EFFECT OF PHYSICAL GELATION STRUCTURE ON VISCO-ELASTICITY IN POLYPROPYLENE.

H. Uematsu, M. Sugimoto, T. Taniguchi, K. Koyama

Yamagata Univ. Jonan 4-3-16, Yonezawa, 992 JAPAN   uematsu@ckpss.yz.yamagata-u.ac.jp

In this study we investigated effects of the network structure of sorbitol nucleator containing 0.5wt% on non-linear visco-elasticity of the polypropylene (PP). We used (1,3:2,4-bis-O-(p-methylbenzylidene)-D-sorbitol) (PDTS) as a geleator in this study. From the data of linear visco-elasticity, it was found that the blend sample (PP/PDTS) exhibited a physical gel behavior at 170 ^{o}C. On the other hand, PP/PDTS did not show a physical gel behavior at 210 ^{o}C. These results mean that the network structure of PDTS depends on temperature. In order to clarify the role of the network structure, we investigated a non-linear visco-elasticity at 170 ^{o}C. First, we carried out steady shear viscocity measurements. In the measurements, we observed stress overshoots and found in the range of strain rate less than $0.1s^{-1}$ that the stress at the steady state does not depend on strain rate. Secondly, we performed measurments of uniaxial elongational viscosity of PP/PDTS. The PP/PDTS showed a non-linearity of viscosity in lower strain rate less than $0.1s^{-1}$. We concluded that the non-linearity of viscosity of start up shear and elongatinonal flow are caused by breakage of PDTS network because network is fragile gel.

Introduction

Nucleator agent has been effectively used to enhance the crystallization of crystalline polymer. Sorbitol nucleator is usually used in polypropylene (PP) as a nucleation agent. It is reported that crystallization temperature (*Tc*) of PP and crystallization rate are increased by addition of sorbitol nucleator[1]. 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] In polymer processing, polymer melt and polymer liquid go though a large deformation and are molded into shape.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 (1,3:2,4-bis-O-(p-methylbenzylidene)-D-sorbitol) (PDTS) provided by New Japan Chemical co. LTD.. Figure1 shows the chemical structure of MDBS. The matrix polymer is isotactic polypropylene provided by Chisso petrochemical Corporation.
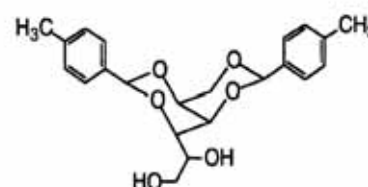
-Coordination of sample-
We mixed PDTS (0.5wt%) and PP by a mixer (Toyo Seiki Seisaku-sho,LTD.). Mixing temperature is 210°C, screws revolution speed is 50rpm and mixing time is 5 minutes. Test specimens for dynamic visco-elasticity were molded by a hot press (Toyo Seiki Seisaku-sho,LTD.) at 230°C. Hereafter the blend sample is referred as PP/PDTS.
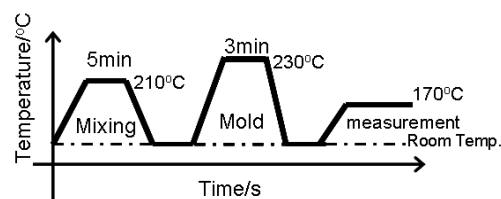
-Analysis-
Both dynamic visco-elasticity and uniaxial elongational viscosity measurement were performed by ARES (TA instruments). Steady shear viscosity measurements were performed by using Physica MCR (Anton-Paar). History of temperature is shown in Figure 2.

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-
Dynamic visco-elasticity of PP and PP/PDTS were measured by frequency sweep mode at different 6 temperatures (170, 180, 190, 200, 210, and 220 °C), which are substantially above their melting temperature, Tm. At high temperature, the slopes of G' and G" for PP respectively approach to 2 and 1 in the low frequencies. The time-temperature superposition could be applied over the entire temperature range.

In contrast, the PP/PDTS system expressed a gel behavior at low temperatures (T ≤ 190 °C). The slopes of G' and G" in the PP/PDTS system showed almost the same values at each temperature. However, at high temperatures (T ≥ 200 °C), the PP/PDTS indicated same viscoelastic of PP. Figure 3 shows the tan δ at different ω vs. T plots for the PP/PDTS system. From the ω-independent tan δ point, the critical gel temperature (T_c) and n values could be

determined. It was found that T_c = 193 °C and n = 2/3. This n value is in agreement with the value reported by Takenaka et al.[3].

Therefor PDTS network depends on temperature, at low temperature network forms in PP and at high tempearture network disappers in PP.

-S*tart-up shear flow*-

Figure 4 shows time dependence of steady shear viscosity (η_S) at various strain rate for PP/PDTS at 170 °C. We observed stress overshoots in this system although PP did not show non-linear viscosites. It seems that decrease of viscosities followed by the stress overshoot are caused by breakeage of PDTS network in shear flow process.

-S*tart-up uniaxial elongational flow*-

Figure 5 shows time dependence of uniaxial elongational viscosity ($\eta_E(t)$) at various strain rates for PP/PDTS at 170 °C. Solid line and dotted-line stand for $3\eta^+(t)$ that are evaluated by using data of dynamic visco-elasticity of PP/PDTS and PP, respectively. It is found that the $\eta_E(t)$ exhibited strong strain-softening. $\eta_E(t)$ decreased with increasing $\dot{\varepsilon}$ at $\dot{\varepsilon} \leq 0.1 s^{-1}$. Above 0.5 s^{-1}, $\eta_E(t)$ is in good agreement with $3\eta^+(t)$ of PP. These results imply that the network structure of PDTS was destroyed at higher strain rates. Figure 6 shows the maximum elongational stress σ_{Max} plotted against $\dot{\varepsilon}$ for the PP/PDTS system at 170 °C. σ_{Max} is the rupture stress of the strand sample under the elongational process. Closed and open symbols respectively denote σ_{Max} of iPP and PP/PDTS. The σ_{Max} values of PP/PDTS at high $\dot{\varepsilon}$ (0.5s^{-1}) agree with those of iPP. However, they deviate from those of iPP at low $\dot{\varepsilon}$ (0.1s^{-1}) and indicate a constant value of 10^4 Pa. This result implies that the network structure of PDTS was broken above critical stress about 10^4 Pa.

Conclusion

We have investigated the linear and non-linear viscoelastic measurements of a PP/PDTS system. It was found that the PP/PDTS system exhibited a sol-gel transition (T_c) at 193 °C. In large deformation flow, non-linear properties were caused by breakege of network because PDTS network is fragile gel.

Acknowledgements

We would like to thank New Japan Chemical co. LTD. for supplied the sorbitol nucleator (PDTS) and thank Dr. Aoki for having a valuable discussion with about a sol-gel transition.

References

1) R-D. Mair, C. Wang, R. Yhomann, C. Friedrich, R. Mulhaupt Proceedings of Aannual Meeting Polymer Processing Society PPS 16 in Netherlands, 2000
2) S. Yamasaki, Y. Ohashi, H. Tsutsumi, and K. Tsujii *Bull. Chem. Soc. Jpn.*, **68**, 146-151 (1995)
3) Takenaka M, Kobayashi T, Saijo K, Tanaka H, Iwase N, Hashimoto T, Takahashi M *J Chem Phys* 121, (7), 3323-3328 (2004)
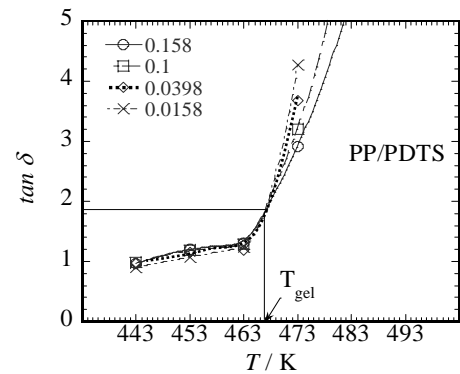
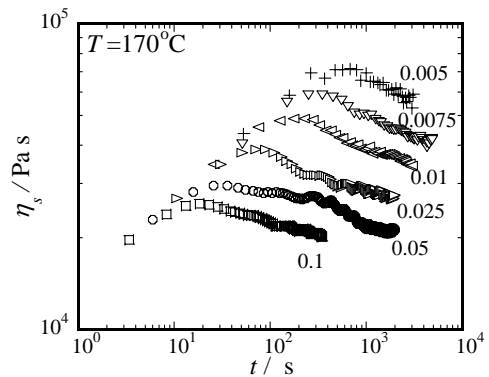Figure 3 Tanδ plotted against temperature T for the PP/PDTS at various frequency.

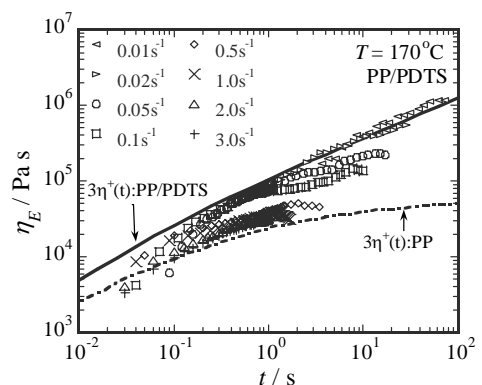Figure 4 Time dependence of shear viscosity at various strain rates for PP/PDTS at 170 °C.

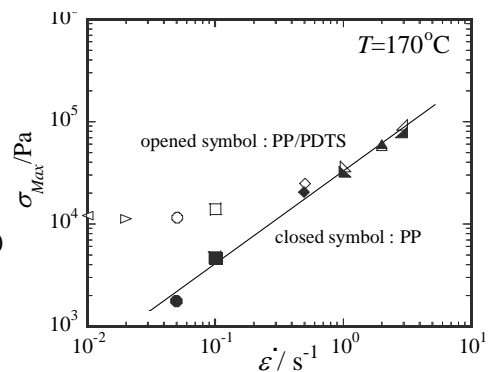Figure 5 Time dependence of uniaxial elongational viscosity at various strain rates for PP/PDTS at 170 °C.

Figure 6 Maximun stress plotted against strain rate for PP/PDTS and PP at 170 °C.