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Polymer 41 (2000) 523–531

polymer

Development of shear flow thermal rheometer for direct measurement of crystallization fraction of polymer melts under shear deformation

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Received 28 December 1998; accepted 18 March 1999

Abstract

Recently viscoelastic measurement has received considerable attention as a complementary method to estimate the crystallization dynamics under shear. However, because of the complex relationship between the crystallization fraction and dynamic mechanical results, it has been difficult to obtain accurate crystallization fraction under shear. To conduct the direct determination of crystallization fraction under shear, the shear flow thermal rheometer (SFTR) having differential thermal analysis (DTA) has been successfully developed using a rotational shear rheometer. Two thermocouples to measure the reference and the sample temperatures were installed at each optimal position as DTA equipment. Two sheets of polyetheretherketone (PEEK) were put on two aluminum plates to prevent heat transfer between the sample and the aluminum plates for accurate measurement of DTA. The influences of using PEEK, instead of an aluminum plate and the thermocouple on rheology results were confirmed to be negligible. In the SFTR, shear strain was given from the lower plate. Both stress and differential temperature responses were simultaneously detected by the upper plate and thermocouples, respectively. The advantage of the SFTR over conventional rheometers was that the crystallinity fraction was able to be directly determined from DTA. In non-isothermal and isothermal preliminary experiments of iso-polypropylene, it was demonstrated that the SFTR provided two kinds of data by the simultaneous measurement of DTA and viscosity. The crystallinity fraction under shear was directly estimated from DTA in the SFTR.

Keywords: Shear flow thermal rheometer; Differential thermal analysis; Crystallization under shear

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1. Introduction

Various synthetic polymeric materials have been commercialized over the last half-century. These macromolecular materials become useful end-use products, such as fibers, rubbers, and plastic materials for films, packaging, and bottles, through the processing of polymeric materials. This processing has been considered as a very significant step for producing useful macromolecular materials.

In the polymer processing of semi-crystalline polymers, studying crystallization dynamics under deformation is quite important. In general, it has been recognized that the crystallization rate increases by flow during processing, i.e. flow induced crystallization [1–4]. This idea has been practically applied in the melt spinning of fiber, film molding etc. [5]. In recent years, computer aided engineering (CAE) including flow induced crystallization and crystallization experiments have been carried out in injection molding process [6–10]. The crystallization behavior of polymer melts at a static condition has been extensively studied before [11]. However, a few experimental studies about the measurement of crystallization under a simple strain, such as shear, uniaxial elongation etc. have been reported in recent years [12–18].

Teh et al. reported the onset of nucleation during crystallization of polypropylene, polyethylene, and their blends using the viscoelastic method [14]. The results of their data were discussed with those of the differential scanning calorimeter (DSC). Ishimuro et al. studied the viscoelastic behavior of the crystallization of poly(phenylene sulfide sulfone) from *N*-methylpyrrolidone (NMP) solutions [15]. Khanna reported that the rheological technique is more sensitive to crystallization kinetics than DSC [13]. The relationship between the crystallization fraction and the rheological measurements was presented as follows:

$$\phi = (G'_t - G'_0)/(G'_\infty - G'_0), \tag{1}$$

where G'_0, G'_t, and G'_∞ are the melt stiffness values, i.e. storage modulus, at time 0, t, and infinity, respectively. Kashiwabara et al. showed the dynamic viscoelasticity of polybutene-1 under isothermal crystallization and discussed

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0032-3861/00/$ - see front matter
PII: S0032-3861(99)00226-8

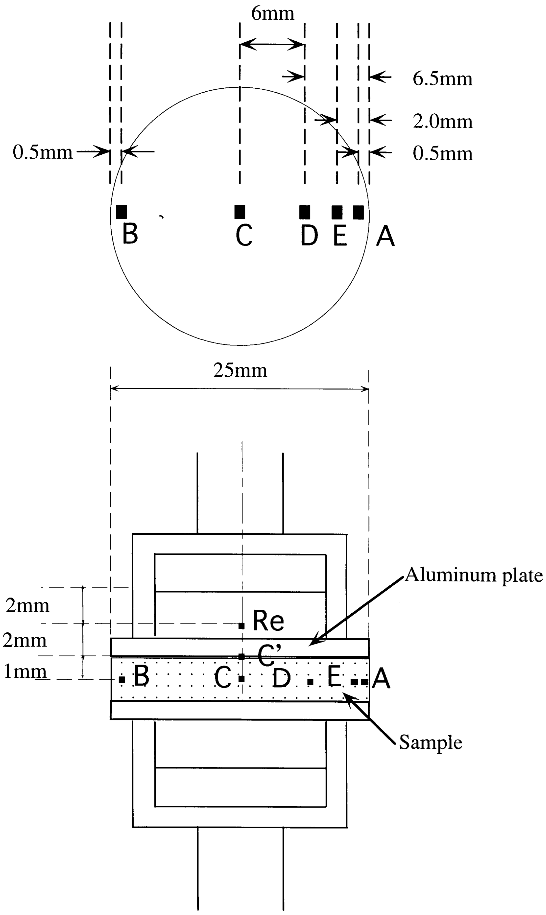

Fig. 1. A schematic illustration of the rotational plate apparatus and the locations of thermocouples to measure temperatures at various points in a sample.

the crystallinity fraction using Eq. (1) [16,17]. They found that the crystallinity fraction calculated from the storage modulus is almost equivalent to that from the loss modulus. To investigate the relation between the crystallinity fraction and viscoelastic data, Boutahar et al. presented the morphology observation and viscoelastic data [18]. They divided crystallization into two categories, suspension-like and colloid-like materials, and discussed the relation in each case. The rheological technique to estimate the crystallization fraction under shear flow is an indirect method and it has been pointed out that the remaining problem about the relationship between the crystallization fraction and viscoelastic data, because of its complex relation, which is easily influenced by types of crystallization growth. So far no one has tried to carry out the direct experimental measurement of the crystallization fraction during flow.

In this paper, to conduct the direct experimental determination of the crystallization fraction under shear, the development of the shear flow thermal rheometer (SFTR) having differential thermal analysis (DTA) using a rotational shear rheometer (Rheometrics Model ARES) is described. In non-isothermal and isothermal crystallization experiments of isotactic-polypropylene, the results of the simultaneous measurements of rheological and thermal data by using SFTR are presented.

2. Experimental

2.1. Development of shear flow thermal rheometer

The shear rotational rheometer of the Rheometrics model ARES was used as the base for modifying the machine. Thermocouples (K type, Sheath thermocouple) were purchased from the Thermocoax Company, and were used as received for DTA. The optimal locations of two thermocouples to detect the reference and sample temperatures were examined and installed. The sensitivity of the thermocouples is 0.1°C. The sampling interval time of the thermocouples is 0.5 s. The differential temperature was calculated by the subtraction of the temperatures between two thermocouples. The thermocouples were installed from the top of the upper parallel plate by making holes in the upper parallel plate. This installation did not have any influence on the temperature control of ARES itself. The parallel plates (aluminum) with 25 mm diameter were used. Polyetheretherketone (PEEK) sheets with 1 mm thickness were used in order to prevent heat transfer between the aluminum plate and the sample. Epoxy type adhesive (ECCOBOND 24 PT.A) was purchased from Grase Japan Ltd. and used as received between PEEK sheets on aluminum plates.

2.2. Sample

Isotactic-polypropyrene (PP, JHH-G) was kindly supplied by the Mitsuichemical Company and used as received. The weight averaged molecular weight is 180 000 and the molecular weight distribution index (M_w/M_n) is 6.5. The tacticity of polypropyrene was 91%. In all the experiments in this paper, the iso-PP was utilized. Disk-like samples with 25 mm diameter and 2 mm thickness were made using the hot press machine from pellets. These disk samples were used for the measurement of SFTR.

2.3. Measurement by shear flow thermal rheometer

The sample thickness between parallel plates (25 mm diameter) were 2 mm. All the measurements were conducted under nitrogen atmosphere. All experiments including non-isothermal and isothermal conditions were started, after keeping the PP sample at 180°C for 20 min to eliminate the pre-heat history completely. Crystallization dynamics was studied in non-isothermal and isothermal conditions. The non-isothermal crystallization behavior was studied under dynamic shear and isothermal crystallization dynamics was studied under steady shear. Both DTA data and viscoelastic data were measured simultaneously. In the dynamic measurement, 3% of shear strain, which was in the linear viscoelastic region, was given. In all experiments, reproducibility of data was carefully confirmed.

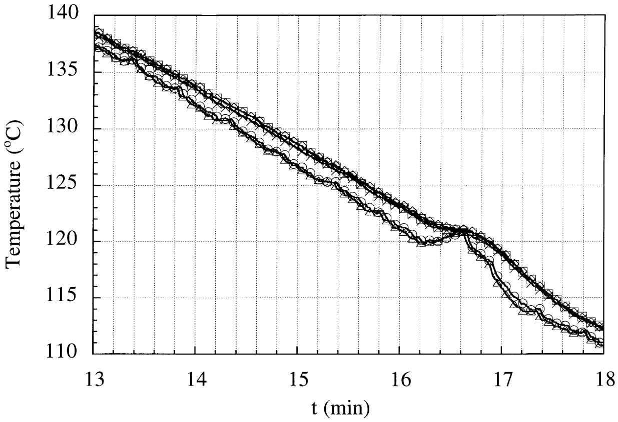

Fig. 2. Temperature change as a function of time under the cooling rate of 5°C/min for iso-PP at various points (A(○); B(□); C(△); D(◇); E(×)) which are located on a horizontal line shown in Fig. 1. The measurement was carried out without any shear flow.

3. Results and discussion

3.1. Development of shear flow thermal rheometer

3.1.1. Location to measure the sample temperature

To install DTA equipment in the Rheometrics ARES, the location of thermocouples is important. We used two thermocouples, one for the sample temperature and the other for the reference temperature. When the thermocouples were put in the atmosphere of the oven, the complete linear temperature decrease was not obtained by setting the cooling rate of 5°C/min and a slight fluctuation was detected. The slight fluctuation seemed to be influenced by the change of the blown nitrogen amount during cooling. From the above result, the location of reference thermocouples needed to be fixed in the metal. Thus, the location of thermocouples for the reference temperature was fixed in the position that was the center of the upper plate and was 2 mm from the surface. We have studied the influence of the thermocouples' location on temperature for samples to determine the optimal position. Fig. 1 shows a schematic illustration of the rotational plate apparatus and tested locations of thermocouples from side and top views. The tested positions (A, B, C, D, E) were located in the middle between two aluminum plates and were on a line as shown in Fig. 1. The positions, A and B were located 0.5 mm from the edge, the positions, E, D, and C were located at 2, 6.5 and 12.5 mm from the edge and position C was in the center.

Fig. 2 represents temperature change as a function of time under the cooling rate of 5°C/min from 180°C at various points using molten PP without shear flow. The peak around 120°C in the SFTR agreed with the crystallization peak, which was measured in the DSC, and attributed to crystallization. The temperature change of location A was almost similar to that of location B, and the decrease of temperature was not completely linear. The instability of decrease may come from the influence of the atmosphere, because of a slight fluctuation of the nitrogen amount. The temperature changes of locations among C, D, and E were almost equal to one another, and the decrease of temperature was very stable. It was interpreted that temperature at inside positions (C, D, E) did not accurately follow the setting temperature change, resulting in the difference between A, B and C, D, E. The stability in the decrease of temperature is more important. Between position C and E, the completely same linear decrease of temperature was obtained. The applied strain only gave in the edge position. Therefore, the sample thermocouple had to be put as close to the edge as possible, for the temperature stability to be achieved. By balancing the two factors, the location E, which is 2 mm from the edge, was selected as an optimal position to measure sample temperature.

It should be important to confirm whether the reference temperature linearly decreases at the rate of 5°C/min or not, when the cooling rate of the nitrogen atmosphere is 5°C/min. Thus, we have measured the temperature change at three positions, E, C′ and Re under the cooling rate of 5°C/min. Fig. 3 shows temperature change as a function of time under the cooling rate of 5°C/min at three positions, E, C′ and Re. It was found that the decrease of temperature at Re was not linear and was equal to that at C′. Fig. 3 showed that the position of the small peak of the lines of Re and C′ were almost similar to that of E. The small peak of Re was assumed as the heat flow from the sample (E′) to the aluminum plate (Re). We considered that the heat flow should be prevented to obtain accurate DTA data.

3.1.2. The influence of PEEK sheets

The heat conductivity of the aluminum plate is very large. To prohibit the heat flow, we have put two polyetheretherketone (PEEK) sheets with 1 mm thickness on parallel plates. PEEK was selected, since it has high temperature resistance ($T_g = 134$°C, $T_m = 334$°C). Epoxy type adhesive was used between the PEEK sheets and aluminum plates.

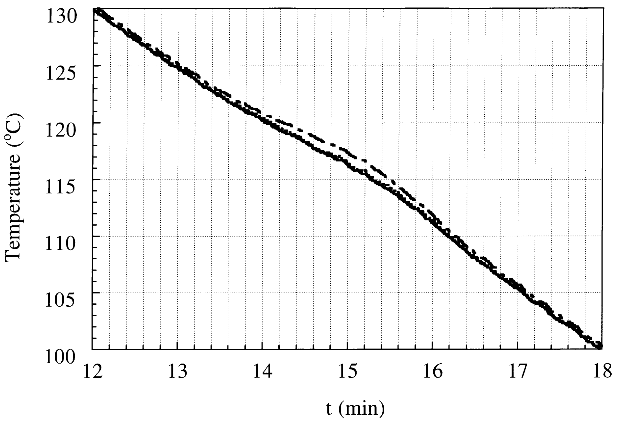

Fig. 3. Temperature change as function of time under the cooling rate of 5°C/min for iso-PP at various points (Re (solid line); C′ (dotted line); E (broken line)) which are located on a vertical line shown in Fig. 1. The measurement was carried out without any shear flow.

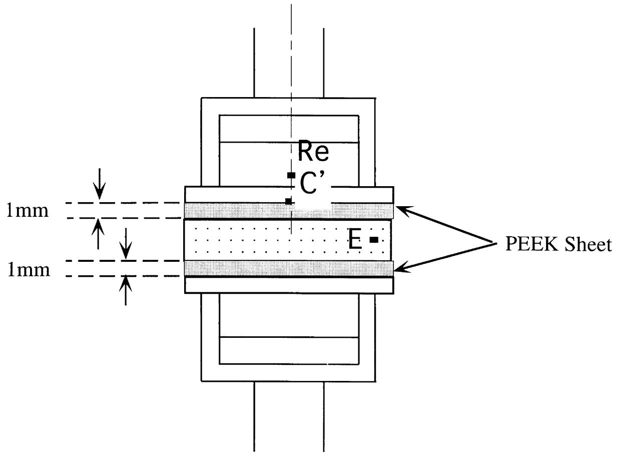

Fig. 4. A schematic illustration of the rotational plate apparatus including PEEK sheets which is examined to reduce the heat transfer between the molten sample and the aluminum plate for accurate measurement of differential temperatures of both points. The measurement was carried out without any shear flow.

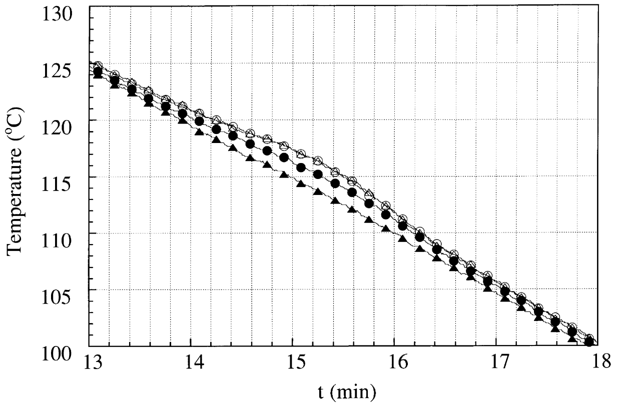

Fig. 6. The effect of PEEK sheet on the temperature difference between the reference (using Aluminum (●); PEEK (▲) and the measurement points (using Aluminum (○); PEEK (△)) shown in Fig. 4 under the cooling rate of 5°C/min. The measurement was conducted under the cooling rate of 5°C/min without any shear flow.

Through using PEEK sheets, both sheets were confirmed to be completely parallel to each other by zero adjustment between the plates. Fig. 4 illustrates the rotational apparatus including PEEK sheets. We have studied the effect of PEEK sheets on the reduction of heat transfer between the sample and the aluminum plate. Fig. 5 gives temperature change as a function of time under the cooling rate of 5°C at three positions, E, C' and Re using PP without shear. It was found that the decrease of temperature at the position of Re became completely linear. Fig. 6 shows the comparison between with and without PEEK sheets at two locations, E and Re, without shear flow. Fig. 6 supported the fact that PEEK sheets effectively prevented the heat flow.

By the introduction of the DTA equipment for the development of the SFTR, some concerns about the influence of PEEK and the existence of thermocouples on viscoelastic data should be pointed out. To examine these influences on viscoelastic data, we have carried out some experiments. Fig. 7 provides the influence of the PEEK surface on the complex viscosity data under a cooling rate of 5°C/min at the dynamic shear condition (1 rad/s, 3% of strain). Fig. 7 suggested that the influence of the PEEK surface was negligible. Fig. 8 gives the comparison between complex viscosity data with only aluminum and that with PEEK sheets and the thermocouples. Figs. 7 and 8 demonstrated that the existence of thermocouples did not affect the shear rheology data.

3.1.3. The improvement of temperature measurement

In DTA, the sensitivity of the thermocouple is important. The heat transfer in itself can affect the sensitivity of thermocouples. Thus, the influence of the diameter of

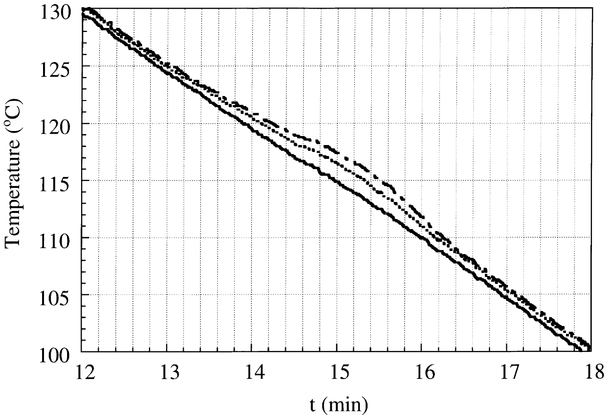

Fig. 5. Temperature change as a function of time under the cooling rate of 5°C/min for iso-PP at various points (Re (solid line); C' (dotted line); E (broken line) which are located on three points shown in Fig. 4. The measurement was carried out without any shear flow.

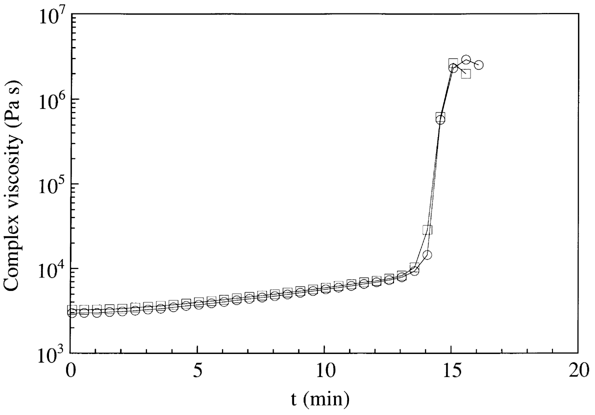

Fig. 7. The influence of PEEK surface on the dynamic shear rheology results of iso-PP. The measurement was conducted under the cooling rate of 5°C/min from 180°C at the dynamic shear condition (1 rad/s, 3% of strain) using the aluminum plate (□) and using aluminum with PEEK sheets (○).

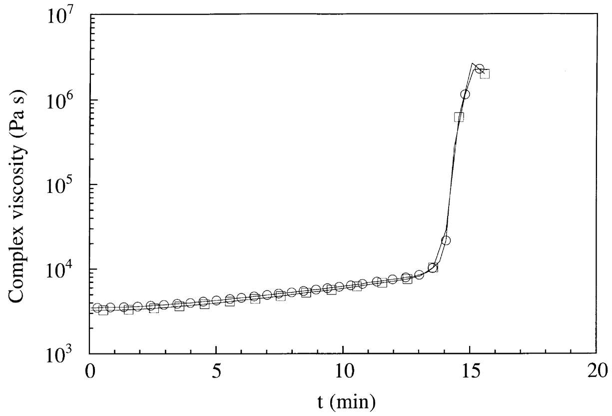

Fig. 8. The influence of the PEEK surface and the existence of the thermocouple on dynamic shear rheology results of iso-PP. The measurement was conducted under the cooling rate of 5°C/min from 180°C at a dynamic shear condition (1 rad/s, 3% strain) with (○) and without (□) PEEK sheets and a thermocouple.

thermocouples and the polyfloroalkoxy (PFA) tube around the thermocouples on the temperature measurement was examined. Fig. 9 shows the effect of thermocouple types on the differential temperatures (between the sample and the reference points) as a function of time under the cooling rate of 5°C/min without shear flow. Fig. 9 revealed that the thermocouples of 0.5 mm diameter with the PFA tube was the best among the three in terms of sensitivity. It was also confirmed that the thermocouples of 0.5 mm diameter with the PFA tube gave a stable temperature decrease as a function of time. It was significant to note that the starting and finishing points of the crystallization peak was not influenced by different types of thermocouples. In the determination of the crystallization fraction, the larger peak should be better in terms of the reduction of errors. Our major purpose is not obtaining the accurate peak area, but obtaining a reproducible large peak having little error to calculate the crystallization fraction, which is obtained by the partial peak area divided by the total peak area. Thus, we think that thermocouples of 0.5 mm diameter with the PFA tube are enough to perform DTA.

The other point, which should be checked, was temperature stability when temperature was set to a constant under shear flow. Fig. 10 shows the temperature stability as a function of time at the isothermal condition and at the dynamic shear condition (1 and 100 rad/s). Fig. 10 suggested that the temperature fluctuation was very little

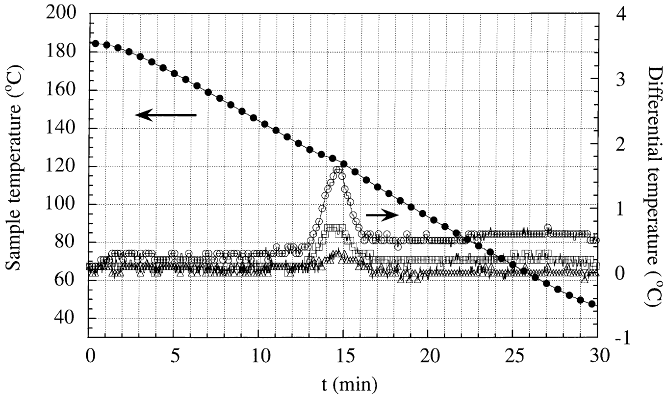

Fig. 9. The effect of thermocouple types on the differential temperatures (between the sample and the reference points) as a function of time for iso-PP. The diameters of the tested thermocouples are 1 mm (△), 0.5 mm (□), and 0.5 mm covered with the PFA tube (○,●). The measurement was conducted under the cooling rate of 5°C/min without any shear flow.

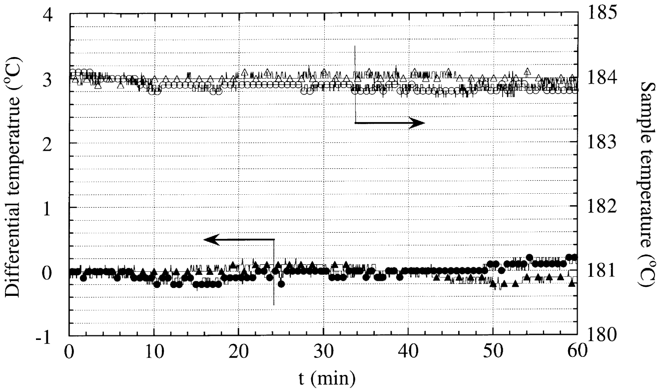

Fig. 10. The temperature stability as a function of time for iso-PP at an isothermal condition under dynamic shear conditions (3% strain, frequency of 1 rad/s (△, ▲) and 100 rad/s (○, ●)).

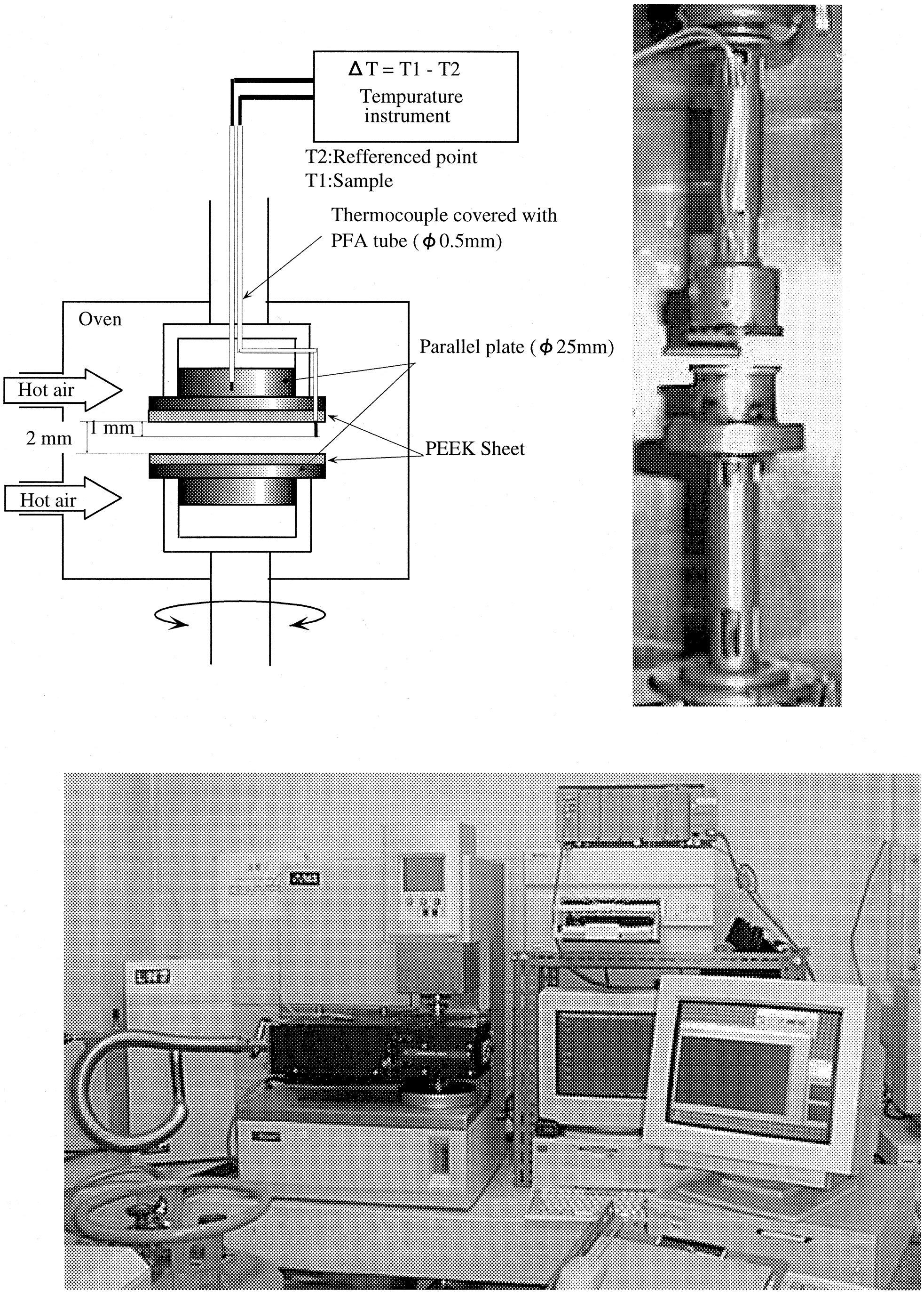

Fig. 11. A schematic illustration of the developed SFTR apparatus and its photographs.

and was less than 0.1°C within 1 h. This stability was sufficient to calculate crystallization fraction which is obtained from the division of partial peek area as a function of time by total peek area, since the peek top of DTA is around 1.0°C. With the above various examination, we have found that our developed SFTR could provide the simultaneous measurement of rheological and thermal data with accuracy. Fig. 11 illustrates the developed SFTR and photographs.

3.2. Non-isothermal crystallization

By using the SFTR, crystallization dynamics under the non-isothermal condition was studied. Fig. 12 shows differential temperature and complex viscosity as a function of time under the cooling rate of 5°C at the dynamic shear condition (3% of strain, 1 rad/s). The crystallization fraction as a function of time was calculated by two ways. One was using DTA data and the crystallization fraction values were

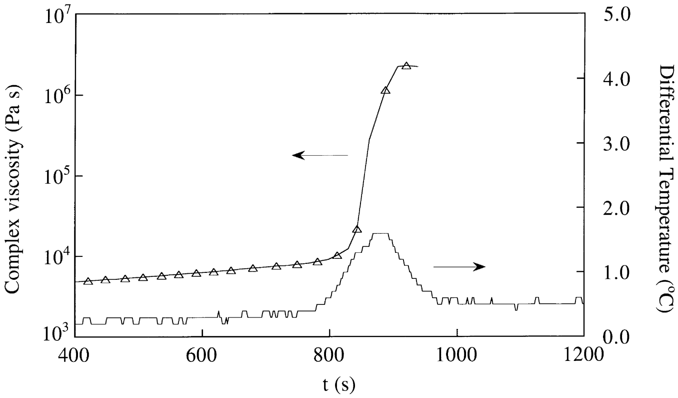

Fig. 12. Differential temperature (solid line) and complex viscosity (△) for iso-PP as a function of time under non-isothermal crystallization (cooling rate of 5°C/min) at the dynamic shear condition (3% strain, 1 rad/s).

obtained by the division of the partial peak area as a function of time by the total peak area using the following equation:

$$X_c(t) = \frac{\int_{t_0}^{t} H\,dt}{\int_{t_0}^{t_\infty} H\,dt}, \qquad (2)$$

where X_c is the crystallization fraction, i.e. relative crystallinity, t_0 is the starting time of the crystallization peak, t_∞ is the finishing time of the crystallization peak, H is the heat capacity which is obtained from the DTA measurement. The other way was using complex viscosity data and the crystallization fraction values were calculated by using Eq. (1), which was proposed by Khanna [13]. Fig. 13 compares the relative crystallinity as a function of time between the two methods. Fig. 13 suggested that, at the initial crystallization time, the estimation of relative crystallinity from complex viscosity was much lower than that from DTA. It was interpreted that when the crystallinity was lower than 50%, DTA could detect the crystallization behavior, however, the complex viscosity was not sensitive, because of independent particles, which had not started the aggregation process with one another, when using Eq. (1). Fig. 13 revealed that rapid viscosity increase appeared after the relative crystallization becomes about 50%.

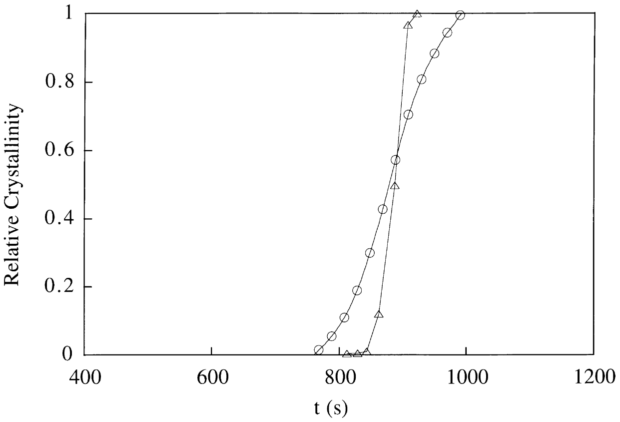

Fig. 13. Comparison of relative crystallinity (non-isothermal condition, dynamic shear) calculated from differential temperature (○) and complex viscosity (△) in Fig. 12.

The above difference pointed out a question about the relationship between the viscosity data and relative crystallinity using Eq. (1). Boutahar et al. also recently proposed other equations to describe the relationship [18]. They discussed relative crystallinity from the rheological data and that from the DSC data. They did not confirm whether relative crystallinity increase in the DSC measurement was equal to that in the shear rheometer. There should be a difference of sample amounts between the DSC (around 10 mg) and the rheometer (around 1 g) data. It was also pointed out that there is a slight difference between the setting temperature and the real temperature of samples in the rheometer. The combination of viscoelastic data from rheometer and thermal data from the DSC could provide some useful information. However, the thermal data of the DSC could not provide the thermal property, which is induced by shear flow. Thus, we stress the importance of direct measurement of temperature to observe the accurate crystallization dynamics under shear flow.

3.3. Isothermal crystallization

In general, in isothermal crystallization experiments, one must cool the sample to the setting temperature as fast as possible to eliminate crystallization during cooling. However, when isothermal experiments of iso-PP were carried out at 140°C, no crystallization occurred during the cooling period in any cooling rate and after reaching 140°C, if no shear flow was given. This was confirmed in both the DSC and SFTR measurements. Thus, the isothermal condition at 140°C was an appropriate condition to observe flow induced crystallization behavior for iso-PP.

Fig. 14 gives differential temperature and viscosity as a function of time under isothermal crystallization at 140°C. Fig. 15 represents the comparison between the relative

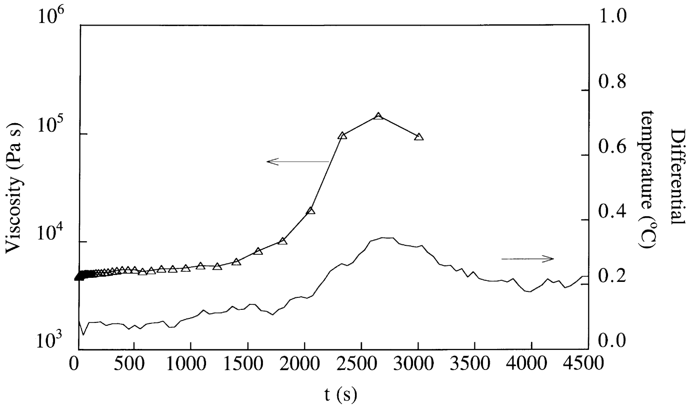

Fig. 14. Differential temperature (solid line) and viscosity (△) for iso-PP as a function of time under isothermal crystallization (at 140°C) under steady shear condition (0.2 s^{-1}).

crystallinity as a function of time from DTA and that from viscosity. Fig. 15 suggested that, at the initial crystallization time, the estimation of relative crystallinity from viscosity was lower than that from DTA. It was reconfirmed that when the crystallinity was lower than 50%, DTA could detect the crystallization behavior, however, the viscosity was not sensitive. The reason seems to be associated with independent crystallized particles, which were not aggregated with one another in the initial crystallization time, resulting in the low sensitivity of shear viscosity. Kashiwabara suggested a similar phenomenon by comparing shear data with the DSC data in isothermal experiments of polybutene-1 [17]. Thus, the present experiments demonstrated the usefulness of the direct measurement of DTA in the SFTR to calculate the relative crystallinity under shear flow.

4. Conclusion

The present study provided the following new findings:

1. To conduct the direct determination of the crystallization fraction under shear, the SFTR having DTA has been successfully developed using a rotational shear rheometer. Two thermocouples to measure the reference and the sample temperatures were installed at each optimal position as DTA equipment. Two sheets of PEEK were put on two aluminum plates to prevent heat transfer between the sample and the aluminum plates for accurate measurement of DTA. The influences of using PEEK, instead of an aluminum plate, and the thermocouple on rheology results were confirmed to be negligible.
2. By using the SFTR, preliminary experiments on direct measurement of DTA were carried out in two conditions; under non-isothermal with dynamic shear condition and under isothermal with steady shear condition. At the initial crystallization time, the estimation of relative crystallinity from viscosity (Eq. (1)) was lower than that from DTA (Eq. (2)) for both cases. The usefulness and high sensitivity of direct measurement of DTA in the SFTR was demonstrated to calculate the relative crystallinity under shear flow.

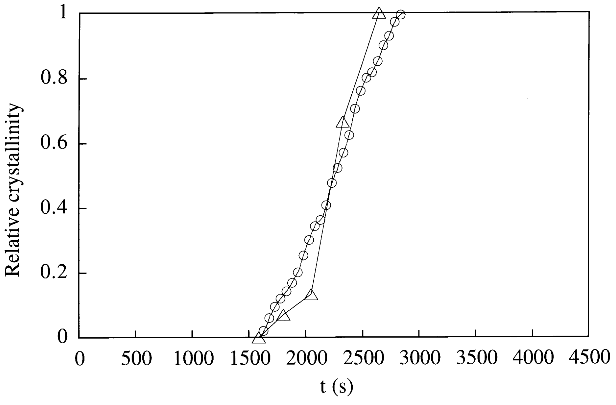

Fig. 15. Comparison of relative crystallinity (isothermal condition, steady shear) calculated from differential temperature (○) and viscosity in (△) Fig. 14.

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