Polypropylene Reactive Nanocomposites with Functional Nanoclays

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Introduction

The most interesting polymer nanocomposite is the one that made of a polymer and nanofiller called nanoclay or organoclay. Here in this work, the nanoclay was prepared from Thai bentonite and common sodium montmorillonite. Two kinds of surfactants were used to modify both clay minerals and thus nano(organo)clay was obtained (Fig. 1). The nanoclays were blended with polypropylene (PP) and ionomer as a reactive compatibilizer.

Experimental

Two types of clay minerals with different CEC were used, local sodium bentonite (Na-BN) with 52.55 meq/100 g and common montmorillonite (Na-MMT) with CEC of 115 meq/100 g, respectively. Polypropylene (Moplen HP500N, 12.0 MFI) was from HMC Polymer Co., Ltd. Sodium-neutralized ethylene-co-methacrylic acid (Surlyn® PC350, 4.5 MFI) was purchased from DuPont Co., Ltd. Two alkylammonium agents with same carbon length (C_{18}), dihydrogenated tallow dimethyl-ammonium chloride (DTDM) and Methyl di-(palm carboxyethyl)-2-hydroxyethyl-ammonium methylsulfate (DCEM) with ester linkage and hydroxyl group were selected for the preparation of organomodified clay by ion exchange.

The 3 wt% organoclays were blended with PP and 6 wt% Surlyn in the twin screw extruder (80, 160, 170, 180, 190, and 200°C from hopper to die, 50 rpm) and the pellets were added to injection molding (barrel temperature of 200°C, mold temperature of 45°C, injection pressure of 1000 bar) to get specimens for tensile test (ASTM D638).

Results and discussion

The results show in Figure 1 confirm the intercalation of two alkylammonium agents in both Na-BN and Na-MMT. The functional nanoclays (DCEMs) show peaks at lower angle region suggesting that the silicate layers were expanded largely [1]. Moreover in Figure 2, the PP/DCEM-nanoclay nanocomposites show no peaks at low angle region indicating the good exfoliation of silicate layers while those with DTDM (linear quarternary ammonium ion) shows some shoulders. Thermal properties of the nanocomposites reveal that the nanoclays can initiate early crystallization but do not change crystal structure [2] and thus resulting in higher crystallinity (Table 1).

Table 1. Melting and crystallization behavior of PP and nanocomposites (using Perkin Elmer DSC-7, 30-250 °C at 10 °C/min)

Material	T_c (°C)	T_m (°C)	ΔHm	% Crystallinity
PP	110.8	161.7	66.46	31.80
PP + Surlyn + DTDM-B	108.9	160.7	63.05	32.83
PP + Surlyn + DCEM-B	109.6	157.7	65.56	34.17
PP + Surlyn + DTDM-M	108.1	158.8	63.34	33.01
PP + Surlyn + DCEM-M	109.1	158.0	65.22	33.77

Effect of functional group on polymer nanocomposites

Functional groups on DCEM can provide dipole interaction and hydrogen bond to carboxylic groups of Surlyn. Figure 3 shows that PP/Surlyn blend has improved modulus and becomes tougher than PP. So Surlyn acts successfully as a reactive compatibilizer. The nanocomposites with DCEM show higher breaking strain and modulus than the ones with non-functional nanoclay (with DTDM) due to in situ interaction by those reactive groups to make reactive nanocomposites. Thermal properties show that the reactive nanocomposites have relatively higher crystallinity suggesting better mechanical properties but their melting temperatures were slightly reduced due to the interaction interrupting crystal growth.

Effect of CEC on polymer nanocomposites

Na-BN (less CEC than Na-MMT) has more impurities. So far, CEC is not an important parameter for making nanoclay and nanocomposites. Clay with lower CEC tends to exfoliate easier (Figures 1-2). It seems that the impurity is not a siginificant parameter for intercalation and PP crystal structure. However, PP nanocomposites with BN-nanoclays (low CEC) have poorer mechanical properties than those with MMT-nanoclays (high CEC), see Figure 3 [3].

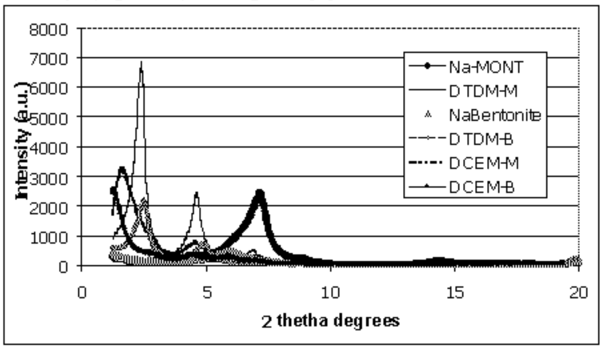

Figure 1. XRD results for the modified nanoclays

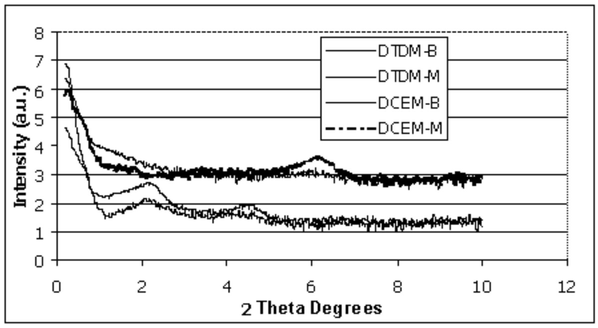

Figure 2. XRD results for PP/nanoclay nanocomposites

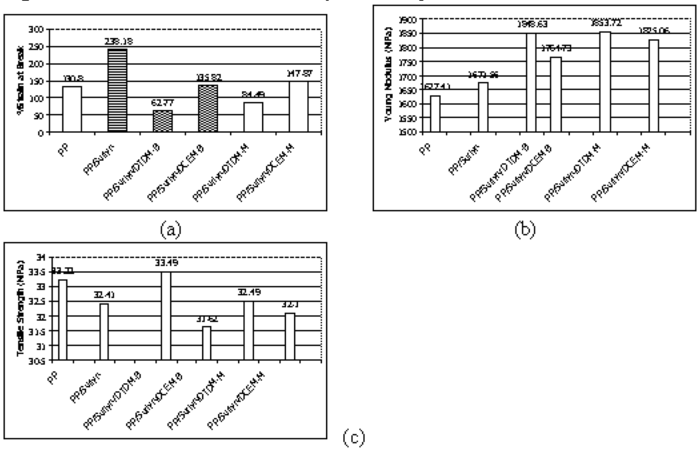

Figure 3 Tensile properties of PP-nanoclay nanocmposites

Conclusion

PP-nanoclay nanocomposites were successfully obtained by both simple and reactive melt mixing (with an ionomer compatibilizer and functional alkylammonium agents). The reactive nanocomposites show slightly higher crystallinity and better mechanical properties. However, the interaction between components and clay impurities affect obviously on mechanical properties rather than thermal properties.

Acknowledgement

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