Sustainable Nanocomposite Materials from Cellulosic Plastics

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ABSTRACT

Injection molded nanocomposites were successfully fabricated from triethyl citrate (TEC) plasticized cellulose acetate (CA) and organically modified clay. Maleic anhydride grafted cellulose acetate butyrate (MA-g-CAB) was used as a compatibilizer. The effect of compatibilizer contents on the performance of these nanocomposites were evaluated. The mechanical properties of these nanocomposites were correlated with the XRD and TEM observations. Cellulosic plastic-based nanocomposites with 3 wt.% compatibilizer showed better exfoliated structure than the counterpart having 0 or 7.5 wt.% compatibilizer contents. The use of compatibizer improved the tensile strength, modulus of elasticity, and thermal stability of these nanocomposites as compared to the counterpart nanocomposite in absence of the said specific compatibilizer.

Keywords: Biopolymers, clay, nanocomposites, cellulose ester, compatibilization,

1 Introduction

Renewable resource-based biodegradable polymers including cellulosic plastic (plastic made from wood), polylactic acid (PLA; corn-derived plastic) and polyhydroxyalkanoate (PHA; bacterial polyesters) are potential biopolymers, which by effective reinforcement with nanoclay can generate the so-called 'green' nanocomposites [1]. Cellulose from trees is attracting interest as a substitute for petroleum feedstock in making plastic (cellulosic plastic - cellulose esters) in the commercial market [2]. Cellulosic derived plastics such as cellulose acetate (CA), cellulose acetate propionate (CAP), and cellulose acetate butyrate (CAB) are thermoplastic materials produced through esterification of cellulose. However, the main drawback of cellulose acetate plastic is that its melt processing temperature exceeds its decomposition temperature. In order to overcome this problem, these plastics should be plasticized. The phthalate plasticizer, used in commercial cellulose ester plastic, is now under environmental scrutiny and perhaps poses a health threat raising concerns about their long-term use. One main objectives of this research is to find a viable replacement for phthalate plasticizer with eco-friendly plasticizers such as citrate [3], blends of citrate, and derivatized vegetable oil [4]. Melt processing through extrusion-injection molding was adopted in fabricating the nanocomposites. By adding organically modified montmorillonite clay into plasticized CA matrix during melt extrusion with high shear force, we expect to get exfoliation and/or intercalation of clay inside the continuous matrix. Optimization of processing conditions and effect of different compatibilizer contents are investigated in this paper in order to obtain better exfoliate clay hybrid. Morphological (X-ray diffraction, XRD, Transmission Electron Microscope, TEM), mechanical and thermal properties were evaluated.

2 Experimental Details

Materials: Cellulose acetate, CA (CA-398-30) without additives in powder form and triethyl citrate (TEC, Citroflex 2) were supplied by Eastman Chemical Co., Kingsport, TN and Morflex, Inc, North Carolina, respectively. The degree of substitution of cellulose acetate (CA) is 2.45. Organically modified montmorillonite (organoclay) Cloisite 30B was purchased from Southern Clay Co. The ammonium cations present in Cloisite 30B are methyl tallow bis-2-hydroxyethyl quaternary ammonium. As compatibilizer, maleic anhydride grafted cellulose acetate butyrate (MA-g-CAB) was synthesized [5] and characterized [5, 6].

Melt compounding: Prior to processing, CA, MA-g-CAB and organoclay were dried in a vacuum oven at 80^{o} C for 24 hrs. The CA powder and TEC plasticizer (CA:TEC = 75:25 by wt. %) were mixed mechanically with a high speed mixer for 5 min and this mixture was stored in a zip-lock bag for 75 minutes. The pre-plasticized mixtures were then mixed with 5wt% organoclays and compatibilizer MA-g-CAB 0 to7.5wt% followed by mixing with the high-speed mixer. Then such mixtures various formulations (pre-plasticized CA + organoclay + compatibilizer) were melt compounded and plasticized simultaneously at 200-210^{o} C for 6 minutes at 100 rpm with a micro-compounding molding equipment, DSM Micro 15 cc compounder, DSM research, Netherlands [5].

Table 1. Comparison of tensile, flexural, Notched Izod impact, HDT, and coefficient of thermal expansion (CTE) properties of plasticized CA /Cloisite 30B/compatibilizer (MA-g-CAB) hybrids

Sample No	CA/TEC Matrix (wt%)	Organo-clay contents (wt%)	Compa-tibilizer (wt%)	Tensile Strength (MPa)	Tensile Modulus (GPa)	Tensile Elonga-tion (%)	Flexural Strength (MPa)	Flexural Modulus (GPa)	Impact Strength (J/m)	HDT (^oC)	CTE (um/m ^oC)
a	100	0	0	70.0 ± 5.1	2.20± 0.1	8.8±1.2	65.4 ± 2.0	2.4±0.2	55 ± 6	85± 3	125 ± 7
b	92.5	0	7. 5	74.0± 6.3	3.0 ± 0.9	7.5±0.8	67.3± 0.9	2.4 ± 0.2	35 ± 13	96 ±2	110 ± 9
c	95	5	0	81.8± 5.9	3.6 ± 0.6	10.0±0. 2	74.7± 0.9	2.7 ± 0.5	25 ± 4	90 ±3	102 ± 3
d	92	5	3	84.7± 0.9	3.7 ± 0.6	9.5±1.2	81.7± 0.9	3.1 ± 0.6	29 ± 1	98 ±3	94 ± 10
e	87.5	5	7. 5	84.2± 1.9	3.7 ± 0.4	8.6±0.9	77.4± 1.2	3.0 ± 0.4	13 ± 1	94 ±4	92 ± 6

Characterization of nanocomposites: The samples made by injection molding were used for different characterizations. XRD studies of the samples were carried out using a Rigaku 200B X-ray diffractometer (45 kV, 100 mA) equipped with CuK radiation (= 0.1516 nm). A transmission electron microscope (TEM) (Jeol 100CX) was used to analyze the morphology of nanocomposites at an acceleration voltage of 100 kV. Microtomed ultra thin film specimen with thickness of 70 nm were used for TEM observation. A dynamic mechanical analyzer (2980 DMA, TA instruments, USA) was used to measure the heat deflection temperature (HDT) of nanocomposites with a load of 66 psi according to ASTM D648, and dynamic storage modulus and tan d was measured. Tensile properties and flexural properties of injection mold specimens were measured with a United Testing System SFM-20 according to ASTM D638 and ASTM D790 respectively. Notched Izod impact strength was measured with a Testing Machines Inc. 43-02-01 Monitor/Impact machine according to ASTM D256 with a 1 ft-lb pendulum.

3. Results and Discussion

3.1 Microstructure of hybrids

In order to obtain better exfoliated nanocomposites, compatibilizer synthesized by us was added to pre-plasticized CA /Cloisite 30B composition. Figure 1 shows the XRD patterns of pure Cloisite 30B clay and plasticized CA/ Cloisite 30B nanocomposites with different compatibilizer MA-g-CAB contents. The XRD peak shifted from 5.0° for pure Cloisite 30B to 2.36° for plasticized CA /organoclay (95/5 wt%) nanocomposite without compatibilizer (Figure 1a). This indicates significant intercalation and slight exfoliation in the hybrid structure.

For plasticized CA /Cloisite 30B/compatibilizer nanocomposites with 3wt% and 7.5wt% of compatibilizer, no clear peak was observed at 2.36° (Figure 1b and 1c), suggesting complete exfoliation of organoclays in the CA/TEC matrix. The XRD curves (figure 1) show that about 3-wt%

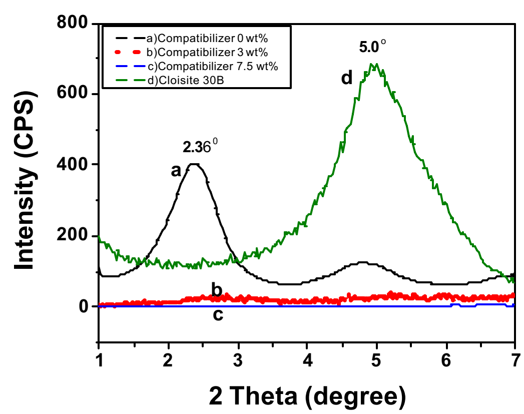

Figure 1. XRD patterns of the plasticized CA / compatibilizer /Cloisite 30B 5 wt% hybrids with different compatibilizer MA-g-CAB: a) compatibilizer 0 wt%, b) compatibilizer 3 wt%, c) compatibilizer 7.5wt%, d) Neat clay (Cloisite 30B).

compatibilizer is needed for almost completely exfoliated clay nanocomposite fromthe plasticized CA /organoclay system. In case of plasticized CA /organoclay hybrid nanocomposites, the maleated CAB will not only enter into the clay gallery but also will react with the free OH groups of the CA structure; thus improving the overall comptibilization of entire system.

Figure 2 shows TEM, which explains the morphology of the composites. The TEM images show that the plasticized CA / organoclay/ compatibilizer hybrid (Figure 2b and 2c) have better exfoliation than the counterparts without compatibilizer (Figure 2a).

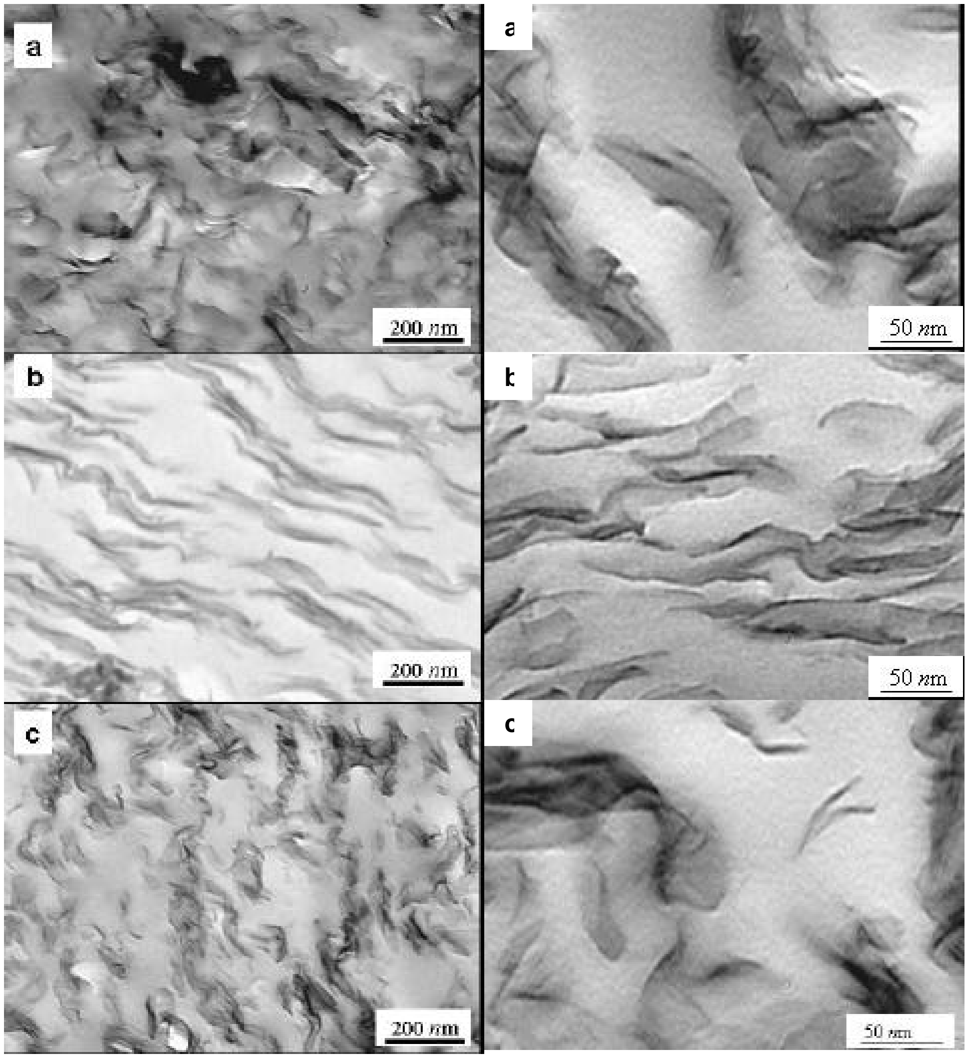

Figure 2 .TEM of the plasticized CA / compatibilizer /Cloisite 30B 5 wt% hybrids with different wt % of compatibilizer MA- g -CAB: a) 0 wt% compatibilizer b) 3 wt% compatibilizer, c) 7.5wt%compatibilizer.

From figure 2a, it can be seen that some the intercalation and aggregation of clay remain in the matrix. It can also be observed from the XRD and TEM results that for exfoliation of clay in CA polymer, the optimum loading of compatibilizer MA-g-CAB is important. The TEM observations of nanocomposites are correlated to validate XRD results.

3.2 Mechanical Properties

Table 1 shows the tensile, flexural, and notched Izod impact, heat deflection temperature (HDT), and coefficient of thermal expansion (CTE) properties of the plasticized CA /Cloisite 30B/MA-g-CAB hybrids with different compatibilizer MA-g-CAB contents. The strength and modulus (flexural and tensile) of the hybrid sharply increased with increasing compatibilizer contents. On the other hand, the notched Izod impact strength and the tensile elongation at break of the hybrids decreased with increasing compatibilizer contents. This indicates that compatibilizer is effective in increasing the adhesion between organoclay and CA molecular chains. The tensile strength and modulus of hybrids with 3-wt% compatibilizer increased by 20%, and 68% respectively compared to hybrid with no compatibilizer. Also flexural strength and modulus were increased about 20 and 25% respectively.

HDT was increased 10% and CTE was decreased 24%, at 3-wt% MA-g-CAB loaded hybrid making the nanocomposites more stable in comparison to the pure matrix. But Izod impact strength was decreased about 50%. HDT property is closely related to the T_g of thermo plastics, therefore, HDT behavior of CA/TEC matrices and hybrids were similar to T_g behavior from DMA curve (Figure 4)

The above results indicate that the better exfoliation and good dispersion of clay in the CA/TEC matrix give good mechanical properties. 3-wt% compatibilizer loading is optimum for HDT, CTE, and mechanical improvement.

3.3 Dynamic Mechanical Properties

Figures 3 and 4 show temperature dependent of storage modulus, tan d, and glass transition temperature (T_g) for the pristine plasticized CA matrix and the hybrid nanocomposites respectively. Storage modulus & T_g of plasticized CA (figures 3) and plasticized CA /clay hybrid composites (figures 4) increased with increasing compatibilizer contents. A possible explanation for improvement of modulus with reinforcement of clay might be attributed to the creation of a three-dimensional network interconnecting long silicate layers, thereby strengthening the material through mechanical percolation [7]. In figure 3 Tg was shifted from 112^{o}C (for 0% compatibilizer, matrix) to 134 ^{o}C (for 7.5% compatibilizer, matrix). Increase in compatibilizer content as well as addition of clay decreases the segmental motions in the CA backbone due to cross-linking and thereby increasing the T_g.

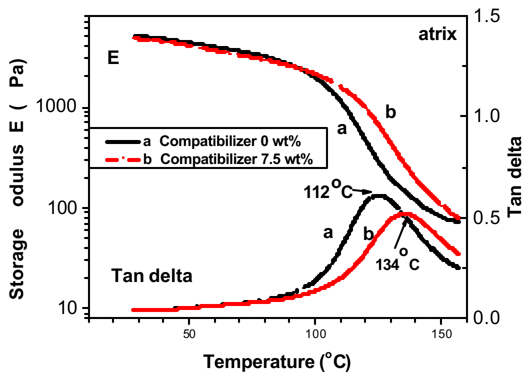

Figure 3. DMA curves of the plasticized CA /compatibilizer matrix with different wt % of compatibilizer (MA-g-CAB) contents.

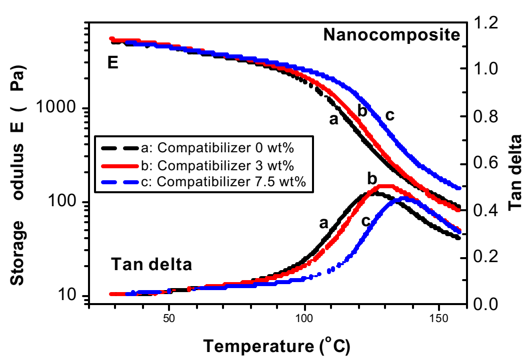

Figure 4. DMA curves of the plasticized CA /compatibilizer / Cloisite 30B hybrid with different wt% compatibilizer (MA-g-CAB) contents.

4 Conclusions

We have successfully developed nanocomposite formulations from cellulose acetate powder, triethyl citrate plasticizer, compatibilizer, and organically modified clay. The tensile strength, modulus and thermal stability of cellulosic plastic reinforced with organoclay was improved by increasing compatibilizer contents where as the impact strength decreased. Nanocomposites with 3 wt.% compatibilizer contents showed better exfoliated structure than the counterpart having 0 or 7.5 wt.% compatibilizer contents.

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References

1. A. K. Mohanty, L. T. Drzal and M. Misra, Polymeric Materials Science & Engineering, 88, 60-61, 2003.
2. S. L. Wilkinson, Chem. Eng. News, January 22, 61, 2001.
3. A. K. Mohanty, A. Wibowo, M.Misra and L. T. Drzal, Polymer Engineering & Science, 43 (5), 1151-1161, 2003.
4. P. F. Bruins, In Plastic Technology; New York Reinhold Publishing Co. Chapman & Hall, Ltd.,:London, 1, 1-7,193-199, 1965.
5. A. Wibowo, A. K. Mohanty, M.Misra, and, L. T. Drzal, Polymer preprint, Spring 2004 (accepted), 227th ACS National Meeting, Anaheim, CA, March 25, 2004.
6. D. Carlson, L.Nie, R. Narayan and P. Dubois, J. Appl. Polym. Sci., 72, 477, 1999.
7. E.P. Giannelis and P.B. Messersmith, US Patent 5554670, Sep. 10, 1996.