Effect of Sequential Mixing and Compounding Conditions on Cellulose Acetate/Layered Silicate Nanocomposites

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Injection molded nanocomposites have been successfully fabricated from cellulose acetate (CA), eco-friendly triethyl citrate (TEC) plasticizer, and organically modified clay with and without maleic anhydride grafted cellulose acetate butyrate (CAB-g-MA) as a compatibilizer. The effects of processing conditions such as mixing methods, pre-plasticizing times, extruder retention times (RT) and addition of compatibilizer on the performance of these nanocomposites have been evaluated. The cellulosic plastic with CA/TEC (80/20 wt%) was used as the polymer matrix for nanocomposite fabrication. The morphologies of these nanocomposites were evaluated through X-ray diffraction (XRD) and transmission electron microscopy (TEM) studies. The mechanical properties of the nanocomposites were measured and have been correlated with the XRD and TEM observations. From all of the sequential mixing methods used, powder-powder mixing leads to the most transparent nanocomposites. Cellulosic plastic-based nanocomposites obtained using increased pre-plasticizing times and RT showed better exfoliated structures. In the system containing compatibilizer, the minimum retention time required for obtaining almost completely exfoliated hybrid nanocomposites was shorter than in the system without compatibilizer.

KEY WORDS: Biopolymer; cellulose acetate; nanocomposites; plasticizing; exfoliated.

INTRODUCTION

Advanced technology in petrochemical based polymers has brought many benefits to mankind. However, it has become evident that the ecosystem is being disturbed because of non-biodegradable plastic materials. The environmental impact of persistent plastic wastes is growing into a more global concern. Currently, there is considerable interest in biodegradable polymers, which can be used as alternatives to traditional plastics, thus reducing the pollution caused by plastic wastes. Tremendous amounts and varieties of plastics, notably polyolefins, polystyrene, and poly (vinyl chloride) are currently produced from fossil fuels, consumed, and discarded into the environment, ending up as non-degradable wastes.

Development of polymer/clay nanocomposites (PCNs) is one of the latest evolutionary steps in polymer technology. Nanocomposites offer the potential for the diversification and application of polymers due to their excellent properties such as high heat distortion temperature, dimensional...
stability, improved barrier properties, flame retardancy, and enhanced physico/thermo-mechanical properties. Polymer layered silicate nanocomposites have been studied for more than 50 years [1] although the concept was reintroduced by researchers from Toyota [2] who made nanocomposites from polyamide 6 and organophilic clay. Extensive literature is now available on nanocomposites with matrices of epoxy [3, 4], polyamide [5], polystyrene [6], polyurethane [7], poly(ethylene terephthalate) [8], and polypropylene [9]. Automakers see opportunities for using polymer clay nanocomposites, especially with polypropylene (PP), thermoplastic polyolefin (TPO) and nylon as matrices [10].

Biobased polymers are moving into the mainstream and the polymers that are biodegradable or based on renewable feedstock may soon be competing with commodity plastics. However, the performance limitations and high cost have limited these biopolymers to niche markets. Nanoreinforcement of biobased polymers with organoclay can create new value-added applications in the 21st century materials world. Biodegradable polymers obtained from renewable resources, for example cellulose plastic, thermoplastic starch (TPS), polyactic acid (PLA, corn-derived plastic), and polyhydroxyalkanoates (PHAs, bacterial polyesters) are some of the potential biopolymers, which with the effective reinforcement with nanoclay can generate nanocomposites [11-16]. However, such newly developing nanocomposites need to be sustainable in order to compete with the existing petroleum-based polymer clay nanocomposites.

Cellulose is attracting interest as a substitute for petroleum feedstock in making plastic (cellulosic plastic, e.g., cellulose esters) in the commercial market [17]. Cellulosic plastics like cellulose acetate (CA), cellulose acetate propionate (CAP), and cellulose acetate butyrate (CAB) are thermoplastic materials produced through esterification of cellulose. Raw materials such as cotton, wood cellulose, and sugarcane bagasse are being used to make cellulose ester biopolymers in powder form. Such cellulose ester powders are extruded in the presence of different plasticizers and additives to produce commercial grades of cellulosic plastics in pelletized form. The main drawback of cellulose acetate plastics is that the melt processing temperatures exceed decomposition temperatures. This dictates that cellulose acetates need to be plasticized. Phthalate plasticizers, used in commercial cellulose ester plastic, however, are now under environmental scrutiny since they are suspected of posing a health threat [18]. Thus there is some concern about their long-term use. One of our main targets is to replace phthalate plasticizers with eco-friendly plasticizers like citrates[19] and blends of citrates and derivatized vegetable oil in designing more eco-friendly cellulosic plastic formulations.

In our current investigation of cellulose acetate plastic-clay nanocomposites, we have chosen triethyl citrate (TEC) as the plasticizer. In our previous investigation [20], the optimal content of TEC was found to be 20 wt%. In this study, the CA/TEC ratios used were 80/20 wt%. Melt processing through extrusion followed by injection molding was adopted in fabricating the nanocomposites. Organically modified montmorillonite clays were added at 5 wt% loading into the plasticized CA matrix during melt extrusion with high shear force in order to obtain exfoliated and/or intercalated clay particles inside the continuous matrix. The proper extrusion processing parameters are important for obtaining good exfoliated nanocomposites. In this paper, the effects of processing conditions such as sequential mixing methods, pre-plasticizing times, melt compounding temperature, extrusion retention times, and compatibilizer (CAB-g-MA) content on the performance of these nanocomposites have been evaluated. The morphological and mechanical properties of the resulting nanocomposites were investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM), and mechanical testing (flexural strength and modulus). Furthermore, material damping behavior was assessed by dynamic mechanical thermal analysis (DMTA) to understand whether nanoreinforcement of the material could improve vehicle NVH (noise, vibration, and harshness) for potential automotive applications.

**EXPERIMENTAL DETAILS**

**Materials**

Cellulose acetate, CA (CA-398-30, acetyl 39.7 wt%, hydroxyl 3.5 wt%, (degree of substitution (DS) of CA = 2.45)) and cellulose acetate butyrate, CAB (CAB-381-20, butyryl 37 wt%, acetyl 13.5 wt%, hydroxyl 1.8 wt%) without additives in powder form and triethyl citrate (TEC, Citroflex 2) were supplied by Eastman Chemical Co. and Morflex, Inc., respectively. One organically modified montmorillonite (organoclay), Cloisite 30B, was purchased from Southern Clay Co. The ammonium