

THERMAL ANALYSIS OF NANOCOMPOSITES: AN OVERVIEW OF SELECTED POLYMER/MONTMORILLONITE LAYERED SILICATE SYSTEMS

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Abstract

Numerous polyolefin and polyester nanocomposite systems containing varying amounts of montmorillonite-layered silicates (MLS), were examined by differential scanning calorimetry, thermogravimetric analysis, and dynamic mechanical analysis. Thermal properties such as the glass transition temperature and melting temperature of the nanocomposite vary slightly from the homopolymer while degradation temperatures and modulus values have improved significantly.

Introduction

Nanocomposites are classified as composite systems in which nano-sized inorganic elements are uniformly dispersed within an organic polymer matrix. A homogeneous dispersion of inorganic particles can lead to a large interfacial area between the nano-sized particles and the polymer matrix. It is this large interfacial area that provides superior properties over conventional composite systems at much smaller inorganic loading levels¹.

MLS is a type of clay material that is commonly used in nanocomposite systems. This material consists of layered silicate sheets that range from 100-200nm in length and 1nm in thickness. Montmorillonite is naturally hydrophobic and is typically modified to optimize compatibility with a given polymer. Substituting the hydrophilic alkali metal and alkaline earth interlayer cations of the natural clay with organic ammonium and phosphonium cations, respectively, changes the character of the MLS. This change in character allows for easier dispersion in the host polymer¹⁻².

Thermal property enhancement has been observed in numerous nanocomposite systems. Nanocomposites based on polymers such as poly(lactic acid)^{2,3}, polysiloxane⁴, and nylon-6⁵, have demonstrated improved thermal properties over the neat polymer. Typical thermal properties that have been affected by nanocomposites are heat distortion temperature (HDT)¹, decomposition temperature⁶, thermal expansion coefficient⁶, and crystallization rates⁵.

Fornes and Paul have shown that nylon-6 nanocomposites prepared through injection molding

techniques demonstrated that crystallization kinetics of the nanocomposites were dramatically increased at very low filler concentrations. Processing conditions such as rapid cooling and strain levels also appeared to affect crystallization rates⁵. Alexandre et al. has shown that ethylene vinyl acetate copolymer (EVA), thermoplastic polyurethane, and polycaprolactone-based nanocomposites exhibit greater thermal stability than the neat polymer. Thermal stability enhancement of 60°C was not uncommon in their nanocomposite samples⁷. Interestingly enough, Bharadwaj et al. were able to process crosslinked polyester nanocomposites that display the exact opposite behavior. The onset of degradation is slowly accelerated upon the addition of MLS particles. It is believed that this is due to the presence of increasing amounts of hydroxyl groups in the organic modifier⁸.

It is clear that nanocomposites and their properties are not entirely understood at this time. It is our objective to provide a sampling of the thermal properties of selected nanocomposite systems and their base-polymers in this work. Experimental results will show that property enhancement observed in some nanocomposite systems are not seen in others. In fact, some nanocomposite systems processed in similar fashion behave in completely opposite ways when observing such behaviors as thermal stability and crystal nucleation.

Experimental

Materials

Three nanocomposite systems were examined in this study. The base polymers used to form the nanocomposites were polylactic acid (Natureworks 4041D), low-density polyethylene (6831), and semi-crystalline polyethylene terephthalate (KOSA 1101). Suppliers of these resins are Cargill/Dow, Dow Chemical, and KOSA respectively.

The polylactic acid (PLA) nanocomposite contained 10% by weight plasticizer (Citroflex A-2), and varying amounts of MLS (Cloisite 25A). The plasticizer was necessary in order to extrude flexible films that were not brittle.

The low-density polyethylene (LDPE) nanocomposites contained 2.5% by weight compatibilizer (Polybond 3109) and varying amounts of MLS (Cloisite 20A). Polybond 3109 is a common coupling agent for polymers and inorganics.

Finally, the polyethylene terephthalate (PET) nanocomposites contained 0.5% by weight maleic anhydride as a coupling agent, along with various amounts of MLS (Cloisite 30B). The purpose of the maleic anhydride was to polarize the PET polymer in order to more easily disperse the MLS.

Processing

All of the nanocomposite samples were initially compounded into pellets using a twin-screw extruder. The resins, clays, plasticizers, and coupling agents were added into various zones of the extruder and extruded into a continuous strand. This strand was cooled in a water bath and pelletized. Once pelletized, the nanocomposite pellets were then processed into films. The LDPE and PLA nanocomposite films were formed through blown-film processing on a twin-screw extruder, while the PET nanocomposites were processed via cast-film processing on a single-screw extruder fitted with a chilled-roll system.

Thermal Characterization Methods

A Perkin-Elmer Differential Scanning Calorimeter (DSC) Pyris-1 fitted with Pyris software was used for the determination of the glass transition temperature, T_g , the melting temperature, T_m , and the crystallization temperature T_c of each film sample. Each sample of 5 to 10 milligrams was run in aluminum hermetic pans. Each sample was heated at least 20°C beyond its isotropic temperature and started below its glass transition temperature. Each sample was run through 2 cycles of heating and cooling in order to eliminate their thermal history effects.

The T_m onset of each DSC curve was analyzed for the onset melting temperature and also for ΔH of the melt. It is the ΔH value that describes crystallization in the polymer film as well as the amount of energy it takes to melt these crystals. Liquid nitrogen was used to run all scans below room temperature. Samples of indium and cyclohexane were used to calibrate the DSC. The Pyris software was used for obtaining all transition temperatures and areas under the peaks for enthalpy values.

A TA Instruments thermogravimetric analyzer (TGA) was used to analyze the decomposition temperature of the films, determine the exact amount of clay in the sample, and evaluate the thermal stability of the nanocomposites in comparison to the neat polymer. The percent weight loss was recorded as a function of temperature at a heating rate of 20°C/min. Nitrogen was used as the testing environment to eliminate any weight fluctuations caused by oxidation of the samples in the testing furnace. Residue values (clay remaining) were taken at 800°C to ensure that all moisture and organics had been eliminated from the sample pan.

Results and Discussion

PLA/MLS 25A Nanocomposite Films

As illustrated in Figure 1, 5% by weight MLS additive provided very little effect on the transition temperatures of the films. The glass transition temperature was not significantly altered as a result of the MLS. This trend was also observed at other concentrations of MLS in the PLA polymer. Although the glass-transition temperature was not affected by the MLS, the degree of crystallization in the films was. As shown in Figure 1, the value for ΔH was lower in the nanocomposite than in the neat film. Since ΔH is directly related to the degree of crystallinity, it is safe to assume that the MLS hindered polymer crystal growth. Again, this trend was observed at other concentrations of MLS from 1-5%.

One property that was significantly affected by the MLS additive is thermal stability. Figure 2 shows just how the incorporation of 5% MLS into the PLA polymer shifts the degradation temperature to higher temperatures. In this example, the degradation temperature of the film was raised by 11°C. Again, this behavior was observed at MLS percentages ranging from 1-5% by weight. The explanation for this phenomenon is not entirely known, but various theories have been published. One such theory states that these types of nanocomposites have been shown to produce a "charring" effect when burned. It is believed that this char product may limit diffusion of the combustion gases and could be the main reason for the fire retardant properties of polymer layered silicate nanocomposites⁹.

LDPE/MLS 20A Nanocomposite Films

It was shown in Figure 2 that the thermal stability of polymers was enhanced through the addition of MLS. This effect was also observed in LDPE/MLS 20A nanocomposite films, but at a much higher level. As indicated in Figure 3, the thermal stability of LDPE films increased by as much as 90°C at a MLS loading level of 7.5% and 60°C at a loading level of 5%. The reason for this highly enhanced thermal stability may lie in the nanocomposite morphology. The TEM image of this sample, shown in Figure 4, suggests an overall intercalated system. Lower magnification images will show the quality of MLS dispersion in the polymer matrix. Unlike the PLA/MLS nanocomposite film, MLS 20A does not appear to affect the degree of crystallization in the polymer. Table 1 lists the measured T_m values for the LDPE/MLS nanocomposite films. The glass transition temperature of the films was not detectable in these scans.

PET/MLS 30B Nanocomposite Films

The final system examined was PET/MLS 30B nanocomposite films. Results from this system differ from those found in the LDPE and PLA systems. As illustrated in Table 2, the films were plasticized by the MLS additive. This is observed in examination of the T_g of the neat and nanocomposite films. As the concentration of MLS in the film is increased, the T_g of the film decreases almost linearly. Although very small, the effect of MLS on the glass-transition of the polymer is significant. It is believed that this effect is due to the hindrance of chain motion in the glassy region because of the MLS platelets.

Figure 5 is the TGA analysis of the PET and PET/MLS film samples. TGA reveals that the MLS additive had a completely opposite effect on the thermal stability of the polymer as was seen in the PLA and LDPE systems. The degradation of the film is actually accelerated when the MLS is added. This may be due to the modification of the MLS and the fact that PET polymers must be processed at higher temperatures than many other polymers, which leads to degradation of the MLS.

Conclusions

In conclusion, this study has provided a glimpse into the thermal properties of a few nanocomposite systems. While some systems may demonstrate enhanced thermal stability, greater degrees of crystallization, lower glass-transition values, or greater melting temperatures, some do not. In fact, some systems show completely opposite behavior. While nanocomposites are becoming more widely known, their properties and behaviors are often questionable and baffling. If there is one constant in all of this, it is the fact that more research must be done in this area to maximize the potential of these complex systems.

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References

1. Vaia, Richard A.; Giannelis, Emmanuel P. "Polymer Nanocomposites: Status and Opportunities" *MRS Bulletin*, May 2001, 394-401.
2. Chang, J.; An, Y.; Cho, D.; Giannelis, E. "Poly(lactic acid) nanocomposites: comparison of their properties with montmorillonite and synthetic mica (II)" *Polymer*, 44, 2003, 3715-3720.
3. Thellen, Christopher. "Investigation of the Processing and Characterization of Blown-Film Nanocomposites Consisting of Polylactic Acid and Organically Modified Montmorillonite Clay". MSE Thesis, University of Massachusetts Lowell, 2003.
4. Burnside, S.; Giannelis, E. "Nanostructure and Properties of Polysiloxane-Layered Silicate Nanocomposites" *Journal of Polymer Science*, 38, 2000, 1595-1604.
5. Forns, T.D.; Paul, D.R. "Crystallization behavior of nylon 6 nanocomposites" *Polymer*, 44, 2003, 3945-3961.
6. Zhu, Z.; Yang, Y.; Yin, J.; Wang, X.; Ke, Y.; Qi, Z. "Preparation and Properties of Organosoluble Montmorillonite/Polyimide Hybrid Materials" *Journal of Applied Polymer Science*, 73, 1999, 2063-2068.
7. Alexandre, Michael; Beyer, Gunter; Dubois, Philippe "Layered-silicate polymer nanocomposites: preparation and characterization of physico-mechanical, thermal and morphological properties" www.morris.umh.ac.be/SMPC/Posters/MIALBPG2001.pdf.
8. Bharadwaj, R.K.; Mehrabi, A.R.; Hamilton, C.; Trujillo, C.; Murga, M.; Fan, R.; Chavira, A.; Thompson, A.K. "Structure-property relationships in cross-linked polyester-clay nanocomposites" *Polymer*, 43, 2002, 3699-3705.
9. Paul, Marie-Amelie; Alexandre, Michael; Degee, Philippe; Henrist, Catherine; Rulmont, Andre; Dubois, Phillippe. "New Nanocomposite Materials Based on Plasticized Poly(l-lactide) and Organically Modified Montmorillonites: Thermal and Morphological Study." *Polymer*, 2003, 44, 443-450.

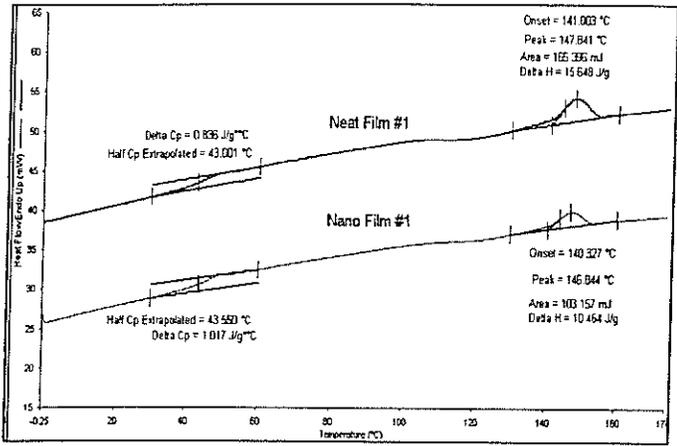


Figure 1: DSC analysis of neat PLA and nanocomposite PLA films.

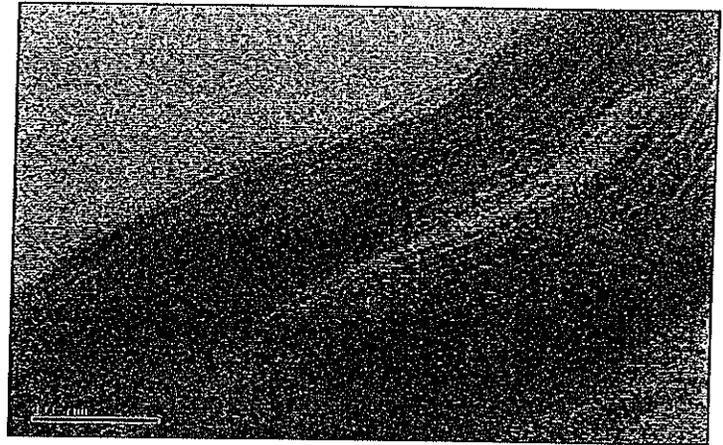


Figure 4: TEM image of LDPE/MLS nanocomposite film containing 7.5% MLS 20A.

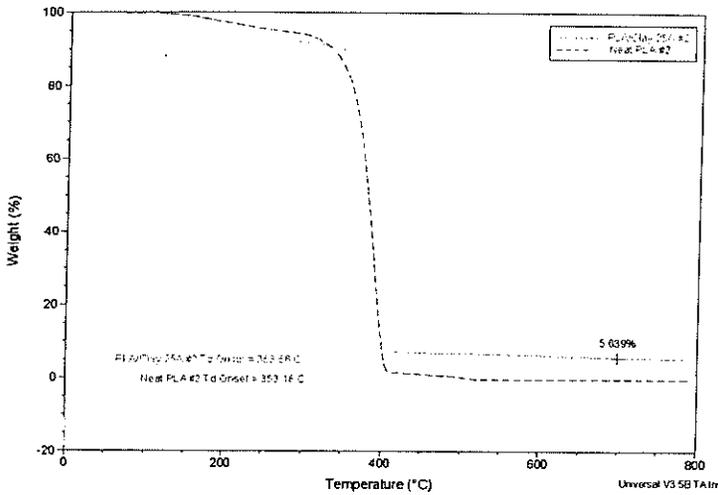


Figure 2: TGA analysis of neat PLA and nanocomposite PLA films.

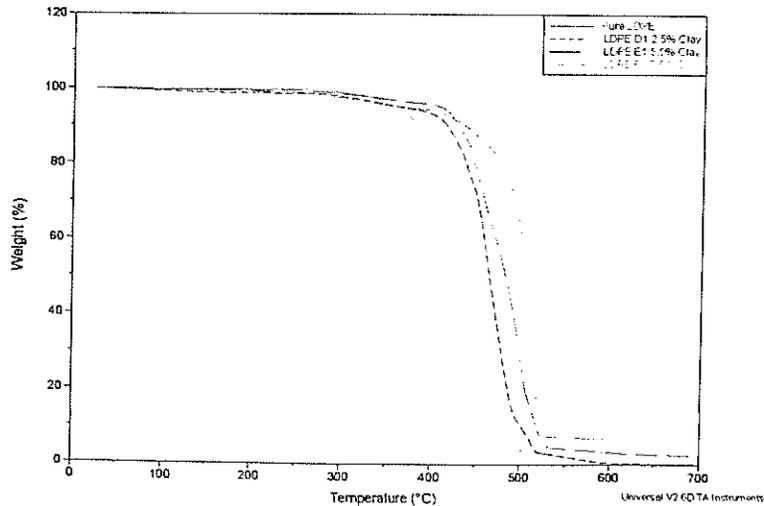


Figure 3: TGA analysis of neat LDPE and nanocomposite LDPE films.

Table 1: Measured Tm Values of LDPE and LDPE/MLS Nanocomposites

Sample	Melt Temperature (°C)
LDPE	109
LDPE/montmorillonite (2.5%)	110
LDPE/montmorillonite (5%)	110
LDPE/montmorillonite (7.5%)	111

Table 2: DSC Results for PET and PET/MLS Nanocomposite Films

Sample	Tg (°C)	ΔH (J/g)	Tc (°C)
Neat PET	81.9	32.8	190.3
PET + MA	80.3	44.6	203.6
PET + 2% MLS	78.2	47.5	209.0
PET + 5% MLS	76.2	49.3	211.9
PET + MA + 2% MLS	78.4	48.5	207.8
PET + MA + 5% MLS	77.5	49.8	210.5

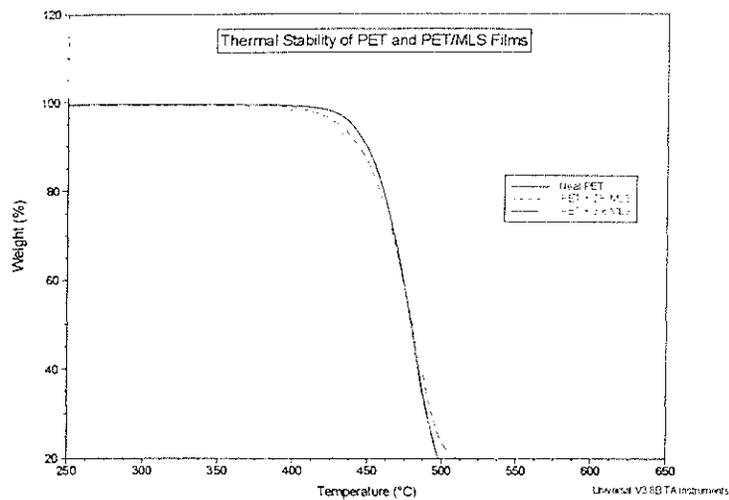


Figure 6: TGA of PET and PET/MLS nanocomposite films.

Keywords: Nanocomposite, Film, Crystallization, Extrusion