

폴리프로필렌과 Clay 로 구성된 나노 복합체의 비선형 점탄성에 관한 연구

김종관, 이승중, 이재욱\*

서울대학교 응용화학부, 서강대학교 화학공학과\*

**Nonlinear Viscoelasticity Polypropylene-Organoclay Nanocomposite.**

Jongkwan Kim, Seung Jong Lee and Jae Wook Lee\*

School of Chemical Engineering, Seoul National Univ.

\*Department of Chemical Engineering, Sogang University,

**Introduction**

Recently, the nanocomposites prepared from polymer and inorganic clay have attracted a great interest from researchers since they frequently exhibit unexpected hybrid properties synergistically derived from two components. However, the exfoliated and homogeneous dispersion of the silicate layers could be achieved only in a few cases, such as polymers containing polar functional groups. Since the silicate layers of the clay have polar hydroxyl groups thus, they are compatible only with polymers containing polar functional groups. PP is one of the most widely used polyolefin polymers. Since it does not include any polar groups in its backbone, it is thought that the homogeneous dispersion of the silicate layers in PP would not be possible. Recently, it is reported a novel approach to prepare a PP-clay nanocomposite by using a functional oligomer.[1] PP was mixed with clay and a polyolefin oligomer with polar OH groups as a compatibilizer. From processing and application points of view, the mechanical and rheological properties of these nanocomposites are very important. In this paper, we focus on the thermal stability and the various viscoelastic properties of the prepared nanocomposite.

**Experimental**

Organically modified montmorillonite, Cloisite 20A, which has an organic salt of dimethyl dihydrogenated tallow ammonium, was provided by Southern Clay Products. PP was supplied by Daelim Industrial Company, which has a melt flow index of 5.9g/min, Mw of 127000, and Mn of 13000. MAPP, Polybond 3150 (melting point of 160°C, melt flow

index of 5g/min at 230 °C) from Uniroyal Chemical is also used to prepare the nanocomposite.

1 wt % nanocomposite was prepared by mixing 28g of PP, 12g of MAPP and 0.41g of clay in a Haake mixer for 10 minutes at 180°C with 50 RPM. With similar way of 1 wt % nanocomposite, other nanocomposites (3 wt %, 5 wt %) also were prepared. For a reference, PP/MAPP blend whose weight ratio is 7/3 was prepared. X-ray diffraction (XRD) was carried out using a Rigaku D/MAX-IIIC X-ray diffractometer. Several rheological tests were conducted on an Advanced Rheometrics Mechanical Spectrometer (ARES) with a parallel plate fixture.

### Results and discussion

Figure 1 shows XRD curves of clay and nanocomposites. Clay powder shows a 001 peak at  $2\theta=3.6^\circ$  corresponding to an interlayer spacing of  $d=24.1\text{\AA}$ . The nanocomposites show no clay peak. Absence of 001 and subsequent peaks is interpreted as defoliation of clay layers into the polypropylene matrix. However, weak 001 peak was observed in some XRD tests on same sample. Therefore it is thought that the prepared nanocomposite contains not only exfoliated clay layers but also intercalated ones.

The linear viscoelastic response was measured by the storage and loss moduli ( $G'$  and  $G''$ , respectively) for the PP/MAPP blend and the nanocomposites. Figure 2 shows the storage modulus measured at 180°C. Both  $G'$  and  $G''$  (not shown) show an increase with clay loading at all frequencies. For homopolymers, it generally shows characteristic terminal behaviour, i.e.,  $G' \propto \omega^2$  and  $G'' \propto \omega$ . The terminal zone dependence of  $G'$  and  $G''$  for nanocomposites shows nonterminal behaviour with power law dependencies for  $G'$  and  $G''$  much smaller than the usual 2 and 1, respectively. Furthermore, there also appears to be a gradual decrease in the power law dependence of  $G'$  and  $G''$  with increasing clay loading. The nonterminal behavior at lower frequency observed in nanocomposite could be attributed to the retardation of molecular relaxation process produced by the tethering of one end of polymer chain and clay surface.[3,4]

The stress relaxation was observed after cessation of steady shear rate for 170seconds. Figure 3 shows stress relaxation patterns of PP/MAPP blend and the nanocomposites. The nanocomposite shows viscous character like usual homopolymer in short time range. However in long time range solid like response was found, and this phenomena is more

conspicuous at higher concentration of clay nanocomposite. Figure 4 shows stress relaxation patterns of PP/MAPP blend and 5 wt % nanocomposite. Short time response of the nanocomposite is similar to that of PP/MAPP blend that rapidly relaxes. However, in long time range solid-like response of 5 wt % nanocomposites was observed, in other words stress relaxation occurs slowly. This is surely due to the existence of clay. Solid-like nonterminal behavior from oscillatory shear is confirmed by solid-like relaxation pattern from different deformation modes.

Nonterminal low frequency rheological behavior has also been observed in ordered block copolymers and smectic liquid crystalline polymer.[5, 6] Koppi et al.[5] have suggested that defects in the layers might contribute to the low frequency viscoelastic response in layered block copolymer. Larson et al.[6] in the study on smectic small molecules and short ordered block copolymers have suggested that the nonterminal low frequency response is due to the long range domain structure and the presence of defects.

### Conclusions

The end-tethered structure of the nanocomposite also enhances the shear viscosity and dynamic moduli. The power law dependence of  $G'$  and  $G''$  in the terminal region shows a dependence on the concentration of the clay. Furthermore the magnitude of frequency dependency for  $G'$  and  $G''$  of nanocomposite is different from that of usual homopolymer. The nanocomposite also exhibits solid-like relaxation pattern from other relaxation modes. From linear and nonlinear viscoelastic experiments performed in this study the nanocomposite exhibits pseudo-solid-like behavior. Similarities of the rheological response of the nanocomposite and block copolymer and liquid crystalline polymer are also introduced..

### Acknowledgments

The authors deeply acknowledge the financial support of Korea Science and Engineering Foundation (Grant No. 98-0502-11-01-3) for this study.

### References

1. M. Kawasumi, N. Hasegawa, M. Kato, A. Usuki, and A. Okada, *Macromolecules*, 30, 6333 (1997).

2. S.D. Burnside, and E.P. Giannelis, *Chem. Mater.*, 7, 1596 (1995).
3. R. Krishnamoorti, R.A. Vaia, and E.P. Giannelis, *Chem. Mater.*, 8, 1728 (1996).
4. R. Krishnamoorti, and E.P. Giannelis, *Macromolecules*, 30, 4097 (1997).
5. K.A. Koppi, M. Tirrell, F.S. Bates, K. Almdal, and R.H. Colby, *J. Phys. II (Paris)*, 2 1941 (1993).
6. R.G. Larson, K.I. Winey, S.S. Patel, H. Watanabe, and R. Bruinsma, *Rheol. Acta*, 32 245 (1993).

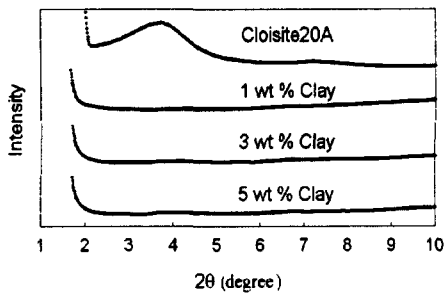


Figure 1. XRD curves of clay and nanocomposites.

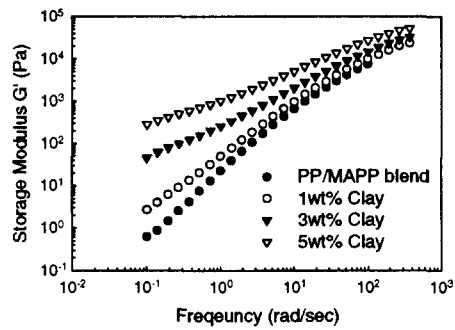


Figure 2. Storage modulus ( $G'$ ) for PP/MAPP blend and nanocomposites ( $\gamma=0.04$ ,  $180^\circ\text{C}$ )

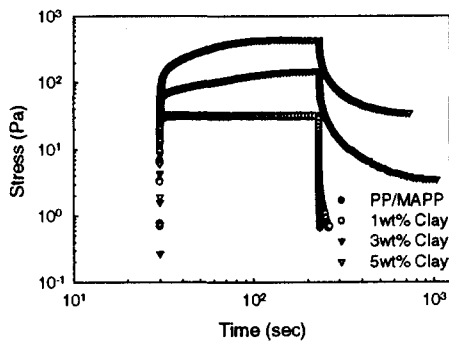


Figure 3. Start up and relaxation of stress for unfilled polymer blend and nanocomposites at  $180^\circ\text{C}$ .

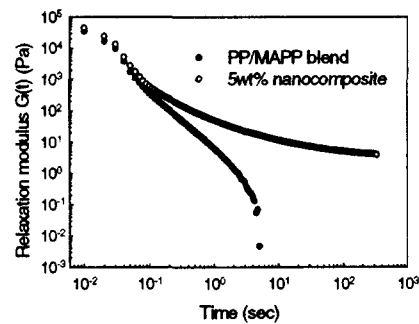


Figure 4. Stress relaxation of PP/MAPP blend and 5 wt % nanocomposites ( $\gamma=5.0$ ,  $180^\circ\text{C}$ ).