Effect of added ionomer on morphology and properties of PP/clay nanocomposites

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Introduction

Recently, the very large commercial importance of polypropylene (PP) has been driving an intense investigation of polypropylene nanocomposites derived from layered silicates. However, it is a great challenge to prepare PP-clay nanocomposites (PPCN) with well-exfoliated structure due to the incompatibility of the hydrophobic polymer with hydrophilic silicates, although the commercial clays usually have been modified with alkylamonium via ion-exchange reaction. Until now, the most successful alternative is the addition of maleic-anhydride grafted PP (PP-g-MA) as a compatibilizer during melt compounding. Actually, the presence of the functionalized ologomer remarkably improves the exfoliation degree of clay platelets. Unfortunately, the same expected improvement in properties (e.g. mechanical properties) as PA6 nanocomposites was not achieved for PP until now. Two aspects of reasons could be responsible for this failure. One is the still unsatisfactory exfoliation degree; the other is high loading of PP-g-MA to achieve desired exfoliation effect, which in turn partly weakens the resulting improvement of mechanical properties due to the inferior properties of the used oligomer.

As a kind of commercial ionomers, there have been few reports about the studies on Surlyn-clay nanocomposites. The presence of the pendant ionic groups and the polar methacrylic acid groups in its backbone potentially create favorable interactions between them and the aluminosilicate clays, resulting in a much more exfoliated morphology compared to nanocomposites prepared from LDPE. [1,2] On the other hand, the kind of ionomer owns good compatibility with many polar and non-polar polymers owing to its unique molecular characteristics and was often used as a compatibilizer for blends of polyolefin and polar thermoplastics, e.g. PP/PBT [3]. Therefore, the main purpose of our work is to investigate the compatibilizing role of added Surlyn on PPCN. In addition, their mechanical properties and wettability are examined, respectively.

Experimental

Table 1. Characteristics of raw materials used

Name	trademark	Characteristics	Supplier
PP	HP562T	MFR (230°C, 2.16Kg) = 6.0g/min, M_w=127,000, M_n=13,000	Polymirae Company Ltd (Korea)
Ionomer	Surlyn®8945	MFR (190°C, 2.16Kg) = 4.5g/10min, specific gravity=0.96, mathacrylic acid content=15.2, sodium content=1.99wt%, neutralization=~40%	DuPont company in Korea
PP-g-MA	Polybond®3200	MFR (190°C, 2.16Kg) = 11.5g/min M_w=84,000, MA content= 1.0wt%, T_m=163°C, T_d=325°C	Crompton Corp.
OMMT	Cloisite®20A (i.e. Dimethyl bis(hydrogenated-tallow) ammonium montmorillonite)	CEC=95 meq/100g, Organic content=39.6wt%	Southern Clay Products

The specific characteristics of the raw materials used were listed in Table 1. Melt compounding was prepared using an intermeshing, co-rotating twin-screw extruder (Bautek, Korea) with a screw speed of 100rpm and 190°C. For convenience, the amount of OMMT is fixed at 5phr based on total weight of the used resins (including PP and Surlyn). As a comparison, the corresponding PP/PP-g-MA/OMMT nanocomposites were also prepared under the same condition. For the convenience of expression, PPxCN represents PP/Surlyn/OMMT and PPxMCN does PP/PP-g-MA/OMMT. Among them, the number x refers to the concentration of the added compatibilizer.

X-ray diffraction data (XRD) were collected on Rigaku D/MAX-IIIC X-ray diffractometer (Cu-Kα radiation, wavelength=1.5418) with accelerating voltage of 40KV. Diffraction spectra were obtained over a 2θ range of 1.2-10°. Rheological measurement was performed in small amplitude oscillation shear (SAOS) on a parallel plate rheometer (Rheometrics RMS800). Data were collected over a frequency range of 0.1-100rad/s at 180°C in a nitrogen environment. Prior to frequency sweep, a strain sweep test is performed to ensure that the strain used is within the linear viscoelastic range.

Results and discussion

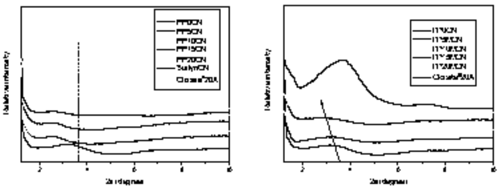

Figure 1. XRD patterns of PP/Surlyn/OMMT (left) and PP/PP-g-MA/OMMT (right), respectively.

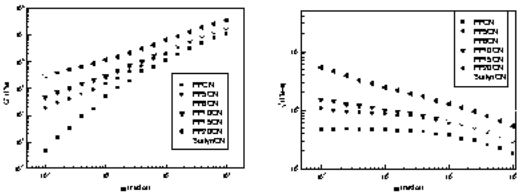

Figure 2. Rhological data of PP/Surlyn/OMMT nanocomposites: storage modulus (left) and complex viscosity (right).

Figure 1 shows XRD spectra of PP/clay nanocomposites as a function of concentration of compatibilizers. In the case of PP/Surlyn/OMMT, when only 5wt% Surlyn was added, the d_{001} diffraction peak is markedly shifted to lower angle, compared to uncompatibilized PP/clay nanocomposite (i.e. PP0CN). However, upon the further addition of Surlyn, the measured interlayer spacing remains unchanged, which is just opposite to the results observed in the PP/PP-g-MA/OMMT nanocomposites. However, it is noticeable that over 15wt% Surlyn, the d_{001} diffraction peaks became broadening remarkably and its intensity peak becomes very weak. As a result, the interlayer spacing is difficult to determine due to peak's broadness. This result indicates that the stacks of layered silicates become more disordered, although maintaining a periodic distance. Figure 2 presents the storage modulus (G') and complex viscosity (η^*) of PP/Surlyn/OMMT nanocomposites. It can be found that especially at low frequency, both G' and η^* values increase progressively with the addition of Surlyn. In order to isolate the effect of effect of dispersion state of the nanofillers, the relative viscosity is defined as the magnitude of the complex viscosity, η_c^*, of the composites divided by the complex viscosity of the silicate-free matrix (i.e. either PP or PP-Surlyn), η_m^*. It is found that the nanocomposite with the highest loading of Surlyn (PP20CN) exhibits greatest enhancement of relative viscosity (not shown here) and it could indicate that the greatest degree of clay exfoliation, consistent with the observation from XRD and TEM.

Conclusions

The results demonstrated that Surlyn can act as an effective compatibilizer for PPCN. The PP/Surlyn/OMMT system exhibited the improved interlayer spacing compared to the analogues of the PP/PP-g-MA/OMMT system.

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