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INVESTIGATION OF IDENTIFICATION OF COMPOSITION IN POLYMERIC MATERIALS BY USING DSC

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The composition of the Peugeot automobile bumper was studied by using DSC. The effects on the DSC curve of quenching from the melt, heating rate, cooling rate, partial scanning, and partial scanning → isothermal scanning were studied. The experimental results indicate that the sample is a blend of two polymers and it is identified as a blend of PP and HDPE by Barta's additive thermal analytical method and IR spectroscopy. A set of methods to determine the composition of polymeric materials is created by using DSC.

Semicrystalline polymeric materials often show double melting peaks in their DSC curves. This phenomenon is possibly attributed either to the melting of the blending components or to the thermal history memory of the homopolymers [1, 2]. Researchers can erase the thermal history and reset up the thermal history when they judge the cause of the multiple melting of some polymeric materials. After erasure of the thermal history of a polymeric material, if the same multiple melting peaks still appear, it can be judged to be a blend; if a single peak appears, it must be a homopolymer [1]. In identifying the composition of the Peugeot automobile bumper sample by DSC, we study the effects on the DSC curve of heating rate, cooling rate, partial scanning and partial scanning → isothermal scanning, besides adopting the method of the former researchers. The sample proved to be a blend of two polymers. Furthermore, by identification via Barta's additive thermal analytical method and IR spectroscopy, the sample was confirmed to be a blend of polypropylene (PP) and high-density polyethylene (HDPE). Thus, a set of methods for determination of the composition of polymeric materials by DSC has been set up.

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Experimental

The automobile bumper sample was obtained from the Peugeot Corporation. Each sample of approximately 5 mg was weighed on a Perkin-Elmer AD-2^{Z} autobalance. DSC scans were recorded on a Perkin-Elmer DSC-2^{C} thermal analyzer with a 3600 data station. All scans were carried out in nitrogen at a scanning rate of 20 deg/min unless otherwise indicated. The additives used in additive thermal analysis were PP KY6100, $M_{i} = 4$-6, from Brazil and HDPE $M_{i} = 5.93$, from Qilu Petrochemical Corporation.

The samples of bumper and PP were dissolved in toluene, filmed on a NaCl window, and then scanned in a Hitachi 270-30 IR spectrophotometer.

Results and discussion

As shown in Fig. 1.a, the sample displayed double endothermic peaks in its DSC curve. The low temperature endothermic peak (LM) appeared in the range of 382 K to 404 K with a peak temperature of 399 K and an enthalpy of 1.57 cal/g; the high-temperature endothermic peak (HM) appeared in the range of 404 K to 443 K, with a peak temperature of 435 K and an enthalpy of 13.7 cal/g. In order to investigate the nature of the peaks LM and HM, the effects on the DSC curve of heating scanning → cooling scanning → reheating scanning were examined.

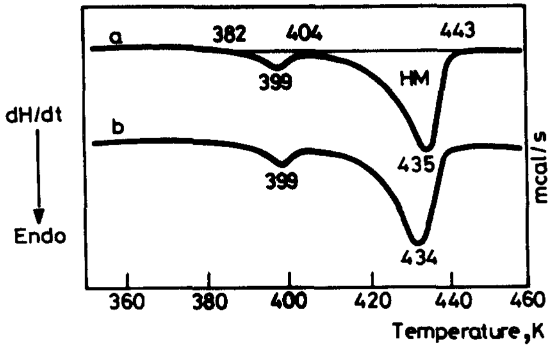

Fig. 1 DSC curves of original sample (a) and quenched sample (b)

The sample was heated to 465 K, kept for 10 min at this temperature, allowing it to melt completely, and then cooled to room temperature. The double exothermic peaks were observed in the cooling curve. When the cooled sample was reheated, double endothermic peaks identical with the peaks LM an HM appeared. Consequently, the peaks LM and HM can be judged to be the melting peaks of the sample due to the above reversible thermal transition process. In order to inspect whether the peaks LM and HM are attributable to the melting of the blending components or to the thermal history memory of the homopolymer, the following methods were adopted:

1. Reheating scanning after quenching from the melt

The sample (original sample) was melted completely and quenched in ice-water, and the quenched sample was reheated As shown in Fig. 1.b, the double melting peaks still appeared, the peak temperature of the low-temperature melting peak was still 399 K and its enthalpy was decreased by only 0.35 cal/g than that of the peak LM; the peak temperature of the high-temperature melting peak was 434 K, which was 1 deg lower than that of the peak HM, and its enthalpy was decreased by 1.1 cal/g than that of the peak HM. The peak temperature remained constant, which indicates that the original sample consists of two crystalline components. The enthalpy decreased, which resulted from a reduction in crystalline perfection due to quenching of the original sample from the melt. If the original sample contained only one crystalline component, then according to the viewpoint of structural reorganization, after its quenching from the melt and a reheating scan, a single melting peak should appear in the DSC curve [3, 4].

2. Changing the heating rate

After their thermal history memory had been erased, the original samples were scanned at a heating rate of 5, 10, 20, 40, or 80 deg/min. As shown in Fig. 2, the peaks LM and HM appeared in their DSC curves. Each peak temperature and enthalpy rose slightly with the increasing of the heating rate, the peak temperature by 3 deg, and the total enthalpy by 1 cal/g. The former is caused by the thermal lag, while the latter may result from a reduction in resolution. The experimental results accord with the law that two crystalline components in the sample retain their melting characteristics [1]. If the sample contained only one crystalline component, then according to the viewpoint of structural reorganization, a high heating rate would suppress recrystallization while a low heating rate would facilitate recrystalliza-

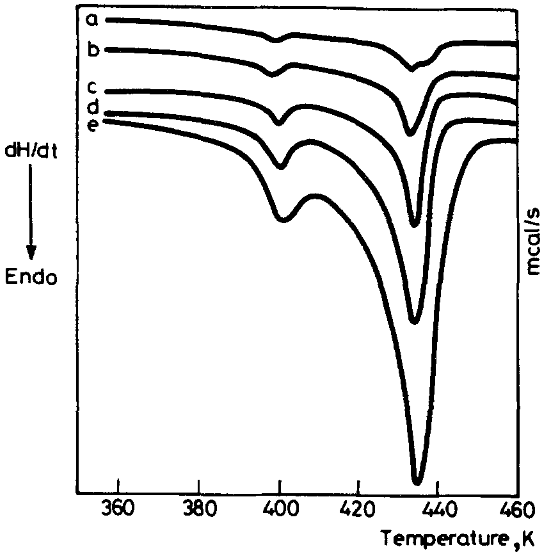

Fig. 2 DSC curves of original sample scanned at different heating rates after it being subjected to the same thermal history. Heating rate (deg/min): a, 5; b, 10; c, 20; d, 40; e, 80

tion, the enthalpy of LM should increase gradually, and the enthalpy of HM should decrease gradually to zero as the heating rate is increased [5].

3. Changing the cooling rate

The original samples were melted completely and scanned at a cooling rate of 5, 10, 20 or 40 deg/min. As shown in Fig. 3, the double crystalline peaks (LC, HC) appeared at cooling rates of from 5 deg/min to 20 deg/min, while only one crystalline peak appeared at (or above) 40 deg/min. The peak temperature of the crystalline peak decreased with increasing cooling rate, which is the normal law for the supercooling of semicrystalline polymers, while the difference between the peak temperatures of the double crystalline peaks (T_{Hc}-T_{Lc}) decreased linearly with increasing cooling rate (V) (see Fig. 4), which indicates that the degree of supercooling of HC is higher than that of LC.

When crystallized samples were scanned at the same heating rate, double melting peaks identical with the peaks LM and HM appeared in each DSC curve. The peak temperatures remained basically constant and the enthalpies were reduced slightly with increasing cooling rate. The enthalpy of the low-temperature melting peak decreased by 0.31 cal/g, and the enthalpy of

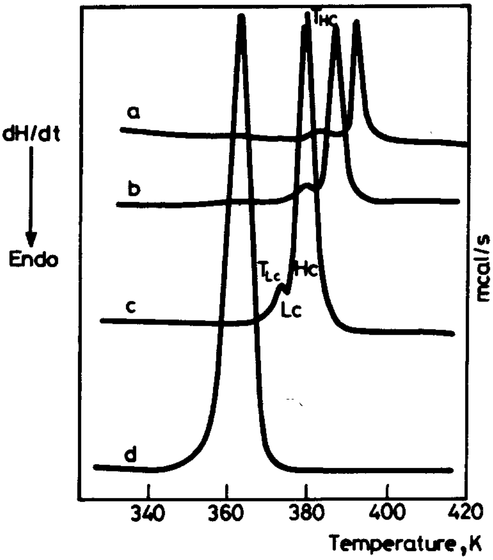

Fig. 3 Crystallization curves of original sample scanned from the melt at different cooling rate. Cooling rate (deg/min): a, 5; b, 10; c, 20; d, 40

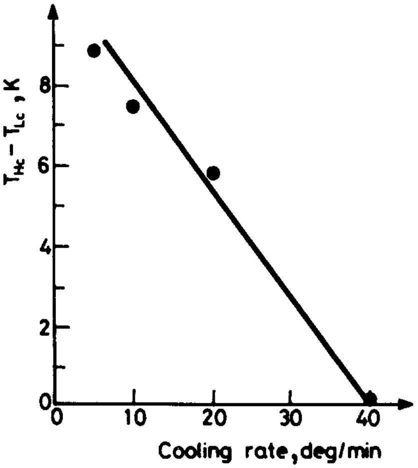

Fig. 4 Effect of cooling rate on the difference between peak temperature of double crystallization peaks

the high-temperature melting peak decreased by 0.91 cal/g from 5 deg/min to 40 deg/min, which is due to the reduction of the crystallizing perfection with increasing cooling rate. Thus, the possibility of polycrystal resulting from different thermal histories was eliminated. If the sample contained only one crystalline component, then according to the viewpoint of structural reorganization, as increasing cooling rate, the peak temperature of the high-temperature melting peak should remain invariable and its enthalpy gradually increase, while the peak temperature of the low-temperature melting peak should shift downwards and its enthalpy gradually decrease until the low-temperature melting peak disappears [4, 6].

4. Partial scanning

As shown is Fig. 5, the original sample was scanned to a temperature just beyond that of the peak LM, followed by immediate cooling scanning, when a single crystalline peak appeared in the cooling curve. The cooled sample was reheated, and double melting peaks identical with the peaks LM and HM still oppeared. Their peak temperatures were the same as those of the peaks LM and HM, and their enthalpies were increased slightly. Further, a shoulder appeared on the forward side of the high-temperature melting peak, which will be discussed later. This phenomenon indicates that there are two crystalline components in the sample.

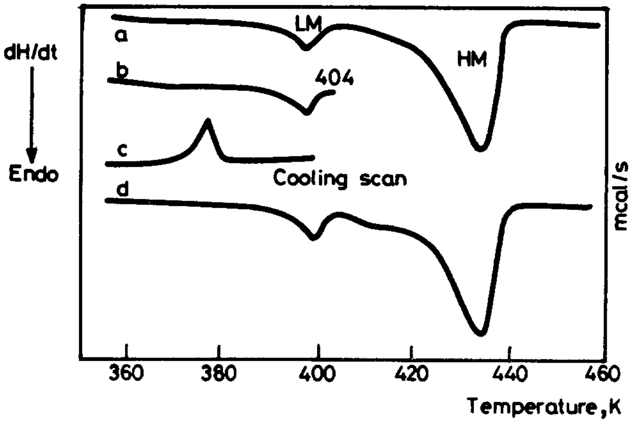

Fig. 5 The judgement of original sample containing two kinds of crystalline components: a, heating the original sample; b, heating to 404K just beyond that of LM peak; c, cooling; d, reheating the cooled sample

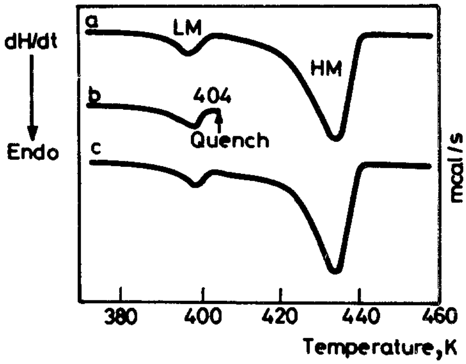

Fig. 6 The judgement that the crystallites symbolized by LM peak did not produce structural reorganization during heating scanning: a, heating the original sample; b, heating to 404K just beyond LM peak, then quenching; c, reheating the quenched sample

As shown in Fig. 6, the original sample was scanned to the temperature just beyond that of the peak LM and quenched in ice-water at once; upon rescanning of the quenched sample, double melting peaks identical with the peaks LM and HM still appeared. Their peak temperatures were identical with those of the peaks LM and HM. The enthalpy of the low-temperature melting peak was lower than that of the peak LM, and the enthalpy of the high-temperature melting peak was slightly larger than that of the peak HM. A shoulder still appeared on the forward side of the high-temperature melting peak. If the sample contained only one crystalline component, then according to the viewpoint of structural reorganization, a single melting peak

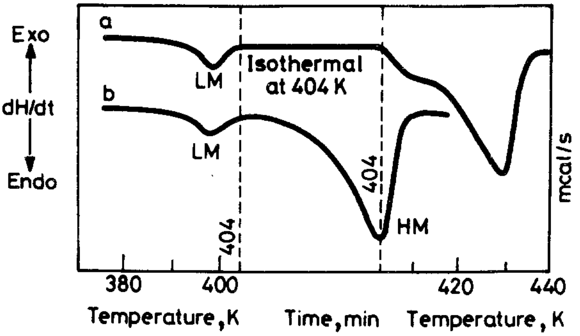

Fig. 7 The judgement on nature of shoulder peak: a, heating to 404K → isothermal scanning for 5 min at 404K → heating continuously to 450K; b, heating the original sample

should appear in the reheating curve, and its enthalpy should be almost equal to the sum of the enthalpies of the peaks LM and HM [4, 7].

5. Partial scanning → isothermal scanning → continuous scanning

As shown in Figs 5.d and 6.c, there is a shoulder on the forward side of the high-temperature melting peak. In order to investigate the reason why the shoulder formed, an ingenious experiment was carried out as follows. As shown in Fig. 7, the original sample was scanned to the temperature just beyond that of the peak LM, and kept isothermally at this temperature for 5 min, no recrystallization peak was observed. On continouosly scanning, a high-temperature melting peak with a shoulder still appeared. The peak temperature was identical with that of the peak HM, and the enthalpy was increased by 0.93 cal/g over that of the peak HM. If the shoulder stemmed from the melting of crystallites formed by the recrystallization after the melting of LC, a recrystallization peak must appear during the isothermal scanning. The enthalpy of the high-melting peak with a shoulder should be equal to the sum of those of the peaks LM and HM [8]. Hence, the shoulder is confirmed as stemming from the multiple melting caused by HC through isothermal annealing.

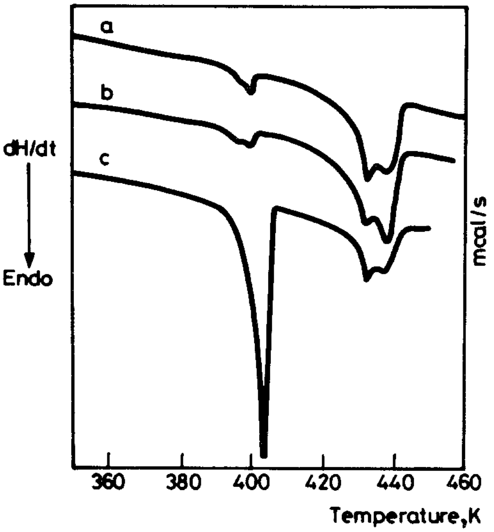

Fig. 8 The foundation that the original sample is judged to be the blend of HDPE and PP. a, heating the original sample; b, heating the original sample + PP; c, heating the original sample + HDPE

6. Additive thermal analysis

The above experimental results testify that the original sample consists of two crystalline components. With a view to elucidating these components the DSC curve of the original sample was studied. It was found that the peak temperatures and melting ranges of the peaks LM and HM approximated to those of HDPE and PP, respectively. Furthermore, blends of PP and HDPE are used as common anti-impact, tough materials, with the properties required for automobile bumpers. Therefore, Barta's additive thermal analysis was adopted to identify whether the original sample belongs among these blends or not [9]. HDPE or PP was added to the original sample. After the thermal history memory of the mixed samples had been erased and a new thermal history set up, the mixed samples were scanned at a very low heating rate (2.5 deg/min) in order to determine whether or not the additive melted separately from the components in the original sample by reducing

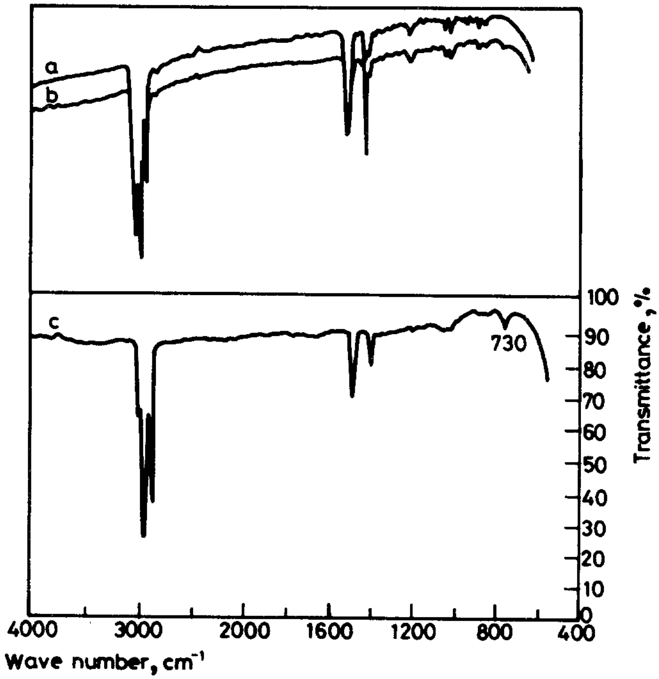

Fig. 9 IR spectra of original sample (b) of PP (a) and their subtraction IR spectrum (c)

the heating rate to increase the resolution. As the resolution was raised, a shoulder appeared on the peak LM, while a double peak emerged at the position of the peak HM (see Fig. 8.a). When PP was added to the original sample, the peak LM remained constant, while the enthalpy of the peak HM increased. Hence, the peak HM is attributed to the melting of crystallites of PP (see Fig 8.b). When HDPE was added to the original sample, the shape of the peak HM remained constant, while the enthalpy of the peak LM increased. Hence, the peak LM is attributed to the melting of HDPE (see Fig. 8.c).

7. IR analysis

In order to prove the reliability of the above thermal analytical method, the subtraction IR spectrum of the original sample and PP was recorded (see Fig. 9). It was found that their IR spectra resemble each other basically, which indicated that the PP content in the original sample is rather high; moreover, the characteristic band of PE (730 cm^{-1}) was observed in the subtraction IR spectrum, with much weaker intensity. This indicates that the PE content in the original sample is rather low, which is identical with the analytical results of DSC.

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Zusammenfassung — Mittels DSC wurde die Zusammensetzung von Peugeout Kfz-Stoßstangen untersucht. Der Einfluß von Abschrecken aus der Schmelze, von Aufheizgeschwindigkeit, Kühlgeschwindigkeit, partiellem Scanning und partiellem Scanning → isothermem Scanning auf den Verlauf der DSC-Kurve wurde untersucht. Die experimentellen Daten ergaben ein Gemisch aus zwei Polymeren, das mit Hilfe des additiven thermischen Analysenverfahrens nach Barta und mittels IR-Spektroskopie als ein Gemisch aus PP und HDPE identifiziert werden konnte. Eine Reihe von Verfahren zur Bestimmung der Zusammensetzung polymerer Materialien unter Anwendung von DSC wurde ausgearbeitet.