

Study on the Morphology and Properties of Metallocene Polyethylene and Ethylene/Vinyl Acetate Blends

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ABSTRACT: Two commercial polymer materials, metallocene linear low density polyethylene (m-LLDPE) and ethylene/vinyl acetate copolymer (EVA) have been used to form binary blends of various compositions. The mechanical properties, morphology, rheological behavior, dynamic mechanical properties, and crystallization of m-LLDPE/EVA blends were investigated. It was found that with the addition of EVA, the fluidity and processability of m-LLDPE were significantly improved, and the introduction of polar groups in this system showed no significant changes in mechanical properties at lower EVA content. As verified by morphology observation and differential scanning calorim-

etry analysis, miscible blends were formed within certain weight ratios. Dynamic mechanical property studies showed that flexibility of the blends was enhanced in comparison with pure m-LLDPE, where the peak value of loss modulus shifted to lower temperature and its intensity was enhanced as EVA content increased, indicating the existence of more amorphous regions in the blends. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 905–910, 2004

Key words: metallocene polyethylene; ethylene/vinyl acetate copolymer; blends

INTRODUCTION

In comparison with conventional low density polyethylene (LDPE) produced with Ziegler–Natta catalysts, it is known that metallocene polyethylene (mPE) possesses superior properties in many aspects, such as optical transparency, higher mechanical properties, and improved heat encapsulation. However, owing to the molecular characteristics of mPE, its market potential is limited for poor processabilities, which can be seen as high melt viscosity, inferior fluidity, and low melt intensity.¹ Many studies have already been undertaken to modify the processing and molding characteristics of mPE, and the efforts mainly focus on (1) using catalysts with different metallocene site or mixed catalysts to widen the molecular weight distribution (MWD) of mPE, or to produce a binary molecular weight distribution products²; (2) introducing long chain branching onto the backbone of mPE resin^{3,4}; (3) modifying the present facilities to meet the particular requirement of mPE processing⁵; (4) blending mPE with additives or other resins to improve the processability.⁶ In practice, blending is the simplest way to be carried out among all these methods described. Related to the corresponding fields, the pre-

vious work investigated involve the blends of mPE with low density polyethylene (LDPE), fluoroelastomer, talcum, diatomite, etc., as modifiers, whereas the study on mPE and ethylene/vinyl acetate copolymer (EVA) blends has not been reported so far. On the other hand, as to conventional LDPE and EVA blends, a number of research works had been reported, whereas most of them have focused on radiation-induced crosslinking systems.^{7–9}

Different from polyethylene, the existence of vinyl acetate groups result in lower crystallinity of EVA; consequently, superior flexibility, impact resilience, transparency, and better miscibility with fillers are formed. In view of these characteristics, it can be expected that the interactions between chain segments and the corresponding properties in metallocene linear low density polyethylene (m-LLDPE)/EVA should be different from those of m-LLDPE/LDPE. Therefore, the phase behavior and the properties of m-LLDPE/EVA blends should be of great interest. In this work, m-LLDPE/EVA blends were prepared in order to improve the processability of mPE. In the meantime, the introduction of ester groups into the blends was expected to provide better miscibility with fillers, which offered the possibility to adopt inorganic nanoparticles for further modification of m-LLDPE. In this article, the mechanical properties, morphology, rheological behavior, dynamic mechanical properties, and crystallization behavior of m-LLDPE/EVA blends were extensively investigated with varied EVA contents.

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TABLE I
Characteristics of the Materials Studied

Sample	Density (g/cm ³) ^a	MI (g/10 min) ^a	\bar{M}_n ^b	\bar{M}_w ^b	\bar{M}_w/\bar{M}_n ^b
m-LLDPE	0.917	1.0	43529	113030	2.60
EVA	0.935	0.7	23068	95704	4.15

^a Obtained from the supplier.

^b Measured by PL-210 GPC.

EXPERIMENTAL

Materials

The m-LLDPE used was supplied by ExxonMobil (USA) as Exceed350D65 grade. EVA copolymer was provided by Beijing Organic Chemical Plant, Beijing, China, with vinyl acetate content of 14%. The molecular parameters of materials, \bar{M}_n , \bar{M}_w , \bar{M}_w/\bar{M}_n , were measured on a PL-210 gel permeation chromatography (GPC) instrument. The molecular and physical parameters of the materials are listed in Table I.

Preparation of m-LLDPE/EVA blends

M-LLDPE and EVA blends of different weight ratios were mixed at 160°C using a RM-200 rheometer mixer (Harst Technology Development Company, Harbin, China), and the melt viscosities of the blends were characterized by torque measurements at a fixed speed of 35 rpm. Then the samples were compression molded at 160°C for tensile, dynamic viscosity, and dynamic mechanical analysis (DMA) measurements.

Characterizations

The tensile tests were carried out on a universal tensile tester (WD-3000, Changchun Kexin Company, China) according to ASTM-D638. The tests were conducted at 23°C, and a crosshead speed of 100 mm/min was employed.

Dynamic viscosity measurements were undertaken using a rheometer (Rheometric Scientific ARES) in the parallel-plate mode. The diameter of both upper and lower plates was 25 mm, and the gap between the two parallel plates was 1 mm. The measurements were conducted at constant strain of 15% (within the linear viscoelastic range) over a frequency range of 10^{-1} – 10^{+2} rad/s at 180°C.

The melt flow index of the blends was measured by a μ pXRZ-400C apparatus (Scientific Research Instrument Factory, Jilin University, China) at 190°C and 5 kg load.

The morphology of m-LLDPE/EVA blends was assessed via a Hitachi-800 transmission electron microscopy (TEM) using cryogenically microtomed ultrathin sections. Phase contrast between the components was

achieved by exposing the sections to vapors of OsO₄ to stain the EVA phase.

Dynamic mechanical properties were measured with a DMA 2980 from TA instruments. Rectangular plaques were compressed and the mean dimensions for the sample plaques were 35 × 12.5 × 2 mm. The storage modulus E' and loss modulus E'' were determined at 1 Hz in the temperature range between –150 and +150°C. The frequency was fixed at 1 Hz and the heating rate was 5°C/min.

Differential scanning calorimetry (DSC) was employed to investigate the crystallization behavior of the blends, performed on a Perkin-Elmer DSC-2C calorimeter. The temperature and heat flow were calibrated before the measurement. All samples were heated from room temperature to 150°C at 10°C/min in nitrogen atmosphere, held at 150°C for 5 min, then cooled down to 25°C at a rate of 10°C/min.

RESULTS AND DISCUSSION

Mechanical properties

As can be seen in Figure 1, with the increase of EVA weight ratio, the tensile strength of m-LLDPE/EVA blends held almost unchanged at first, then a decreasing trend was observed. At the same time, the elongation at break for all the blends was higher than that of pure m-LLDPE. These phenomena are quite different with the reports on m-LLDPE/LDPE blends, in which the tensile strength and tensile elongation simultaneously decreased with the addition of LDPE.¹⁰

As mentioned above, the two polymers in the system under investigation, i.e., the blends of m-LLDPE and EVA with 14% VA content, have a structural difference in the sense that the former is a completely nonpolar methylene chain, and the latter is a copolymer of a nonpolar methylene chain with polar acetate groups. Accordingly, these two polymers differ in the degree of crystallinity and also in their polarity. With

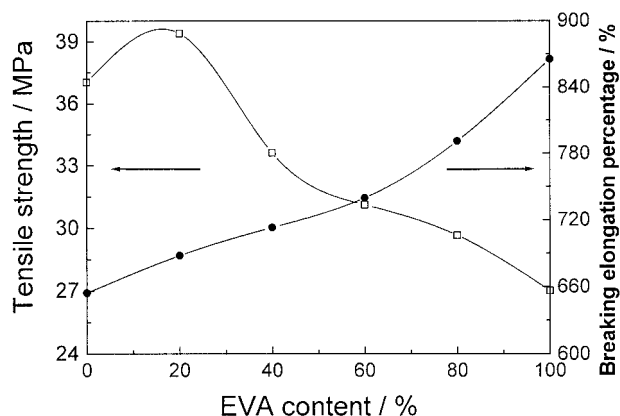


Figure 1 Mechanical properties of m-LLDPE/EVA blends vs EVA content.

regard to the tensile strength of m-LLDPE/EVA blends, we conclude that as EVA content increases, the changing trend of compatibility and the intermolecular interactions between the two components might lead a cooperation effect under some circumstances. At the same time, due to the introduction of polar vinyl acetate groups, with an increase in the EVA content, the effective energy-dissipation process of the blends becomes easier, which gives rise to an increase in the tensile elongation. Namely, EVA turns from separate phase into a continuous phase; it does, of course gradually bear the main loading in the deformation, which leads to the increasing tendency of tensile elongation of the blends. These will be verified by the morphology observation and DSC analysis below.

Morphology

In order to get insight into the compatibility of the two components, as well as the relationship between mor-

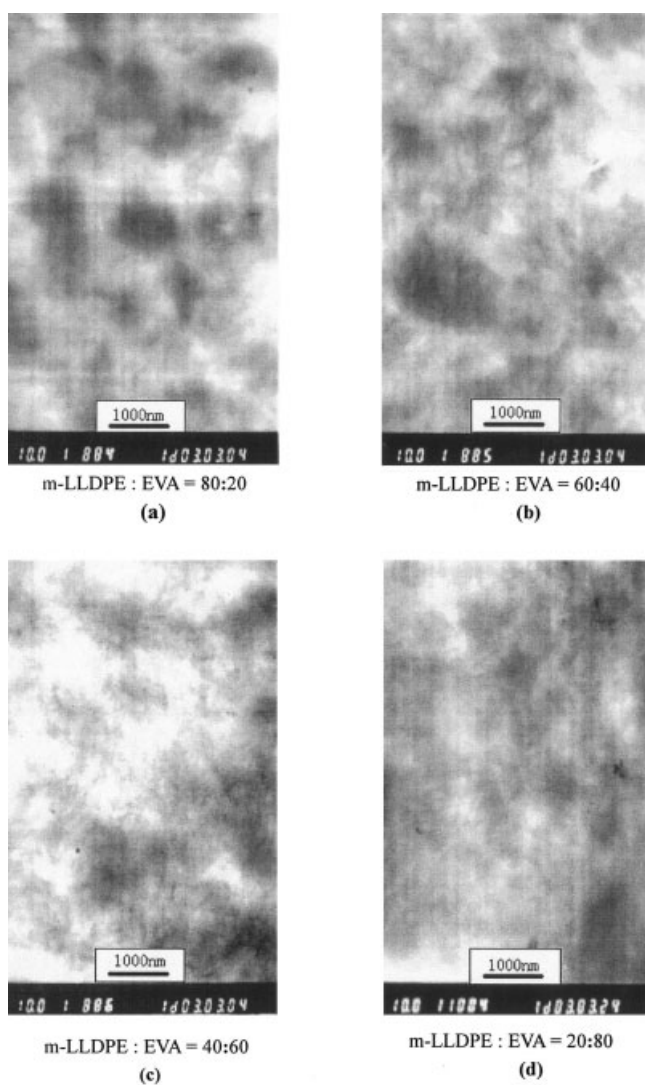


Figure 2 TEMs of m-LLDPE/EVA blends.

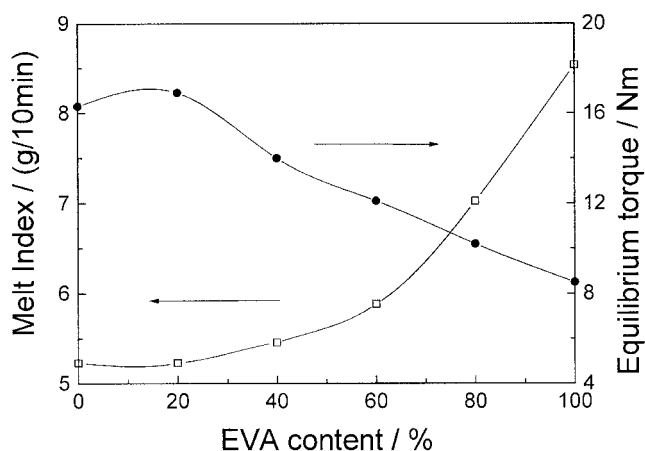


Figure 3 Melt index and equilibrium torque of m-LLDPE/EVA blends vs EVA content.

phology and properties of m-LLDPE/EVA blends, the electron micrographs of the samples were examined with TEM (as illustrated in Fig. 2). With increase in EVA weight ratios, the microstructure of the blends took on compatibility to a certain extent. For instance, at 20% EVA weight ratio, a comparatively good dispersion of EVA was observed, and the interfacial characteristics showed that the two components were compatible, which could be in favor of the improvement on bearing the external stress. Meanwhile, the EVA phase took on irregular figures and certain distribution of the disperse size. When EVA content increased above 40%, the enrichment of EVA phase occurred, and the compatibility became worse accompanying the appearance of phase reversion.

Rheology

As described above, the processability of metallocene polyethylene is a key factor in its industrial production. Therefore, it is of significant importance to investigate the rheological behavior of m-LLDPE/EVA blends with varied weight ratios. Figure 3 shows the changing trend of melt flow index and the equilibrium torque of the blends as EVA content increased. With the addition of EVA, the values of melt flow index increased gradually, indicating improved fluidity of m-LLDPE, which can lead to the improvement of material processing. With regard to the equilibrium torque, the value went up slightly first, then decreased sharply as EVA content further increased. The decrease in equilibrium torque should correspond to lowered melt viscosity, which is also in favor of m-LLDPE processing.

The dynamic rheological behavior of m-LLDPE/EVA blends is shown in Figure 4. As can be seen in Figure 4(a), the dynamic viscosity (η^*) of m-LLDPE decreased slightly within the frequency range investi-

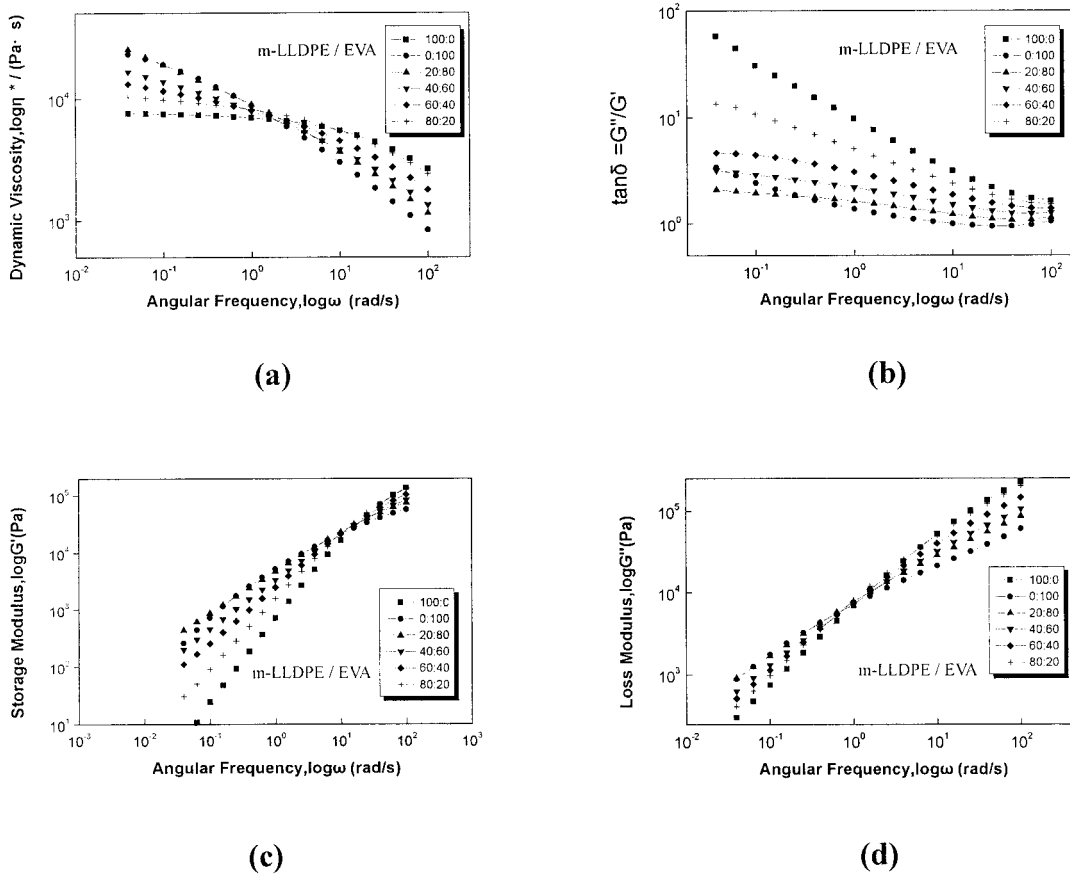


Figure 4 Dynamic rheological behavior of m-LLDPE/EVA blends: (a) η^* vs frequency; (b) $\tan \delta$ vs frequency; (c) G' vs frequency; (d) G'' vs frequency.

gated, indicating the nonsensitivity of η^* to the shearing stress. This should be attributed to the molecular structure of m-LLDPE, especially the absence of high molecular weight proportion, which brought on a simultaneous response of macromolecular chains under external stress. Accordingly, this characteristic nonsensitivity of η^* is responsible for the high viscosities and high motor load during m-LLDPE processing. As to m-LLDPE/EVA blends, the dynamic viscosity was higher than that of pure m-LLDPE at low frequency, whereas at high frequency, as EVA content increased, the changing extent became more significant, which indicates more sensitivity of η^* to the shearing stress.

Figure 4(b) illustrates the variation in loss tangent ($\tan \delta$) with frequency. It can be seen that within the frequency range investigated, $\tan \delta$ of all the samples showed a decreasing trend, in which pure m-LLDPE manifested the most obvious change. As EVA content increased, the changing extent became much slightly, and the curves turned to parallel with each other when EVA weight ratio was above 20%. This phenomenon also indicates the changes in the supermolecular structure and phase behavior of the melt blends, which bring about a transformation in rheological properties, namely, the decreasing viscosity and viscous dissipation.

The effects of increasing EVA content on the storage and loss modulus of the samples at 180°C are presented in Figure 4(c) and (d). We can see that as the frequency increased, both the storage modulus (G') and loss modulus (G'') were increased, and the changing extent of G' and G'' became smaller with the increase of EVA content. In addition, all the curves in (c) and (d) came across together where G' was higher than G'' for each sample, indicating faster elastic response of the materials as the frequency increased.

It is well understood that a linear behavior of $\log G'$ vs $\log G''$ plots could be a compatibility criterion of polymer blends.^{11,12} In our experiments, a linear relationship between G' and G'' appeared when the EVA content was less than 40%, while a slanting behavior appeared as EVA content was much higher (see Fig. 5). This implies the deterioration of the compatibility of the two components. This result is consistent with the morphology observation discussed above.

Dynamic mechanical properties

The storage modulus (E') and loss modulus (E'') curves from the DMA measurements of all the samples are displayed in Figure 6. It can be seen that

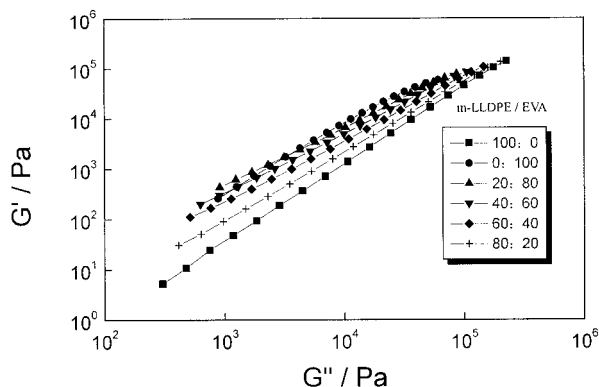


Figure 5 Log G' vs log G'' plots for m-LLDPE/EVA blends.

above the glass transition temperature, the values of storage modulus (E') of all the blends were lower than that of pure m-LLDPE, indicating the decrease in material rigidity, which may be related to the changes in the molecular architecture caused by the addition of EVA. At the same time, the peaks in the loss modulus curve shifted to lower temperature as EVA content increased.

The dynamic loss modulus, E'' , is a measure of the dissipated heat during deformation. At the point of peak temperature in the loss modulus curve, the polymer mobility is undergoing the maximum change, which corresponds to the chemical definition of the glass transition temperature T_g . As indicated in many corresponding reports,^{13–15} the shift of the peaks in the loss modulus curve corresponds to the content of amorphous regions near the short chain branches. With the increase of EVA content, the shift of the peaks to a lower temperature as well as the increase in the peak intensity illustrated in Figure 6(b) showed that the addition of EVA lowered the intermolecular interactions and the regular arrangement of m-LLDPE segments went into more randomly, accordingly led to the formation of more amorphous regions in the blend systems.

Nonisothermal crystallization behavior of m-LLDPE/EVA blends

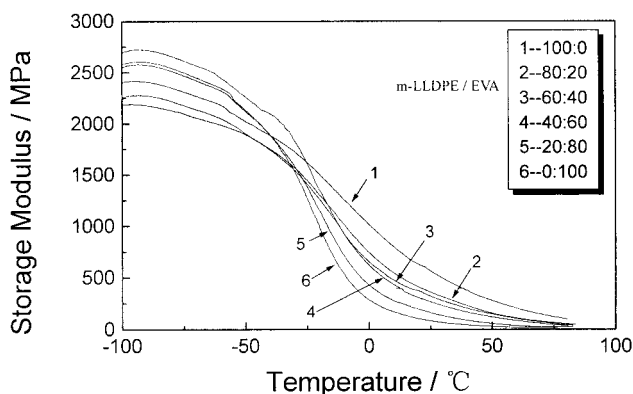
The curves of DSC scans for m-LLDPE/EVA blends are plotted in Figure 7. It can be seen that the blend of 20% EVA content showed only one melting and one crystallization peak respectively, indicating the existence of one type of crystal species. Therefore, it appears that cocrystallization of m-LLDPE and EVA took place.

As EVA content increased, a gradual appearance of two separated peaks during cooling process manifested that liquid–liquid and solid–liquid phase separation happened. In the meantime, the crystallization

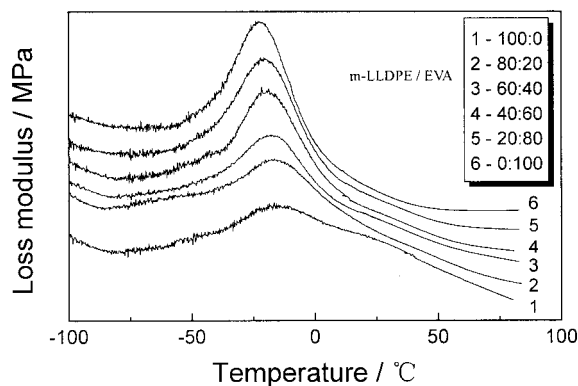
temperature of m-LLDPE decreased gradually accompanying a gradual increase of EVA crystallization temperature; consequently, these two temperatures came close each other with the increase of EVA content, which means that partial cocrystallization might exist in the blends. With regard to the melting process, the changing behaviors with varied EVA content were in agreement with the cooling course.

CONCLUSION

Miscible blends of m-LLDPE/EVA can be formed at lower EVA content, and the obtained materials possess almost unchanged tensile strength compared with pure m-LLDPE, where polar functional groups are introduced to the blend systems. When EVA content becomes higher, the compatibility will be deteri-



(a)



(b)

Figure 6 Storage modulus (E') and loss modulus (E'') curves of m-LLDPE/EVA blends.

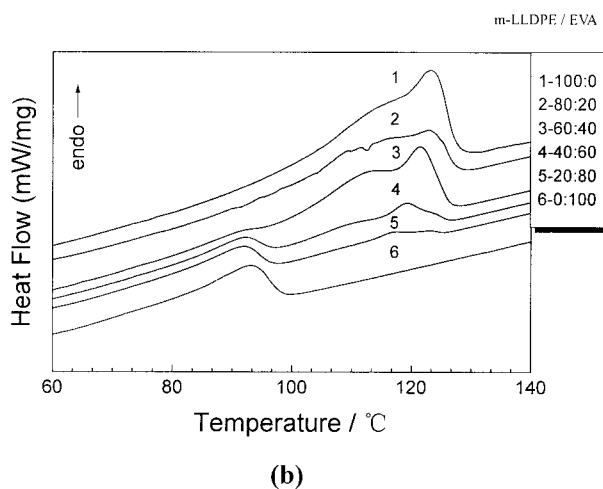
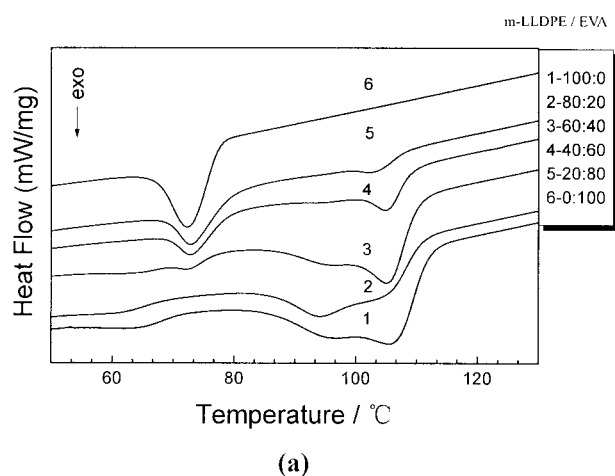


Figure 7 DSC traces for m-LLDPE/EVA blends: (a) cooling process; (b) melting process.

orated, which give rise to the decrease in tensile strength, though the tensile elongation is increased gradually. The introduction of EVA is favorable to improving the sensitivity of m-LLDPE to external shearing stress, leading to decreased melt viscosity and increased melt fluidity; therefore the processability of m-LLDPE can be significantly improved. As shown by dynamic mechanical analysis, the introduction of EVA results in the decrease of rigidity as well as the expansion of amorphous regions in the blend systems. DSC analysis shows the occurrence of cocrystallization with lower EVA content, indicating good compatibility between the two components, which is consistent with the morphology observation.

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