

Effect of sorbitol nucleator on nonlinear visco-elasticity in polypropylene

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Abstract

We investigated effects of the network of sorbitol nucleator on non-linear visco-elasticity of the polypropylene (PP). We used Bis(p-methylbenzylidene)sorbitol (MDBS) as a nucleator in this study. We blended MDBS of 0.5wt% (MDBS0.5) and PP at melting state (210 °C). From the data of linear visco-elasticity, it was found that the blend sample (PP/MDBS0.5) exhibited a physical gel behavior at 170 °C. On the other hand, the PP/MDBS0.5 did not show a physical gel behavior at 210 °C. These results mean that the network structure of MDBS depends on temperature. In order to clarify the role of the network structure, we investigated a nonlinear visco-elasticity at 170 °C. First, we carried out steady shear viscosity measurements. In the measurements, we observed stress overshoots and found in the range of strain rate less than 0.1 s^{-1} that the stress at the steady state does not depend on strain rate. Secondly, we performed measurements of uniaxial elongational viscosity in the blend sample. The blend PP/MDBS0.5 showed a non-linearity in viscosity at a lower strain rate less than 0.1 s^{-1} . From the relation between stress and strain rate of PP/MDBS0.5 we estimated a critical stress where the network was broken.

Introduction

Nucleator agent has been effectively used to enhance the crystallization of crystalline polymer. Among others sorbitol nucleator is usually used in polypropylene (PP) as a nucleation agent. It is reported¹⁾ that crystallization temperature (T_c) of PP and crystallization speed are increased by addition of sorbitol nucleator. However the effect of sorbitol nucleator is not only an enhancement of crystallization but also a change of linear visco-elasticity due to a network formed by sorbitol nucleator in molten polymer.²⁾ We focus on network structures formed by sorbitol nucleators and study the effect of sorbitol nucleator on non-linear visco-elasticity in PP.

Experimental

-Materials-

As a nucleator we selected Bis(p-methylbenzylidene)sorbitol (MDBS) provided by Shinnihonrika Corporation. Fig.1 shows the chemical structure of MDBS. The matrix polymer is isotactic polypropylene provided by Chisso petrochemical Corporation.

-Coordination of sample-

We mixed MDBS(0.5wt%) and PP by a mixing machine (Toyoseiki corp.). Mixing temperature is 210°C, Screws revolution speed is 50rpm and mixing time is 5 minutes. Test specimens for dynamic visco-elasticity were shaped by a hot press (Toyoseiki corp.) at 230°C. Hereafter the blend sample is referred as PPLMD05.

-Analysis-

Both dynamic visco-elasticity and uniaxial elongational viscosity measurement were performed using ARES (TA instruments). History of temperature is shown in Figure 2.

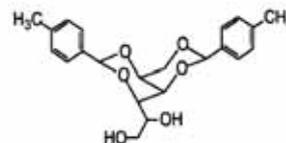


Figure 1 Chemical Structure of Sorbitol nucleator used in this study

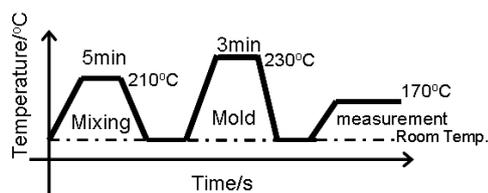


Figure 2 History of temperature used in this study

Results and Discussion

-Linear visco-elasticity-

Fig.3 shows linear visco-elasticities of the blend sample and neat-PP. This experiment was performed after the history of temperature shown in Fig.2. The result that a gel behavior is appeared indicates that network structures are formed at 170°C .

-Uniaxial elongational viscosity-

We measured uniaxial elongational viscosities after the history of temperature shown in Fig.2. In Fig.4, solid line and dotted-line stand for $3\eta^*(t)$'s that are evaluated by using data of dynamic visco-elasticity of PPLMD05 and neat-PP, respectively. The result shows that the elongational viscosity of PPLMD05 is in good agreement with $3\eta^*(t)$ of neat-PP in a higher strain rate than 0.5 s^{-1} , but not in agreement with $3\eta^*(t)$ of neat-PP in a lower strain rate than 0.1 s^{-1} . These results imply that there is a critical stress where the behaviors of elongational viscosity can be divided into two cases.

-Critical stress-

To investigate the effect of network formed by sorbitol nucleator on elongational viscosity, we focused on a relationship between strain rate and maximum stress that is the elongational stress just before the break of the sample in uniaxial elongational flow. On the assumption that maximum stress indicates a break point of network structures in uniaxial elongational flow, we plotted the maximum stresses as a function of strain rate in Fig.5. When the strain rate is faster than 0.5 s^{-1} , the maximum stress of PPLMD05 agrees to that of neat-PP. On the other hand, when the strain rate is lower than 0.1 s^{-1} , the maximum stresses of PPLMD05 are almost constant. At the elongational stress higher than about 10^4 Pa , a network structure of MDBS is broken and elongational stress of PPLMD05 approaches to that of neat-PP. On the other hand, when the elongational stress is lower than about 10^4 Pa , a network structure of MDBS is not broken and elongational stress of PPLMD05 is increased by elongated networks formed by sorbitol nucleator.

Conclusion

From the measurement of non-linear visco-elasticity, we found that non-linearity in viscosity depends on the critical stress ($\approx 10^4\text{ Pa}$) at which the network formed by sorbitol nucleator is broken.

Reference

- 1) R-D. Mair, C. Wang, R. Yhomann, C. Friedrich, R. Mulhaupt. "Self Organization and Nucleation of I-PP by Sugar Acetals" Proceedings of annual Meeting Polymer Processing Society PPS 16 in Netherlands, 2000
- 2) S. Yamasaki, Y. Ohashi, H. Tsutsumi, and K. Tsujii. "The Aggregated Higher-Structure of 1,3:2,4-Di-o-benzylidene-D-sorbitol in Organic Gels", *Bull. Chem. Soc. Jpn.*, **68**, 146-151 (1995)

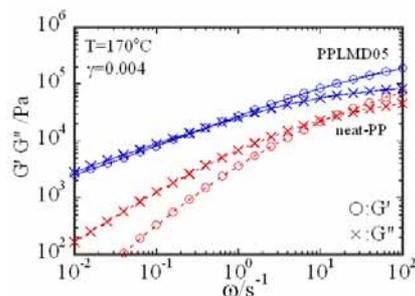


Figure 3 Storage modulus(G') and loss modulus(G'') plotted as a function of angular frequency, ω .

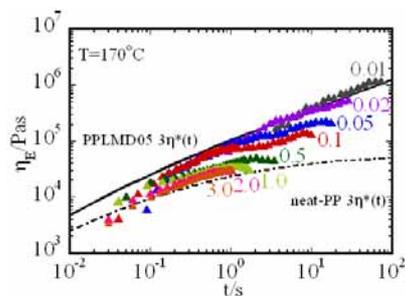


Figure 4 Uniaxial elongational viscosity plotted as a function of time.

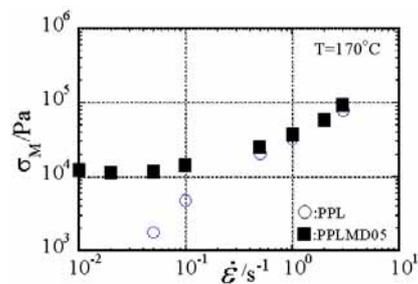


Figure 5 The maximum of stress plotted as functions of strain rate.