A study of the crystal phase separation of mLLDPE/EVA blend

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Abstract. The crystal phase separation of mLLDPE/EVA (40/60) (wt/wt) blend was investigated by FTIR micro-spectroscopy in a sequential cooling process. To reveal microcosmic causation and details during the process, the changes of absorbance ratio corresponding to high and low vibrational states, and the apparent enthalpy differences of vibration energy states transformation (ΔHV) of characteristic groups in pure mLLDPE, pure EVA and mLLDPE/EVA blend were calculated based on FTIR spectra data. By analyzing ΔHV values of individual characteristic group relating to the exothermal peaks examined in the cooling process, it has been found that methylene groups play an important role in the crystal phase separation. Besides, the energy analysis of the corresponding methyl band at A1369.4/A1367.7 cm⁻¹ in blend indicated that the chain segments of EVA were involved in the phase separation and crystallization process of mLLDPE taking the form of cocrystallization, which further illuminate the results of DSC analysis. Simultaneously, the worse miscibility of ester and alkyl groups was proved by the absence of enthalpy changes at 110°C.

Keywords: Metallocene linear low density polyethylene; Ethylene/vinyl acetate copolymer; Crystal phase separation

1. Introduction

The research interest in polyolefin blends has lasted for several decades both in academic and industrial scopes [1-3]. Concerning the transition from melting to crystalline state, the compatibility between the components, the liquid-liquid and liquid-solid phase separation, as well as the crystal structure formed by the balanced competition among the kinetic, relaxation factors and the thermodynamic equilibrium not only have considerable influence on the melting process and the rheological properties, but also directly affect the final properties of the products [4-5]. Crystal phase separation has decisive influence on the morphology and properties of polyolefin blends, and the effect of the constitutive changes on the crystal phase separation process could reflect the interactions and the dispersion state among the components. However, owing to the similarity in the structure and properties of the components, the phase separation or phase behavior of many commercial binary polyolefin blends could not be directly discerned in the melt state, e.g., HDPE/LDPE blend. As the crystal kinetic process could provide relevant information on phase separation, differential scanning calorimetry (DSC) analysis has been exercised to investigate the crystal phase separation of polyolefin blends via the measurement of the energy changes in the phase transition process, along with the profile change of exothermic crystallizing peaks [6-8]. However, the microcosmic causation or details
concerning crystal phase separation are still unclear by DSC analysis.

In view of the congregation structure formed in non-isothermal crystallization, the macromolecular chain segments in the crystal region of polyolefin blends possess special conformational characteristics and form three-dimensional ordered structure. Owing to the strong intermolecular interactions, the crystalline phase will behave distinctly different physical properties from the melting state. As clarified by large numbers of research reports or monographs [9-13], IR spectroscopy displays prominent advantages concerning the investigation on the changes of characteristic groups during phase transition process, and the effectiveness and sensitivity of this method has been widely testified. During the crystallizing process, the infrared spectra of polymers will manifest notable changes in the intensity, frequency, and the profile of absorption peaks, which might be ascribed to two factors: (1) the force constant of interior chemical bonds and the intermolecular interactions of polymer chain segments are changed by heat shrinkage, accordingly resulting in changed characters of the molecular vibration dipole moment; (2) inside the macromolecular chains, the changes of infrared absorbing concentration of characteristic groups would arise as the temperature decreases. Our previous work has proven that the changes of absorbance ratio corresponding to different vibrational states, and that the apparent enthalpy differences of vibration energy states transformation ($\Delta H_v$) of characteristic groups could be analyzed via the collection of FTIR spectra data [14-15]. In this case, particular information about the crystallization process of the blends, accompanying the energy change of corresponding groups could be obtained via FTIR spectral measurement, thus obtaining more detailed information compared to DSC measurement.

In the present study, the morphology of mLLDPE/EVA (40/60) (wt/wt) blend was firstly observed by transmission electron microscopy (TEM), which evidently indicated the formation of individual rich domains. Afterward, by comparison of the infrared spectra of pure metalloocene linear low density polyethylene (m-LLDPE), pure ethylene/vinyl acetate copolymer (EVA), and mLLDPE/EVA blend during a cooling process, the phase separation along with the formation of crystal structure in mLLDPE/EVA blend were discussed, with the intention of supplying a new insight into the thermodynamics investigation on crystal phase separation of polyolefin blends. At the same time, the combination of FTIR with DSC analysis was carried out to give more information.

2. Experimental

2.1. Materials

The mLLDPE used was supplied by Exxon Chemical Company as Exceed350D65 grade. EVA was provided by Beijing Organic Chemical Plant (China), with vinyl acetate content of 14%. The characteristics of the two materials are listed in Table 1, in which the molecular parameters of materials, $M_n$, $M_w$, $M_w/M_n$, were measured on a PL-210 GPC instrument.

2.2. Preparation of mLLDPE/EVA Blend

The blend was prepared by dissolving the two species (40wt % mLLDPE and 60wt % EVA, weighed 2g in all) in 200ml of $p$-xylene, refluxing for 2 hours at constant temperature, and by rapidly precipitating into 400ml of methanol at 0 °C. The sample was placed for 12 hours at room temperature,

| Samples | Density (g/cm$^3$) | MI (g/10 min) | $\bar{M}_n$ | $\bar{M}_w$ | $M_w/M_n$ |
|--------|-----------------|--------------|------------|-------------|-----------|
| mLLDPE | 0.917           | 1.0          | 43529      | 113030      | 2.60      |
| EVA    | 0.935           | 0.7          | 23068      | 95704       | 4.15      |
then filtrated and washed with methanol, and dried in vacuum at 50 °C.

2.3. TEM observation

0.04 g of mLLDPE and 0.06 g of EVA were dissolved in 50 ml of p-xylene, refluxing for 2 hours at constant temperature. Afterward, the solution was droplet taken using a sucker and dripped onto phosphonic acid surface at 150 °C to form thin film, then cooled to the ambient temperature at a rate of -2 °C/min. The film was put over copper mesh and dried after washed by de-ionized water for many times, then dyed using RuO₂. The morphology of corresponding samples was observed with a Hitachi-800 TEM.

2.4. FTIR micro-spectroscopy

The FTIR measurements were performed in 10kHz rapid-scan at a resolution of 4cm⁻¹ on a UMA500 microscope with a Bio-Rad FTS6000 FTIR spectrometer equipped with a MCT detector, and 16 scans were co-added in each scanset. The sample as a clear KBr pellet was laid between KBr windows in ICL Basics™ microscope compression stage equipped with the temperature controller in precision better than ±1 °C over entire temperature range. The samples was heated from ambient to 150 °C at a rate of 80 °C/min, held at 150 °C for 5 min, then a cooling rate of -2 °C/min was adopted from 150 °C to 67 °C.

2.5. DSC analysis

The DSC thermograms were measured using 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 a rate of 80 °C/min in nitrogen atmosphere, held at 150 °C for 5 min, then cooled down to 50 °C at a rate of -2 °C/min.

3. Results and discussion

Fig.1 represents the morphology of mLLDPE/EVA (40/60) (wt/wt) blend via TEM observation. As indicated in the micrograph at low magnification, distinct phase separation has occurred, resulting in the formation of two individual rich domains. Obviously, the dark area represents EVA rich domain, whilst the bright area corresponds to mLLDPE rich domain. More interestingly, it can be seen from the micrograph at high magnification that bundle form configuration has formed in the crystallization process. It might be reasonably supposed that the liquid-liquid and liquid-solid phase separation, as well as the formation of crystal structure in the blend are very complicated. As to the formation of the radial sheet crystals, the circumstances concerning the diffusion, migration and regular stacking of the two species of macromolecular chains need more experimentation results to elucidate, which will be discussed in a further study. Besides, it is noteworthy that the sheet crystals penetrate into each other, at the interface, indicating that there is partial compatibility between the two components.

Fig. 2 depicts the FTIR spectra of pure mLLDPE, pure EVA and mLLDPE/EVA blend recorded during the cooling process, from 150 °C to 67 °C at 5 °C intervals. It can be seen that the intensity of most absorption peaks showed enhanced up trend as the temperature decreased to a certain extent, indicating that the corresponding characteristic groups are correlative to the crystal and/or the conformation in the macromolecular congregation structure. Therefore, whether for the two individual components or mLLDPE/EVA blend, the investigation on the crystallization process could essentially be transferred to a study on the conversion from liquid amorphous state to solid crystalline structure, simultaneously accompanied by the conformation changes of macromolecular chain segments. Apparently this process will lead to incontinuous changes of the vibration mode of correlative groups in FTIR spectra, which might be employed to determine the crystallization temperature. In addition, as mentioned earlier, FTIR micro-spectroscopy possesses the advantages of providing intrinsic and
detailed information on a microcosmic molecular level, by way of inspecting the structural changes during the crystallization process.

Fig. 1. Transmission electron micrograph of mLLDPE/EVA (40/60) (wt/wt) blend.

Fig. 2. Infrared spectra of (a) pure mLLDPE, (b) pure EVA and (c) mLLDPE/EVA blend from 150°C to 67°C at 5°C intervals.
The FTIR spectra of pure mLLDPE, pure EVA and mLLDPE/EVA (40/60) (wt/wt) blend at 67°C is shown in Fig. 3. As to pure mLLDPE, it was found that after the slowly cooling course, the bending distortion vibration band corresponding to methyl and methylene groups at 1461 cm\(^{-1}\) and the rocking vibration band corresponding to methylene around 720 cm\(^{-1}\) all became sharper and divided into double peaks, manifesting the comparatively higher crystallinity formed. The appearance of double peaks is due to the function of crystal force field, which induces the coincidence of molecular vibration and crystal lattice vibration. Once there are two or more macromolecular chains get across one crystal lattice, the split of crystal band might happen. However, similar phenomenon was not found in pure EVA or mLLDPE/EVA blend investigated.

If we regard 150°C as the start-point of the energy changes in the crystallization process, and that 67°C as the end-point, it can be seen that for both the blend and the pure polymers the infrared spectra of the characteristic groups investigated all take on gradual changes in peak intensity, peak profile and absorption frequency with the decrease of temperature. This transformation is considered to be an equilibrium achieved between the two energy states of specific characteristic groups in same vibration mode. According to Ref [14-15], we can obtain the apparent enthalpy differences of vibration energy \(\Delta H_v = -R\partial[\ln(A_H/A_L)]/\partial(1/T)\) (1) states transformation \(\Delta H_v\) using the following equation, namely where \(A_H\) and \(A_L\) are the peak absorbance corresponding to high and low energy states for one single characteristic group, \(T\) represents the temperature. In this way, the enthalpy differences relating to one specific vibration mode of characteristic groups could be acquired via the necessary calculation by determining the peak absorbance ratio at different temperatures, and it provides the possibility to obtain some indications of the contributions made by individual characteristic groups in the crystallization process. Specifically, as to the present study, the crystal phase separation of mLLDPE/EVA blend could be analyzed on a
Fig. 4. The typical plots of $\ln(A1472.7/A1471.0)$ vs. $T^{-1}$ for (a) mLLDPE, (b) mLLDPE/EVA blend, and (c) EVA.

Table 2. Grouped apparent enthalpy of vibration energy states transformation in mLLDPE, mLLDPE/EVA blend, EVA, and the corresponding band assignments.

| Group | AL/AH (°C) | $\Delta H_{80}/(kJ \cdot mol^{-1})$ | $\Delta H_{110}/(kJ \cdot mol^{-1})$ | $\Delta H_{113}/(kJ \cdot mol^{-1})$ |
|-------|------------|-----------------------------------|-----------------------------------|-----------------------------------|
| -CH2- | 2930.0/2941.4 | -2.37 | -1.52 | 2935.9/2939.2 |
| νas (CH2) | 2857.7/2859.8 | -2.06 | -0.86 | 2856.0/2859.4 |
| νs (CH2) | 2847.6/2849.0 | -1.74 | -1.47 | 2848.4/2851.3 |
| δ(CH2) | 1472.3/1471.9 | -5.38 | -3.78 | 1472.7/1471.0 |
| -CH3 | 1369.4/1367.7 | -2.71 | -1.67 | 1368.7/1364.6 |
| δs (CH3) | 1241.1/1239.8 | -1.42 | -1.04 | 1242.4/1239.7 |
| -OOCCH3 | 1020.1/1019.6 | -0.76 | -0.65 | 1020.8/1019.3 |

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molecular level with this method.

The typical plots of ln(A_L/A_H) vs. reciprocal temperature representing methylene bending vibrations in pure mLLDPE, pure EVA and mLLDPE/EVA blend are shown in Fig. 4, subsequently relating ΔH_v values with the temperature. In addition, the grouped apparent enthalpy differences of vibration energy states transformation and band assignments in the samples are listed in Table 2. It can be seen from Fig. 4 that with the given cooling rate, for whether pure mLLDPE and EVA, or mLLDPE/EVA blend, the vibrational absorption peak of the corresponding groups all present sudden changes during the cooling course, showing typical one-stage phase transition in the thermodynamics essence. As indicated from Table 2, the ΔH_v values of characteristic groups all manifest minus values, which is indicative of an exothermal process towards ordered structure. Note that as to EVA, the vibration modes of ester groups only showed sudden changes in the vicinity of 80°C, and the ΔH_v values relating to 1741/1742-cm^{-1}, 1242/1240-cm^{-1} and 1021/1019-cm^{-1} bands are comparatively small, indicating that the vibration modes of methyl and methylene bearing on the main chain play a dominant role during the crystallization process. Especially, the ΔH_v values concerning the bending vibration of methylene near 1472 ± 1/1471 ± 1-cm^{-1} manifest prominent changes in all the samples, showing that methylene is sensitive to the formation of the congregation structure in this process.

Fig. 5 showed the DSC thermograms of pure mLLDPE, pure EVA and mLLDPE/EVA (40/60) (wt/wt) blend in the cooling course. It can be seen that there are two evident exothermic peaks on the curve of mLLDPE/EVA blend, corresponding to the apex values of 80.3°C and 110.3°C, respectively. However, under the same cooling procedure, there is no enthalpy changes around 80°C for pure mLLDPE, as well as the absence of enthalpy changes around 110°C for pure EVA. The corresponding apex temperature of enthalpy changes for pure mLLDPE and EVA occurs at 111.1°C and 78.6°C, respectively. The above results indicate that with a slow cooling rate, liquid-liquid and liquid-solid phase separation arise in the blend, which act as a driving power for the macromolecular chain segments of mLLDPE and EVA to move towards their individual rich domains in the crystallization process, subsequently form the crystal structure via the regular arrangement of chain segments. Accordingly, there are two crystallization peaks come into being in the blend as the temperature decreasing, in which the one at low temperature relates to EVA-rich domain, whereas the other corresponds to mLLDPE-rich domain.

According to Kohji Tashiro et al [16], the crystallization temperature and peak profile of polymer blends might be influenced by the lamellar size and the interaction at the boundary between the two lamellae of the different species. In addition, the lamellae of one species might be surrounded not only
by the amorphous phase of itself but also by the amorphous chains of the other species, for these reasons the crystallization behaviors of each component in the blend system were influenced. As seen in Fig. 5, owing to the insertion of EVA chain segments, the apex temperature relating to mLLDPE-rich domain in the blend was lower than that of pure mLLDPE; likewise, the peak temperature relating to EVA-rich domain in the blend is a little higher than that of pure EVA, owing to the insertion of mLLDPE chain segments. That is to say, although the two characteristic peaks are entirely separated, the corresponding apex values come nearer to each other as compared to their individual species, implying that there is a small quantity of cocrystallization in the blend. Accordingly, the changes of intermolecular interactions could be induced by the interlacement or entanglement among the chain segments of two different species, which might be reflected in FTIR spectra.

Fig.6 depicts the apparent enthalpy differences of vibration energy states transformation corresponding to the bending vibration of methylene in pure mLLDPE, pure EVA and mLLDPE/EVA blend. It can be seen that Fig. 5 and Fig. 6 present much resemble form, manifesting that thermal analysis using FTIR micro-spectroscopy could receive consistent results with DSC measurement. Moreover, it is noteworthy that as indicated in Fig. 6, both pure mLLDPE and EVA manifest much larger $\Delta H_v$ values compared to the blend investigated, showing that in the cooling course, larger changes in absorbance ratio arose in the two pristine polymers than those in mLLDPE/EVA blend. This result further proves the existence of certain compatibility between mLLDPE and EVA in the blend system, which is consistent with the TEM observation mentioned above.

4. Conclusions

TEM observation indicated the occurrence of phase separation during the crystallization process of mLLDPE/EVA (40/60) (wt/wt) blend, and there was compatibility between the two components. In comparison of the $\Delta H_v$ values of various characteristic groups calculated from FTIR spectra data, it was found that for mLLDPE/EVA blend, the bending vibration mode of methylene made prominent contribution to the liquid-liquid and liquid-solid phase separation, as well as the following migration and regular arrangement of mLLDPE and EVA chain segments to form crystal structure in the cooling course. The cocrystallization of mLLDPE and EVA arose during the phase separation process.
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