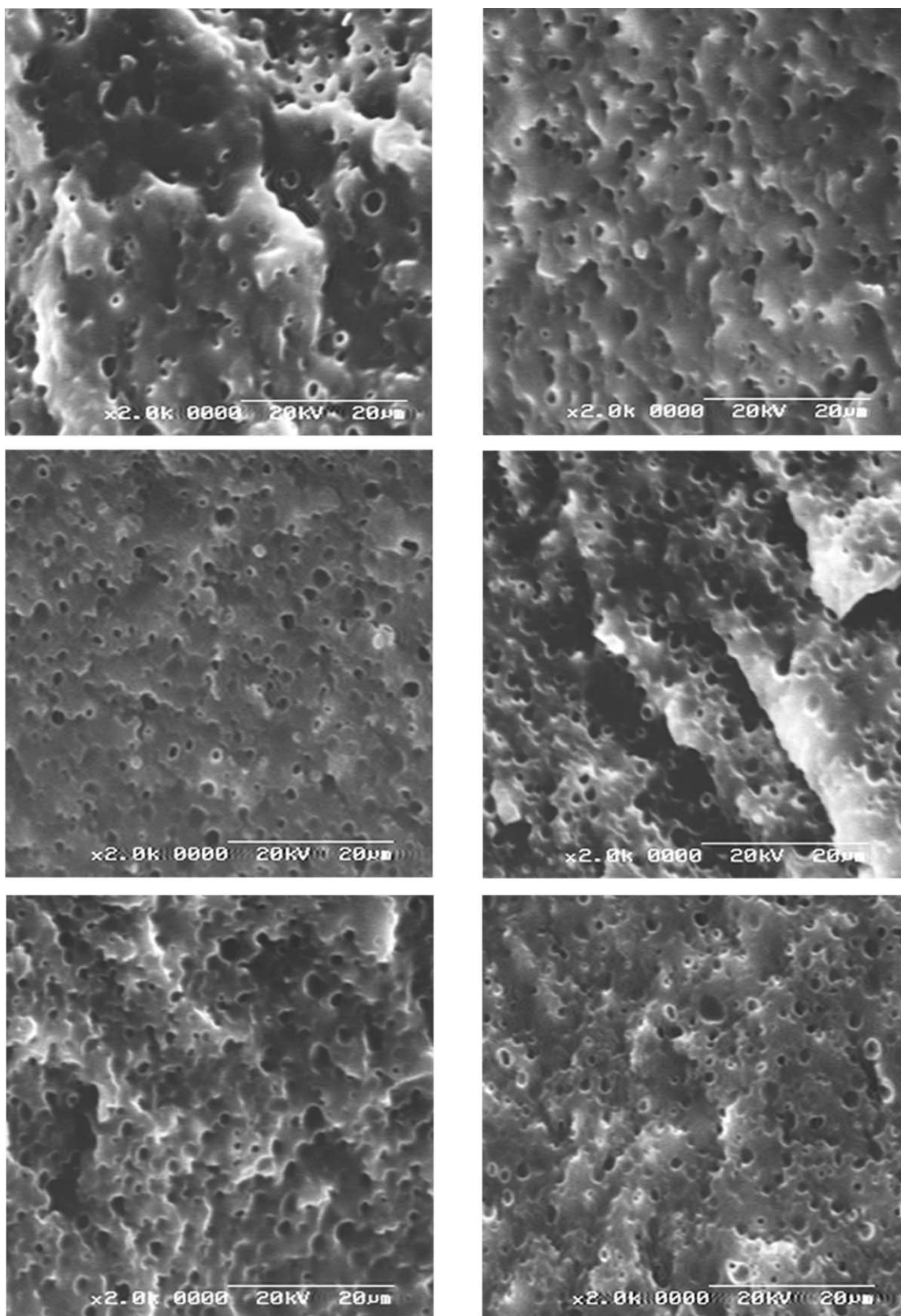


Figure 7. Morphology of Nylon 1010/ACM/Ti(OBu)₄ (wt/wt, min) blends with different mixing time and catalyst content (etched with chloroform). (1) 50/50, 10 min; (2) 50/50, 30 min; (3) 50/50, 60 min; (4) 50/50/1, 10 min; (5) 50/50/1, 30 min; (6) 50/50/1, 60 min.

power law model, η is the complex viscosity, γ is the shear frequency, K is a constant, n is defined as the Power Law Index (PLI). After calculation, PLI of Nylon, ACM, Nylon 1010/ACM and Nylon 1010/ACM/Ti(OBu)₄ is 0.87, 0.36, 0.33, and 0.26, respectively. All PLI values are between 0 and 1, which mean that all the materials appear the shear-thinning behaviors. PLI of Nylon 1010/ACM decreased after adding catalyst, indicating the pseudoplastic behavior of Nylon 1010/ACM/Ti(OBu)₄ is more apparent than that of Nylon 1010/ACM blend.

Morphology

Morphology plays an important role in the properties of polymer blends. The blend samples were etched with chloroform to remove the ACM phase and the morphology of the left parts is shown in Figure 7.

Small cavities can be observed in the morphology, which can be attributed to ACM being etched. All blends showed a sea-island structure independent of blending time and catalyst. After adding catalyst, the average size of the dispersed phase decreased and the number of the cavities increased. This indicates the addition of catalyst can improve the compatibility of the two phases. Comparing the morphology of the blends with different blending time, longer blending time led to a decreased size of the dispersed phase. This indicates longer blending time can also improve the compatibility of the reactive blends. By ¹H NMR analysis in the previous section, it has been proved that catalyst could affect the exchange reaction. Therefore, the exchange reaction can influence the morphological evolution of the blends. The copolymer generated in the exchange reaction might play a role as a compatibilizer and improve the compatibility of the Nylon/ACM blends.

Conclusions

The effects of blending time and catalyst Ti(OBu)₄ on the ester-amide exchange reaction in Nylon 1010/ACM 50/50 (w/w) blend were discussed. Longer blending time and the presence of Ti(OBu)₄ catalyst promoted exchange reactions. Pathway of the reaction was investigated by ¹H NMR, and it was observed that catalyst can enhance the reaction extent. The tensile strength of the blends with catalyst was improved by increasing the blending time from 10 to 30 min, and the MFI was decreased by adding catalyst. The melting temperature (T_m) of all blends decreased with extending the blending time. The initial decomposition temperature of the blends decreased after adding of the catalyst. Thermogravimetry curves showed two-step decomposition, and the rate of the second step decomposition increased with higher extent of reaction between the two polymers. Rheology analysis showed that the complex viscosity and storage modulus increased after adding the catalyst into the blends. SEM images of the blends illustrated that the exchange reactions can influence the morphological evolution of the blends during processing (changing mixing time or catalyst content).

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