

STUDY OF ACOUSTIC EMISSION DURING NON-ISOTHERMAL CRYSTALLIZATION OF POLYPROPYLENE

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ABSTRACT

In this paper we have presented the results of acoustic emission (AE) during non-isothermal crystallization of polypropylene (PP) melt with mean cooling rate $4^{\circ}\text{C}/\text{min}$, and discussed the effects of molecular weight (MW) on AE activity. It is shown that the amount of AE ring-down counts during whole crystallization of PP depends on the MW strongly. The copious AE bursts have been observed at the late stage of PP crystallization. AE bursts are caused by cracking, crazing and cavitation between spherulites and inside spherulites.

INTRODUCTION

Acoustic emission (AE) is a transient elastic wave generated by a rapid release of energy within the material. Local defect area or local fast deformation due to stress concentration or other reasons such as motion of dislocation, phase transformation or growth of cracks in material on loading will cause AE.

Some papers on study of AE of polymers on tensile loading have been published since the 1970s^[1]. AE of glassy polymers on tensile loading has been found to be closely related to stress induced crazing and subsequent growth and development into crack. For nonbrittle polymers on tensile loading copious AE activity is usually observed during yielding and the late stage of necking and at the close proximity to specimen failure. Therefore, AE would be useful to acquire information and understanding of the microplastic flow and microfracture processes.

The study of AE of a structural phase transformation in some alloys and chemical compounds has been a matter of interest to several investigators^[2,3] in recent years. AE activity has been found to be closely related to microstructure transformation. Analysis of the occurrence and character of the AE signals gives valuable information about the kinetics and dynamics of the elastic fields in the crystal lattice.

Galeski et al.^[4] reported the first observation on AE during polymer crystallization in 1987. They showed that AE was closely related to the spherulite growth and the cavitation in material. In our laboratory AE during the crystallization of PP was observed in 1986.

During the plastics fabrication, such as injection-molding, press-molding or extrusion-molding, the melt of polymer is cooled from the temperature of

pre-melting to room temperature. This is a nonisothermal process. Hitherto AE during non-isothermal crystallization of polymer has not been reported yet.

The purpose of this paper is to present the results of AE during non-isothermal crystallization of isotactic PP melt and the effects of molecular weight (MW) of PP on AE activity have been discussed.

EXPERIMENTAL

A single channel AE apparatus Model SFI-1 of Yingkou Instrument Factory was used in this investigation. The transducer was a circular disc of $\phi 10 \times 8$ mm, made of lead zirconotitanate PZT-5. It had a resonance frequency of 120 kHz. It was attached to a quartz waveguide, vaseline being applied for acoustic coupling. The another end of quartz waveguide was immersed into the melt of sample as shown in the block diagram of Fig. 1. A band pass amplifier of pass band 105 — 135 kHz was used for the AE signal. Ring-down counting method was adopted for the detection of AE signal. Each signal event was recorded as a count number. The threshold level for ringing was fixed at 0.3 volt. Time constant was set at 5 sec and the attenuator was set at 0 dB.

Three samples of PP were examined, PP-1 had a *MFI* of 4 g/10 min (230 °C, 2.16 Kg) and a *MW* of 3.0×10^5 (Cosmoplene FY 4012, made in the Polyolefin Company 'Singapore' Pte, Ltd.). Other two samples PP-2 and PP-3, were prepared by chemical degradation from PP-1. Their *MW* and *MFI* were listed in Table I.

Table 1 *MW*, *Q* and *MFI* of samples.
Q: Engineering Characterization of MWD (after Fan et al.⁵).

SAMPLE	PP-1	PP-2	PP-3
M_n	3.0×10^5	1.4×10^5	1.0×10^5
<i>Q</i>	3.2	1.4	1.3
<i>MFI</i>	4.2	29	73

Sample was placed in a small oven which was lining with thin film of PTFE. The thermocouple was inserted into the sample melt at a fixed position. 3.6g samples in the form of pellets was pre-melted at 190 °C to exclude bubbles between pellets. Pretreated sample was melted and held at 190 °C for 20 min, then it was cooled with mean cooling rate 4 °C/min. AE signals during the whole crystallization process and the temperature of sample were recorded simultaneously.

For the study of correlation between AE activity and crystallization process DSC measurements were carried out by a Perkin Elmer DSC-4 instrument at the same cooling rate.

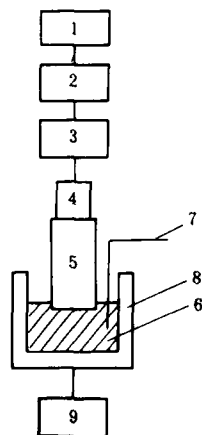


Fig.1 Block diagram for the instrument used for observing AE

1 - Recorder ; 2 - Single channel acoustic emission apparatus ; 3 - Preamplifier ; 4 - Transducer ; 5 - Quartz waveguide ; 6 - Specimen ; 7 - Thermocouple ; 8 - Small oven ; 9 - Temperature controller

The morphology of samples crystallized at above mentioned condition was observed by SEM .

RESULTS AND DISCUSSION

Stress concentration during crystallization of polymer melt can arise from partial changes of density . When the level of internal stress approaches to the cohesion of polymer , the stress is released and acoustic waves are emitted . The cavitation or cracking occurs .

For the samples of PP- 1 , PP- 2 and PP- 3 their AE activity during cooling crystallization were shown in Fig. 2a , b and c respectively . The different features of AE had been observed . Above 148 °C any burst was not recorded for these samples . At the temperature range of 148 — 120 °C a few intermittent AE bursts were observed i. e. at the earlier stage of crystallization . As the MW of PP increased the amount of burst decreased , but the temperature to generate the first AE burst removed to higher temperature .

Very copious AE bursts were observed from 110 °C to 90 °C at the main stage

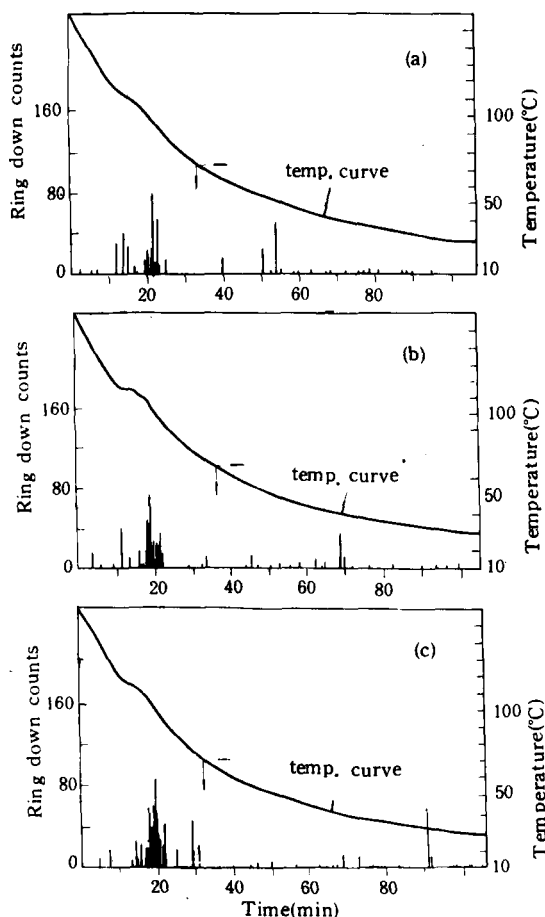


Fig.2 Temperature curve and AE during crystallization . a. For PP-1 ; b. For PP-2 ; c. For PP-3 .
The cooling rate : 4 °C /min .

of crystallization. AE activity increased and temperature range to emit almost continual AE bursts shifted to higher temperature with the decrease of MW .

At the broad temperature range from 70 °C to room temperature some intermittent AE events accrued. In the whole cooling process the recorded amount of AE ring-down counts increased obviously with the decrease of MW , as shown in Table 2.

Table 2 Comparison of AE characteristic of samples

Sample	PP-1	PP-2	PP-3
Sum of AE (Ring down counts)	680	1110	1410
Temperature of emitting the first AE burst (°C)	148	141	138
Temperature of range detected continual AE bursts (°C)	110 ~ 95	112 ~ 95	114 ~ 93

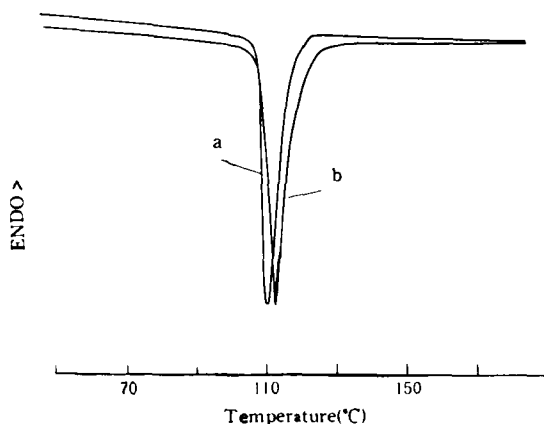


Fig.3 DSC curves; cooling rate 4 °C /min
a. PP-1; b. PP-3

DSC curve of PP-1 measured at the cooling rate 4 °C/min was shown in Fig.3a. The exo-peak (the heat of crystallization) located at 123 — 101 °C. The temperature of the fastest crystallization rate was about 115 °C. The peak temperature was 110 °C. Below 105 °C copious AE events were observed. It means that copious AE signals were generated at the later stage of crystallization process. Similar results were reported by Galeski et al. for PP and by Sawada et al.^[3] for some chemical compounds. For PP-3 having lower MW the crystalline peak on DSC curve shifted to

higher temperature as shown in Fig. 3b . Consequently the temperature to emit very copious AE bursts was higher .

After 90 °C the main crystallization process had been finished . The exo – peak could not be observed . However , the structure of spherulites became more complete . The stresses on inter spherulitic boundaries and within spherulites were increased due to the difference of density between crystalline and amorphous regions . AE activity was observed by releasing stresses .

The results obtained by SEM of samples , for which AE was detected during crystallization , showed that cavities and cracks existed in the specimens as shown in Fig. 4 . Some of cracks were located on interspherulitic boundaries . During later stage of spherulite growth impingement of spherulites occurred , leading to formation of interspherulitic boundaries. The buildup of internal stress on the boundaries was the results from volume shrinkage of spherulites owing to the increase in density . When the level of stress approached a limit , the stress was released , and acoustic waves emitted , and cracks occurred .

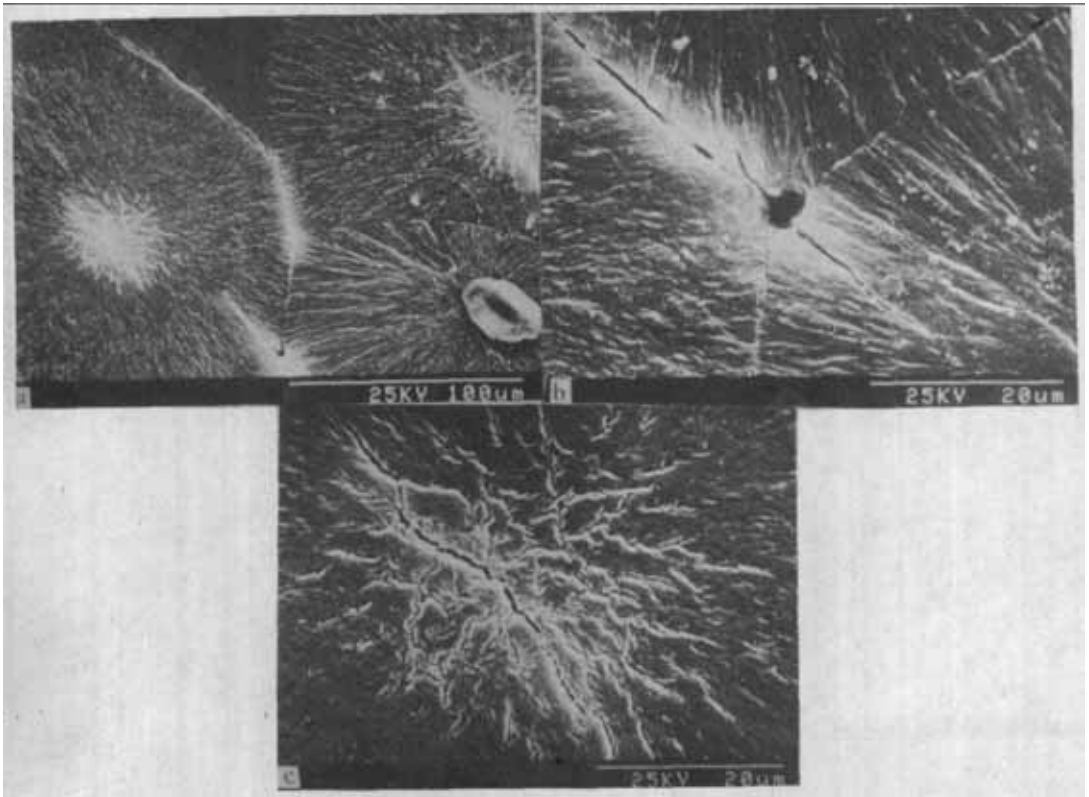


Fig.4 SEM photographs for crystallized samples .

Some cavities or cracks were resulted from occlusion of regions by spherulites as mentioned by Galeski . The crystallization of these occluded areas proceeded without a supply of fresh melt to fill up the deficiency caused by the density change . The buildup of stress in the bulk of sample led to the occurrence of cavitation and AE signals were observed . In Fig . 4b such cavity was shown .

Besides some cracks or crazes inside spherulites had been observed as shown in Fig.4c. They were generated due to the difference of density between lamella and amorphous region in spherulite. The internal stresses increased with spherulite growth. While these cracks and crazes developed, AE bursts were detected.

For sample PP-1, PP-2 and PP-3 the above mentioned various cracks, cavities and crazes were observed, but their quantity was more in sample PP-3 than in PP-1. AE was directly related to the formation of cracks and cavities inside sample. The more amount of AE bursts was, the more defects were caused. These defects must affect the mechanical properties.

Keywords :

Acoustic emission ; Non - isothermal crystallization ; Polypropylene

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