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다양한 냉각속도와 변형률속도에서 폴리프로필렌의 압력-부피-온도 특성에 관한 연구

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Study on the Pressure-Volume-Temperature Properties of Polypropylene at Various Cooling and Shear Rates

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Abstract: To understand the pressure-volume-temperature (PVT) properties of polymer in injection process, a dilatometer with high cooling rate (up to 25 °C/s) and shear rate (up to 320 s^{-1}) was developed. The working pressure and temperature of the dilatometer range from 0 to 100 MPa, and from 30 to 300 °C, respectively. With this instrument, a crystalline polymer polypropylene (PP) was employed to study the effects of cooling rate, shear rate, pressure and their coupling effect on its PVT properties. It was demonstrated that the cooling rate showed a significant effect on the PVT properties. With the increase of cooling rate, the transition temperature of PP from melt state to crystallization decreases gradually and the temperature range of crystallization was also extended. Shear increased the transition temperature of PP from melt state to crystallization. Meanwhile, the initial temperature of shear and crystalline segment was shifted to a higher temperature region with increasing shear duration or shear rate. Above the transition temperature, the effect of shear on the PVT properties weakened gradually with increasing the initial temperature. The coupling analysis of cooling and shear processes showed that increase in cooling rate was enhanced the effect of shear on the transition temperature of PP from melt state to crystallization.

Keywords: pressure-volume-temperature properties, cooling rate, shear rate, crystallization.

Introduction

The PVT properties of polymers are usually used to describe the relationship between specific volume (V), temperature (T) and pressure (P), which offer compressibility and thermal expansion of melting or solid polymer within temperature and pressure range during injection molding process. The simulation software of injection molding usually describes the PVT property of polymer using double domain Tait equation,[1] which is obtained by fitting the experimental data, in which the correctness totally depends on the accuracy of the experimental results of the PVT parameters.[2]

In the past decade, the researchers have been constantly investigating the influence of cooling and shear on the polymer PVT property. Results revealed that increasing cooling rate decreased the transition temperature of polypropylene (PP) while both the temperature range of transformation process and final specific volume was increased.[3-8] Besides, applied shear increased the transition temperature and shifted the crystallization region to the high temperature area, and this phenomenon became more obvious with increasing pressure.[9-12] It is concluded that the cooling and shear conditions can cause the offset of the PVT property curve, which cannot be ignored. Therefore, the offset of the PVT property curve caused by cooling and shear conditions will influence the precision of simulation results. This paper presents a novel PVT testing apparatus with the function of cooling and shear.[13] The dynamic evolution of the PVT properties of PP was explored

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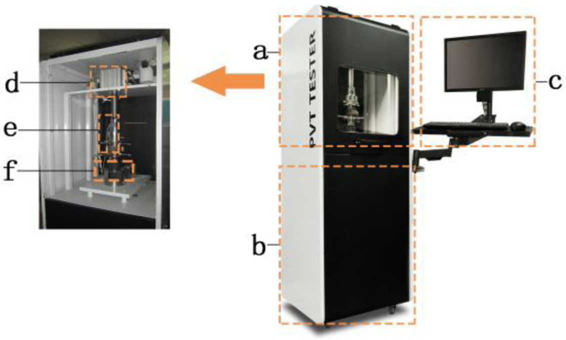

Figure 1. Overall shape of the PVT apparatus. (a) Measuring chamber; (b) control cabinet; (c) operation and display platform; (d) cylinder; (e) measuring module; (f) servo motor.

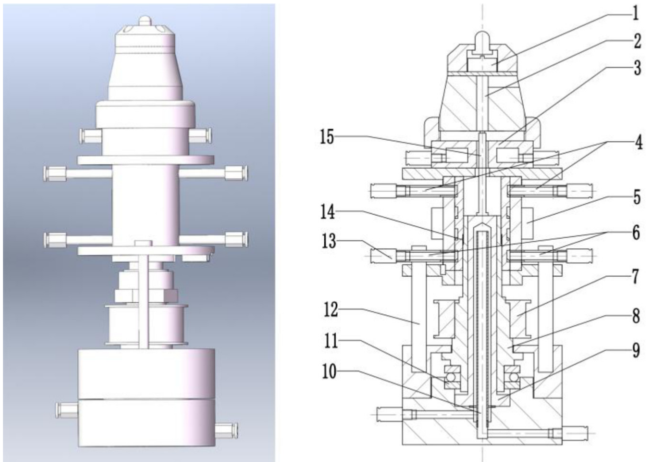

Figure 3. The three-dimensional diagram and detailed outline of the testing module. 1-Pressure sensor, 2-LVDT, 3-Thermal insulation, 4-Spiral cooling outlets, 5-Electrical band heater, 6-Spiral cooling structure, 7-Wheel of timing belt, 8-Rotary piston, 9-Static piston, 10-Nozzle construction, 11-Pressure bearing, 12-Stud for rotation prevented, 13-Safety pin, 14-Sample and seal, 15-Carrier rod.

at high cooling and shear rate. This work provides theoretical basis for the quality control of the molding products.

PVT Measurement Apparatus

Development of the PVT Dilatometer. As shown in Figure 1, a PVT measuring instrument with function of cooling and shear was developed. It was composed of a piston-sleeve testing module, a force support, a control system and a data acquisition and analysis system. In the measurement process, the change of specific volume of the sample could be identified by the relative position change of the sleeve and the plunger, which could be measured by the displacement sensor. In order to achieve uniform distribution of temperature, the test module utilized an annular specimen with inner and outer diameter of 26 and 27 mm and height of 2.5 mm (Figure 2). In addition, six-point temperature measurement was adopted to obtain the accurate temperature parameters of the sample, which were uniformly arrayed on the sleeve and the plunger respectively. The plunger and the sleeve were both embedded with cooling channels to realize higher cooling rate and more even cooling effect. Meanwhile, the plunger or sleeve could rotate to apply shear action to polymer melt. It could eliminate the maldistribution of shear rate due to the speed difference in radial direction. With this measuring equipment, the measurement of the PVT property data could be obtained under the conditions of high pressure (1-100 MPa), high temperature (30-300 ºC), high cooling rate (up to 25 ºC/s) and high shear rate (up to 320 s^{-1}). The detail construction in measuring chamber is shown in Figure 3.

Performance Evaluation of the PVT Dilatometer. All experiments were carried out in isobaric cooling process. Water was employed as cooling medium to verify the performance of PVT apparatus under rapid cooling conditions. The maximum cooling rate could reach 45 ºC/s. However, there was an obvious pressure fluctuation at the beginning of the cooling process. In this work, it was demonstrated that the reasonable PVT data are able to be achieved with the cooling rate of 25 ºC/s. The PVT curves obtained under this condition are shown in Figure 4(b). Compared with the results of the natural cooling, the migration trend of the curves was consistent

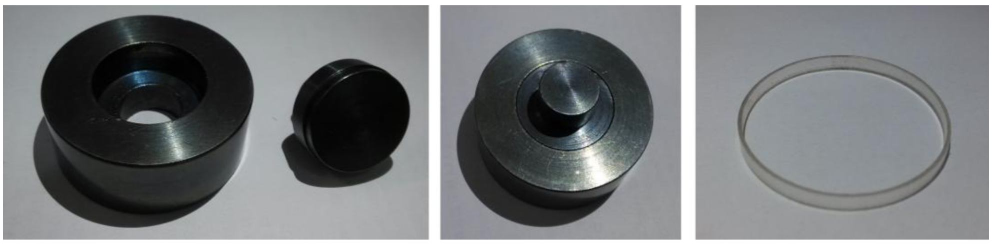

Figure 2. Annular mold and sample.

with the previous studies. Precise shear rate could be achieved due to the servo motor with a good control of rotating speed and angular displacement. The experimental results showed that the maximum pressure was as high as 20 MPa when shear forces were applied.

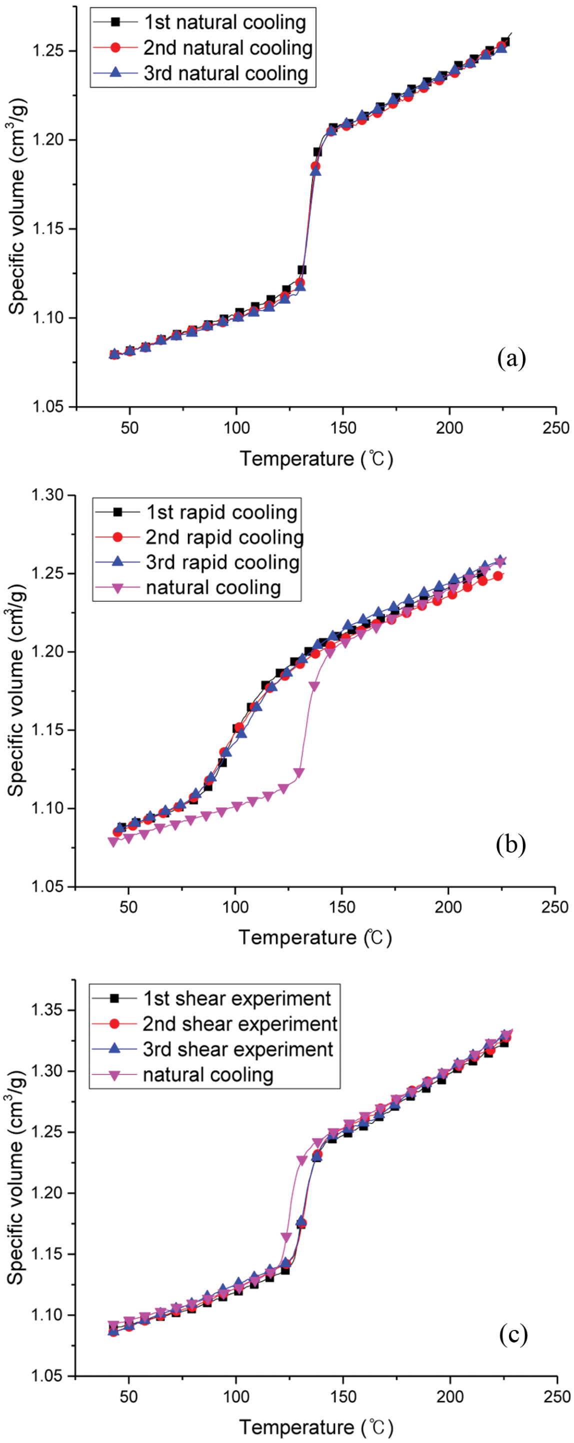

Figure 4. Repeatability experiments under different cooling and shear rates: (a) natural cooling (0.05 °C/s); (b) rapid cooling (25 °C/s); (c) shear experiment.

Repeatability is one of the most important evaluation indexes of the PVT apparatus. Evaluation experiments under rapid and natural cooling conditions were implemented respectively at the pressure level of 40 MPa and the temperature range of 40-220 °C. Evaluation experiments for shearing were carried out at the pressure of 10 MPa, where shear was applied for 2 s with a rate of 160 s^{-1} at 170 °C. The results for the above experiments obtained under various conditions are compared in Figure 4, respectively. The measurement repeatability of PVT apparatus is calculated as

$$\varepsilon = \frac{\nu_{\max} - \nu_{\min}}{\nu_{\max}} \times 100\% \tag{1}$$

where ε, $\nu_{\max}$ and $\nu_{\min}$ represent the deviation, the maximum and minimum specific volume, respectively. The maximum error of the measured results under the conditions of natural cooling, rapid cooling and with shear are 0.28, 0.81 and 0.32% respectively, which are perfectly acceptable and reveal a good repeatability.

Experimental

Materials. The material used in this work was an isotactic polypropylene (PP6331, from LCY Chemical Corporation, Taiwan), whose properties are listed in Table 1.

Rapid Cooling Experiments. The PVT properties of PP were measured at four different cooling rates. All the experiments were carried out under the pressure of 40 MPa, and the range of temperature was 40-220 °C. The four cooling rates were as follows: 1) 25 °C/s with water as cooling medium; 2) 2 °C/s and 3) 0.5 °C/s with compressed air as cooling medium; 4) 0.05 °C/s for natural cooling.

Shear Experiments. Shear process is generally influenced by shear rate, duration of shear and initial temperature.

Table 1. General Properties of PP Used in This Study

Property	Unit	PP6331
Density	g/cm^3	0.9
MFI (melt flow rate)	g/10 min	14
Shrinkage	%	1.5
Tensile stress at yield	MPa	1284
Tensile strain at yield	%	10
Heat deflection temperature	°C	104

Accordingly, we considered three cases. First, the PVT curves were obtained in different shear durations at the shear rate of 160 s^{-1} and the initial temperature of 162 ºC. The duration of shear was 1, 2, 3 and 4 s, respectively. The pressure was 10 MPa. Second, the PVT curves were obtained at the shear rates of 320, 160, 80 and 40 s^{-1}. In order to ensure that all experiments had the same amount of shear, the durations of shear corresponding to the four shear rates were 1, 2, 4 and 8 s, respectively. All the experiments were taken at the pressure of 10 MPa with the same initial temperature of 162 ºC. In addition, the PVT curves were also obtained at different shearing initial temperature with the same shear rate of 160 s^{-1}. The initial temperatures were 152, 177 and 202 ºC. The durations of shear were 2 and 4 s, and the pressures were 10 MPa.

Cooling and Shear Coupling Experiments. In these experiments, compressed air was used as cooling medium whose cooling rate reaches to 2 ºC/s. When the compressed air was released, the air flows through the cooling pipe at high speed which will absorb more heat and provide higher cooling rate. All the experiments were taken at the shear rate of 160 s^{-1} with the same shear duration of 4 s. The initial temperatures were 152, 177 and 202 ºC, respectively. The pressure was 10 MPa.

Results and Discussion

Effect of Cooling Rate on the PVT Properties. The results of PVT curves at various cooling rates are shown in Figure 5. In this figure, the transition temperatures for the cooling rates of 0.05, 0.5, 2 and 25 ºC/s are 140, 138, 134, 118 ºC, respectively. Figure 6 shows the variation of transition tem-

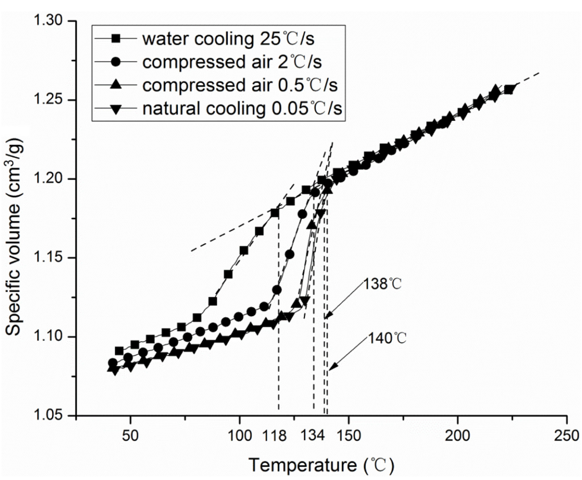

Figure 5. PVT curve at different cooling rates (25, 2, 0.5, 0.05 ºC/s).

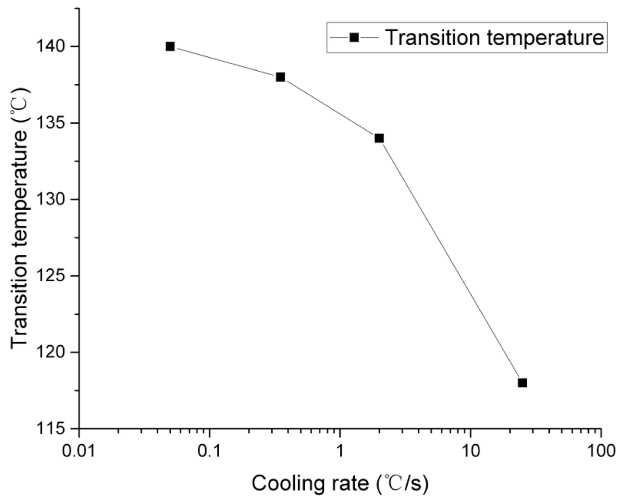

Figure 6. Variation of transition temperature under different cooling rates (25, 2, 0.5, 0.05 ºC/s).

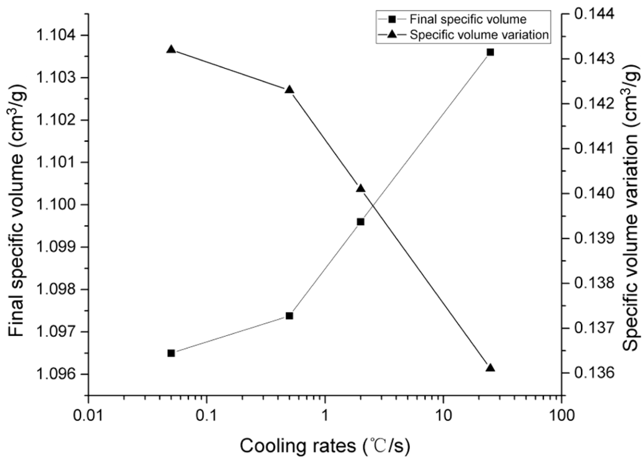

Figure 7. Final specific volume and specific volume variation under different cooling rates (25, 2, 0.5, 0.05 ºC/s).

perature. It is obvious that the crystalline segment of PVT curve was gradually shifted to the low-temperature region with increasing cooling rate. The temperature ranges of the crystalline segment for each cooling rate are about 38, 24, 14 and 12 ºC. Apparently, the temperature range of crystalline transition increases with the cooling rate. However, the changing trend of the specific volume of the polymer in molten and solid states was not affected by the cooling rate significantly. The specific volume of the polymer in the entire solid section increased with the increasing of cooling rate. As shown in Figure 7, there was the final specific volume and the variation of specific volume of the samples at each cooling rate, which increased along with the increase of cooling rate. It was because increase in cooling rate suppressed the formation of large grains, which

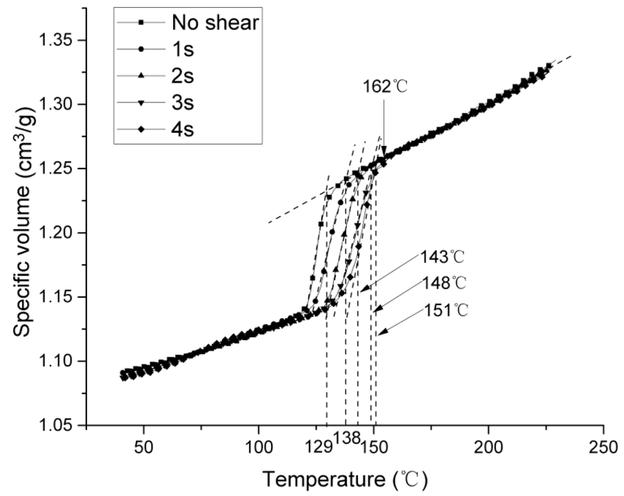

Figure 8. The influence of shear duration (0, 1, 2, 3, 4 s).

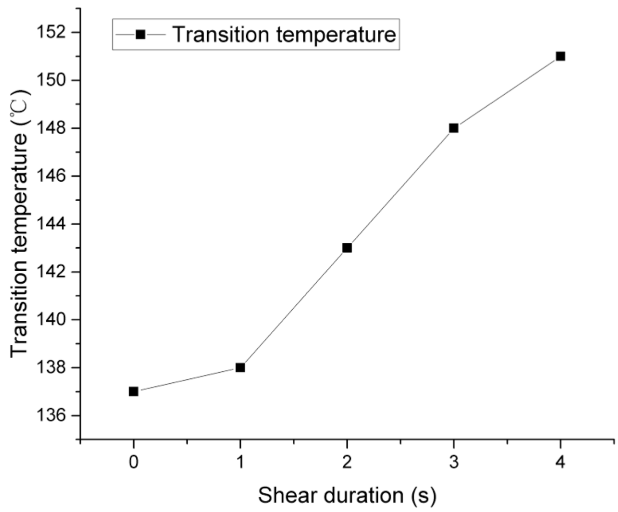

Figure 9. Variation of transition temperature (0, 1, 2, 3 s).

resulted in decrease in overall degree of crystallinity. The nucleation density was increased due to the reduction of the internal crystalline phase caused by elevation of cooling rate, i.e. making the grain smaller and more uniform.[14]

From the perspective of crystallization, crystallization of PP was weakened by increasing the cooling rate, which allows more time for the filling process during injection molding. However, the melt is frozen rapidly due to increasing of cooling rate, which has a greater impact on the filling process than the crystallization. Consequently, an excessive cooling rate would lead to a short shot. On the other hand, the change amount of specific volume decreases with the cooling rate. Higher quality could be achieved for the molding parts with less shrinkage during injection molding.

Effect of Shear on the PVT Properties. PVT curves with shear were studied in this section by comparing them with the ones without shear under the same conditions. The influence of the shear duration on the PVT properties is shown in Figure 8. The square line represents the PVT curve of PP without shear. It was found that the shear accelerated the crystallization of polymer melt, and the crystalline section of the curve was shifted to the high temperature region. Figure 9 shows the variation of transition temperature. The transition temperatures corresponding to each shear duration are 129 ºC for 0 s, 138 ºC for 1 s, 143 ºC for 2 s, 148 ºC for 3 s, and 151 ºC for 4 s. The offset distance was enlarged obviously with the growth of shear duration, while the increasing trend was gradually weakened. The phenomenon mentioned above could be attributed to the orientation of the polymer chains caused by shear, which enhanced the movement of the crystal nucleus. Meanwhile, the

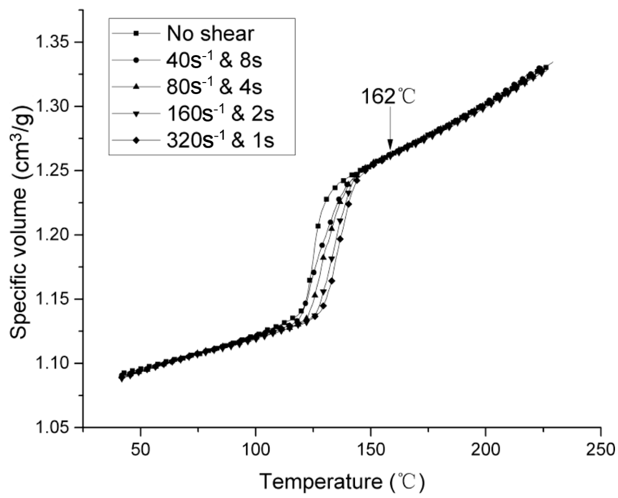

Figure 10. The influence of shear rate (320 s^{-1} & 1 s, 160 s^{-1} & 2 s, 80 s^{-1} & 4 s, 40 s^{-1} & 8 s).

shear also promotes the formation of new crystal nuclei resulting in the accelerated formation of grain, however this impact is extremely limited. The specific volume of solid section was almost the same. It is suggested that shear was able to increase the initial temperature of crystallization, while it has no effect on the eventual degree of crystallinity.[14]

The influence of shear rate on PVT properties is shown in Figure 10. It indicated that the shear rate of 320 s^{-1} with shear duration of 1 s had the greatest impact on the PVT properties, while the offset distance of shear rate with 40 s^{-1} was the smallest among all of the measurements. The results show that the crystallization stage is gradually shifted to high temperature region with the shear rate.

Figures 9 and 10 show that both increasing the shear dura-

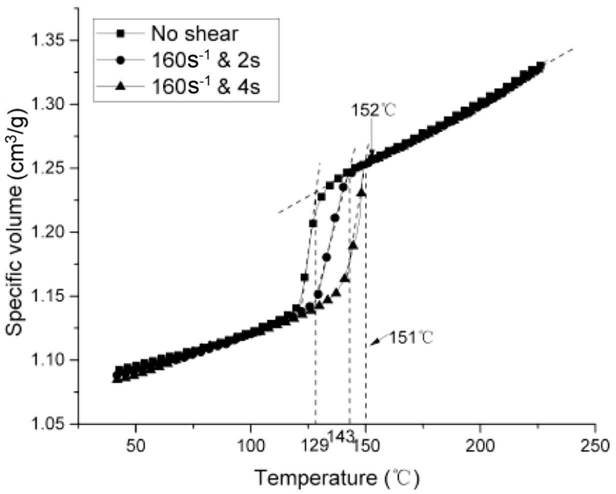

Figure 11. Effect of initial temperature (152 °C).

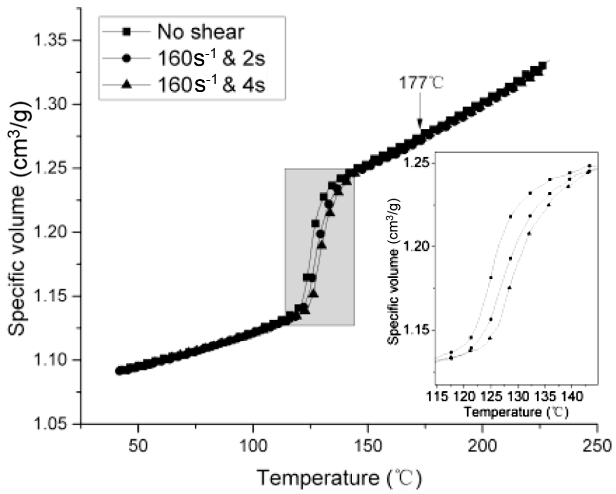

Figure 12. Effect of initial temperature (177 °C).

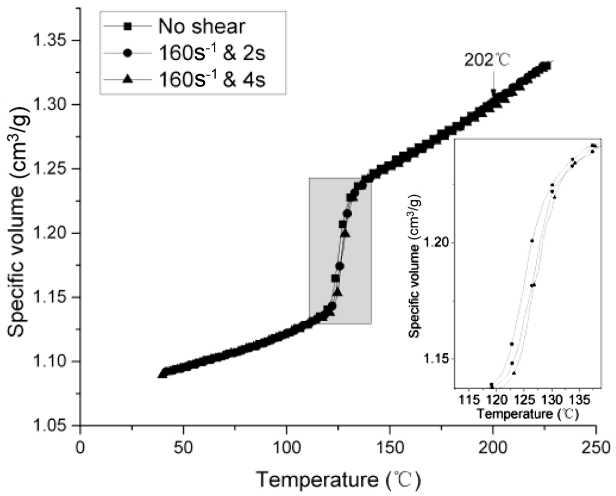

Figure 13. Effect of initial temperature (202 °C).

tion and the shear rate lead to the shifting of the crystallization stage to higher temperature, and the influence of the shear duration was more obvious. Owing to the sample thickness of just 0.5 mm, the drag flow between the melt and the measuring chamber walls could be more apparent compared with thick samples. For ultra-thin products, shear will have more obvious effect on the mobility of the melt.

Effect of Initial Shear Temperature on the PVT Properties. The influence of initial shear temperature on the PVT properties of PP is shown in Figures 11, 12 and 13. The initial temperature in Figure 11 is 152 °C which approaches the transition temperature. It was noted that the effect of shear near the crystallization temperature of PP was remarkable. The transition temperatures are shifted to 143 and 151 °C from 129 °C, respectively. Meanwhile, the initial temperature in Figure 13 was far away from the transition temperature and has no obvious influence on the PVT properties. It indicates that the effect of shear rate on the PVT property was gradually weakened with increasing the initial temperature. A possible explanation for this phenomenon is that shear causes the molecules to orient and leads to a certain amount of crystal nucleus. However, the crystal nucleus could re-melt at high temperatures and the molecular chains became relaxed again. The higher the initial temperature, the more molecular chain was relaxed as well as the weaker effect of shear on the PVT properties. As shown in the figures, the effect of shear duration of 4 s had more significant effect than 2 s, which further demonstrates the above explanation. It should be noted that this experiment was carried out under natural cooling conditions with the cooling rate of 0.05 °C/s.[14]

Coupling Effect of Cooling and Shear. According to the results mentioned above, it was demonstrated that both cooling rate and shear have effects on the PVT properties. However, their coupling effect on the crystallization is not understood clearly yet. Experiments were setup to study the coupling effect of the cooling rate and shear. As shown in Figures 14, 15 and 16, the relatively higher cooling rates promote the effect of shear and consequently result in the crystallization stage shifting to the high temperature region, and the crystallization rate is obviously accelerated. It is understandable that the high cooling rate shortened the re-melting time and reduced the loss of the crystal nucleus. In other words, more crystal nuclei were kept due to the high cooling rate, which raises the transition temperature. Although the high cooling rate was generally considered to inhibit crystallization, the influence of shear

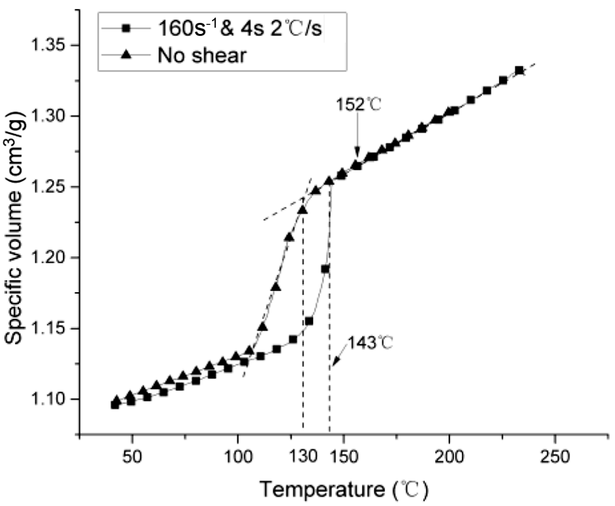

Figure 14. Effect of coupling of cooling and shear.

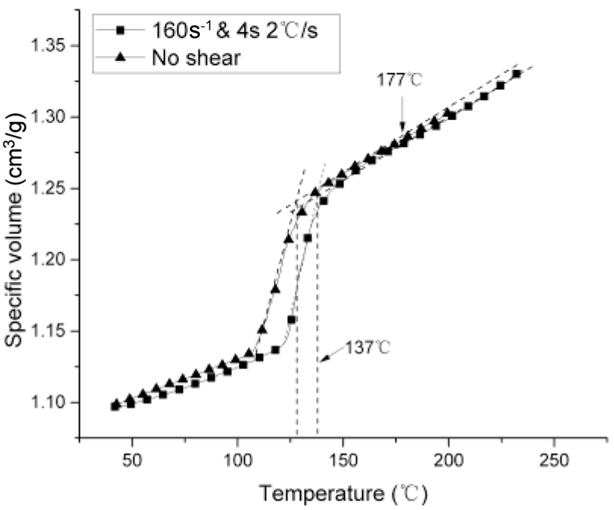

Figure 15. Effect of coupling of cooling and (initial temperature 152 ºC) shear (initial temperature 177 ºC).

loaded at 152 ºC has not been weakened (Figure 14). The transition temperature in Figure 14 with shear is higher than the one without shear. The effect of shear near the transition temperature was more obvious than that of the cooling rate.

Conclusions

In this paper, a PVT measuring instrument with rapid cooling and shearing function was developed. The function parameters of the instrument are as follows: pressure measurement range of 1-100 MPa, temperature measurement range of 30-300 ºC, maximum cooling rate of 25 ºC/s, maximum shear rate 320 s^{-1}, shear function of the pressure measurement of the upper limit of 20 MPa. The reproducibility of the instrument

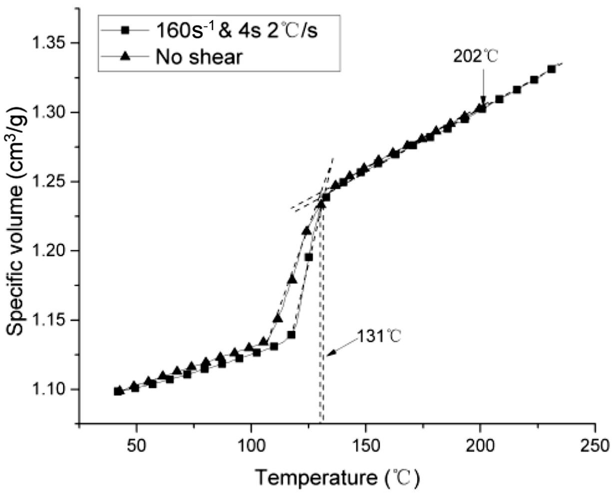

Figure 16. Effect of coupling of cooling and shear (initial temperature 202 ºC).

was verified by repeated experiments. The maximum repeatability error was 0.81%. The effect of cooling, shear and their coupling effect on the PVT properties of PP was investigated by employing this instrument. Rapid cooling could inhibit crystallization and influence the PVT properties of PP. The larger cooling rate, the less specific volume of crystallization stage changes. Meanwhile, shear action increased the transition temperature of the PP. At the same initial temperature of shear, crystalline segment offsets to the high temperature region with increasing the shear time and shear rate. However, this trend was gradually weakened with increasing the temperature. Above the transition temperature, the effect of shear on the PVT characteristics was gradually weakened with the increase of the initial temperature of shear. The coupling analysis of cooling and shear showed that increase of cooling rate can enhance the effect of shear on the transition temperature of PP. The relatively higher cooling rates promoted the effect of shear and consequently result in the crystallization stage shifting to the high temperature region.

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