

입자가 첨가된 폴리프로필렌 용융물의 유변학적 특성에 대한 상용화제의 영향에
대한 실험적 연구

이승환, 조은나리, 윤재륜
서울대학교 공과대학 재료공학부

**An experimental study of the influence of compatibilizer on the rheological
properties of particle-filled polypropylene melts**

Seung Hwan Lee, Enu Na Ri Cho, and Jae Ryoung Youn

School of Materials Science and Engineering, Seoul National University, Seoul 151-742,
Korea

1. Introduction

Polypropylene was the first synthetic polymer to achieve industrial importance and it is presently the fastest growing polymer resin for technical end-users where high tensile strength coupled with low-cost is one of the essential features. There has been much interest in the development of polypropylene composites to improve the properties of this low cost, commodity polymer by reinforcement with various fillers, such as layered silicate organoclay or synthetic fiber. The main target of filling and reinforcing polypropylene are twofold: improving the mechanical properties, mainly modulus or heat deflection temperatures and reducing the overall cost of the material in the case of mineral filler and inexpensive organic fillers. Relevant parameters of fillers are particle size and size distribution, matrix adhesion, hydrophobicity, and the surface polarity of the filler. Furthermore, the effects of additives and processing aids (compatibilizer) have to be considered which can contribute strongly to the dispersion quality and molecular interaction between polymer matrix and filler.

For thermoplastic polymers, the knowledge and moreover the design of flow behavior is essential for all forms of production and processing in the molten state. Additionally, rheology has attained a key portion in polymer research from the fillers over composite and compatibilizer to processing behaviors and final properties. In the case of viscoelastic systems, the rheological consequences of filler is more complex than for the Newtonian case. The addition of filler and compatibilizer leads to a change in the relaxation time spectrum with an addition of long relaxation times resulting from polymer matrix/particle and particle/particle interactions. In dynamic oscillatory measurements, this is well reflected in a plateau development of the storage modulus at low frequencies, similar to network development in crosslinking.

In this work, we prepared layered silicate based polypropylene nanocomposites (iPP/PP-g-MAH/OLS) and glass fiber reinforced composites (iPP/PP-g-MAH/GF) using the compatibilizer (PP-g-MAH). Also we examined the rheological behaviors in shear

and uniaxial elongational flows and compared the effect of filler and compatibilizer on rheological properties.

2. Experimental

The isotactic poly(propylene) homopolymer for extrusion sheet (HP 550K, MFI 3.5 g/10min, Polymirae Co.) was used as base polymer resin in this study. Maleic anhydride grafted polypropylene (PP-g-MAH, Polybond-3150, Crompton Co.) was used as the compatibilizing agent. Its grafted percentage was 0.50 wt% and melt flow index was 50g/10min. The layered silicate organoclay and chopped glass fibers were used as fillers to make the composite materials. The organoclay was a natural montmorillonite modified with a quaternary ammonium salt (Cloisite 15A, Southern Clay Co.) via ion-exchange reaction. Length and diameter of chopped glass fiber (Cratech, Owens corning Co.) was 2~3 mm and 13 μm , respectively.

All samples were prepared by melt compounding with a counter-rotating twin-screw extruder (Brabender PLASTI-CORDER PLE-651). Melt compounding was done at 190°C and at screw speed of 100 rpm. Prior to extrusion, all the organoclay and glass fibers were dried in a vacuum oven at 80°C for 8h. For comparison polypropylene composites with 5 wt% organoclay and glass fiber were prepared in the absence or presence of compatibilizer. The extruded melt was quenched in water and pelletized. For shear rheological measurements the pellets were molded into a disk of 25 mm in diameter x 1.5 mm in thickness and compressed. Also for the elongational rheological measurements, the pellets were molded into a rectangular strip of 57.0 x 7.0 x 1.5 mm³.

Dynamic oscillatory shear flow measurements were conducted using a rotational rheometer (AR-2000, Rheometric Scientific) with parallel plates. Frequencies of 0.01 - 200 rad/s were used at the strain amplitude of 10% in order to be within the linear viscoelastic region. The viscosity growth during uniaxial elongational flow at a constant extension rate was measured using a Meissner-type elongational rheometer (RME, Rheometric Scientific). A sample of rectangular cross-section is elongated between two rotating clamps. A constant speed of the two clamps makes it possible to deform the melt homogeneously and to apply a constant strain-rate to the polymer melt. The constant extension rates were applied at constant elongation rates of 0.05, 0.1, 0.3, 0.5 and 1.0 s⁻¹.

3. Results and discussion

Figure 1 shows the logarithmic plots of storage moduli (G') versus frequency (ω) for iPP/PP-g-MAH/OLS nanocomposites and iPP/PP-g-MAH/GF composites at 190°C, respectively. It is found that more increased elastic modulus and decreased terminal slope were observed in the compatibilized nanocomposites (iPP/05/OLS05) than those of pure polypropylene matrix or uncompatibilized composite (iPP/00/OLS05) at low frequency regions. It is obvious that the iPP/PP-g-MAH/OLS nanocomposites have stronger elastic properties than pure polypropylene or uncompatibilized iPP/OLS nanocomposites. On the

other hands, in the case of iPP/PP-g-MAH/GF composites storage modulus was decreased compared with that of pure polypropylene at low frequency regions. This is probably because glass fibers decrease the interfacial bonding between polypropylene matrix and then slippage occurs in the composites with the addition of compatibilizer.

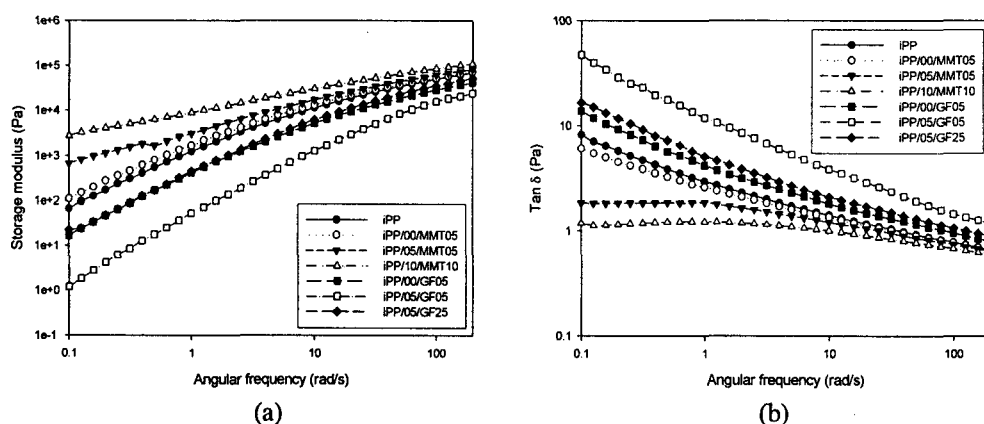


Figure 1. (a) Storage modulus and (b) Loss tangent ($\tan \delta$) of pure polypropylene, iPP/GF composites, and iPP/MMT nanocomposites

Figure 2 shows the transient elongational viscosity with respect to Hencky strain of iPP/OLS nanocomposites and iPP/GF composites. Faster failures observed in the iPP/GF composite melts are compared with those of pure polypropylene or iPP/OLS nanocomposites. Glass fiber filled composites fail at strain of about 2 and show the smaller elongational viscosities than pure polypropylene. But the compatibilized iPP/OLS nanocomposite increases continuously with increasing strain and shows larger transient elongational viscosity than pure polypropylene or iPP/GF composites.

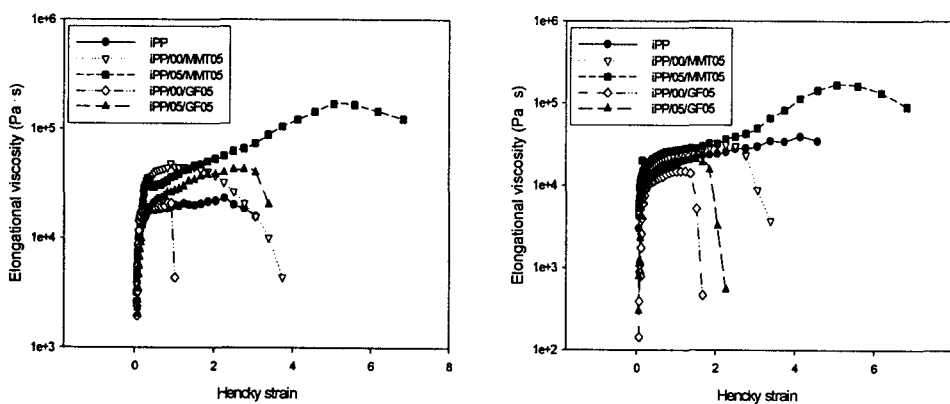


Figure 2. Transient elongational viscosities of (a) elongational rate of 0.1 s^{-1} and (b) elongational rate of 0.5 s^{-1} for organoclay and glass fiber filled composites

4. Conclusion

We have prepared the iPP/PP-g/MAH/OLS nanocomposites and iPP/PP-g-MAH/GF composites by using twin-screw extruder and investigated the effects of fillers and compatibilizer on shear and elongational flow properties. iPP/PP-g-MAH/OLS nanocomposites showed large increase in storage modulus, solid-like plateau behavior at low frequency region, and strong frequency-thinning behavior in dynamic oscillatory shear flow. In uniaxial elongational flow, outstanding strain hardening behavior was observed due to 3-dimensional network structure originated by strong intermolecular bonding between polypropylene matrix and organoclay. However, glass fiber reinforced composites (iPP/PP-g-MAH/GF) exhibited decreased storage modulus and Newtonian behavior at low frequency regions.

* Acknowledgement

This work was financially supported by the Korea Science and Engineering Foundation through the Applied Rheology Center (ARC) at Korea University.

5. References

- Markus, G., 2001, Melt rheology of polyolefins, *Prog. Polym. Sci.*, **26**, 895-944
- Karger-Kocsis, J., 1995, "Polypropylene: structure, blends and composites", Chapman & Hall, London
- Solomon, M.J., A.S. Almusalla et al., 2001, Rheology of Polypropylene/Clay Hybrid Materials, *Macromolecules*, **34**, 1864-1872
- Sinha Ray, S. Okamoto, M., 2003, Polymer/layered silicate nanocomposites:a review from preparation to processing, *Prog. Polym. Sci.*, **28**, 1539-1641
- Giannelis, E. P., R. Krishnamoorti, et al., 1999, Polymer-Silicate Nanocomposites :Model Systems for Confined Polymers and Polymer Brushes, *Adv. Polym. Sci.*, **138**, 107-147
- Shenoy, A. V., 1999, "Rheology of Filled Polymer Systems", Kluwer Academic Publishers, Dordrecht