Bio-Based Nanocomposites of Cellulose Acetate and Nano-Clay with Superior Mechanical Properties

Mehdi Hassan-Nejad, Johannes Ganster, Andreas Bohn, Manfred Pinnow, Bert Volkert*

Summary: Bio-based nanocomposites were manufactured by melt intercalation of nanoclays and cellulose acetate (CA) with and without plasticizer. Glycerol triacetate (triacetin) as plasticizer up to 30 mass%, and different types of organo-modified and unmodified montmorillonites (MMTs) as filler were used. X-ray diffraction (XRD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM), were used to study clay dispersion, intercalation/exfoliation, and structure of the composites. XRD and TEM revealed very good dispersion and exfoliation of modified clay throughout the CA matrix. While for unmodified clay agglomeration and poor dispersion but an intercalated structure was observed. The mechanical properties of injection moulded test bars were determined by a tensile experiment giving tensile strength, Young's modulus and elongation at break. Adding plasticizer facilitated the processing and up to 20 mass%, increased the tensile strength, Young's modulus and elongation at break as well. Higher amount of plasticizer diminished the tensile properties except elongation showing a slight increase. In all plasticized composites, organo-modified clay improved the tensile strength and at the same time, young's modulus and elongation almost remained constant. On the other hand, plasticized CA compounded with unmodified clay revealed lower properties. In a particular case, compounding of unplasticized CA with unmodified clay resulted in superior mechanical properties with a novel structure. So that, in optimum percentage –5 mass%- of unmodified clay, tensile strength and young's modulus increased significantly by 335% and 100%, to 178 MPa and 8.4 GPa, respectively. This is a dramatic improvement in strength and stiffness of CA. Adding organo-modified clay resulted in a little improvement in tensile properties. SEM pictures of the optimum composite showed a core/shell structure with high orientation in the shell part. It is supposed that this behaviour is caused by the interaction between CA hydroxyl groups and free cations existing in the galleries of unmodified clay.

Keywords: cellulose acetate; injection moulding; nanocomposites

Introduction

Nowadays, the long-term increasing price of petroleum and the decline of its resources has affected all related markets including the synthetic plastics field. At the same time, environmental impact and the polymeric material waste problem due to the usual lack in biodegradation is a growing global concern.

Currently, there is strong concern in bio-based polymers such as cellulosic plastic (plastic made from wood), thermoplastic starch (TPS), polylactic acid (PLA, corn-derived plastic), and polyhydroxy alkanoate (PHA, bacterial polyester), which are environmentally friendly, based on renewable resources and have potential to compete with existing commodity polymers.

Fraunhofer-Institute for Applied Polymer Research, Geiselbergstr. 69, D-14476 Potsdam-Golm, Germany
E-mail: ganster@iap.fhg.de

Cellulose is an important part of natural macromolecules, which is the most abundant organic compound on the earth. According to a report of the Food and Agriculture Association of the USA, $3270 \times 10^9\,m^3$ of cellulose exists on earth.[1]

Cellulose derivatives like cellulose acetate (CA), cellulose acetate propionate (CAP), and cellulose acetate butyrate (CAB) are thermoplastics produced through esterification of cellulose. Although, cellulose and its derivatives are known for long time and widely use in fibre producing, coating, etc. yet there are not too many attempts for injection moulding applications.

One problem of melt processing of cellulosic materials is the existence of a narrow window between the melting point and decomposition point. Using plasticizer is a method to facilitate the process and remove this problem. In addition, nanocomposites fabricated through melt intercalation of polymers into layered silicates recently have gained much attention for their easy availability, low cost, and more importantly environmentally friendliness. There are some attempts to improve CA properties by compounding with plasticizer and nanoclay[2,3] and also using a compatibilizer through melt intercalation.[4,5] Alternatively, the solution method can be applied to improve homogeneity and intercalation/exfoliation[6–8] but not for injection moulding applications which are the subject of the present paper.

This new family of composites frequently exhibits remarkable improvements of mechanical and materials properties compared with polymers or conventional micro and macro composites. Improvements can be in terms of high storage modulus, higher tensile and flexural properties, higher heat distortion temperature and thermal stability, increased gas barrier properties and decreased flammability. Nanoreinforcements of biodegradable polymers have strong promise in designing eco-friendly green nanocomposites for several applications.

In the current investigation our concern is improving the mechanical properties of CA by accompanying layered silicate nano clays through melt compounding. In this study on CA, the effect of plasticizer and nanoclays on the properties of plasticized CA and unplasticized CA were studied. Triacetin (glycerol triacetate) was chosen as plasticizer. Melt processing through kneading-extruding-injection moulding is adopted in fabricating the nanocomposites. By compounding unmodified MMTs and organo-modified MMTs with plasticized and unplasticized CA via melt extrusion, an improvement in mechanical properties was attempted.

This paper reports the results of optimised processing conditions, varying the amount of plasticizer and different types of unmodified and organo-modified MMTs. XRD, TEM, SEM, and tensile properties of the resulting plasticized CA and different types of nano-composites were used to evaluate the successful preparation.

Experimental Part

Materials

In this study, cellulose acetate, CA with degree of substitution (DS) = 2.63 without additives in powder form was used. 1,2,3-triacetoxypropane (triacetin or glycerin triacetate) as supplied by Aldrich was used as the plasticizer. Three different layered silicate clays, one unmodified (Dellite LVF, cation exchange capacity (CEC) = 105 mequi/100 g), and two organo-modified (Dellite 67G, modified by dimethyl-dihydrogenated tallow ammonium and Dellite 43B, modified by dimethyl-benzyl-hydrogenated tallow ammonium), were supplied by LAVIOSA, S.p.A Co., Italy.

Melt Compounding and Injection Moulding

Three plasticized CA composites with 10, 20, and 30 mass% of triacetin were prepared and in each case the effect of clay by adding 5 mass% of different clays was studied.

CA and clay were dried in a vacuum oven at 80 °C for 24 h before use. The clay was immersed in triacetin for 24 h, and then was premixed with powder CA in a mechanical-high-speed mixer for 5 min. The unplasticized CA and clay was compounded in the same procedure, just avoiding introducing plasticizer. The mixture of various formulations was kneaded in a Brabender mixer for 20 min at 230 °C followed by extrusion at the same temperature in a co-rotating twin screw compounder (Haake minilab) at 200 rpm. Subsequent injection moulding was performed in a Haake mini-jet with 230 °C barrel and 110 °C mould temperature to obtain dumbbell-shaped test bars according to ISO 527, type 5 A.

Characterization

TEM images were taken from cryogenically microtomed utrathin sections (60 nm) using a Phillips CM 200 at an acceleration voltage of 120 KV. SEM images were taken from JSM 6330 F (Jeol, Japan). XRD studies of the samples were carried out using a Bruker-AXS, two-circle-diffractometer D 5000 (46 KV, 30 mA) equipped with Cu Kα radiation ($\lambda = 0.15418$ nm) and a curved graphite crystal monochromator at a scanning rate of 0.1°/50 sec.

Tensile properties of samples were measured using a Zwick 1445 universal testing machine at 23 °C and 50% relative humidity. Initial clamp separation and crosshead speed were 44 mm and 22 mm/min, respectively. All measurements were performed at least for six replicated of dumbbell shaped specimens and averaged.

Results and Discussion

Wide Angle X-ray Scattering (WAXS)

The extent of MMT intercalation and dispersion is usually judged from WAXS results but has to be complemented by transmission electron microscopy. The X-ray diffraction patterns of samples with unmodified MMT (Dellite LVF) and organo-modified MMT (Dellite 43B) are shown in Figure 1 and 2, respectively.

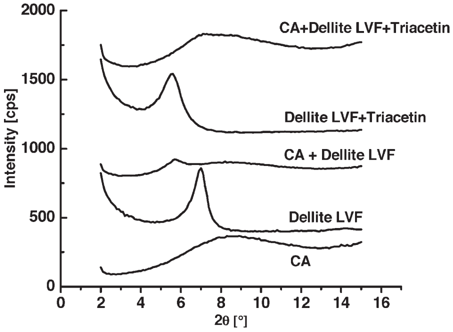


Figure 1.
Wide angle X-ray diffraction scans of compositions using unmodified clay.

The WAXD patterns from Figure 1 show that when unmodified MMT was immersed into triacetin, the diffraction peak of MMT (001) silica sheets moved from 7.0° to 5.5°. According to the Bragg diffraction equation ($2d\sin\theta = \lambda$), the distances d_{001} between the layers were 1.26 and 1.61 nm, respectively, which indicates that the triacetin had intercalated into the layers of Dellite LVF, swelling the clay structure. In contrast, cf. Figure 2, immersed Dellite 43B produces a slight peak shift from 4.5° to 4.8° so distances d_{100} decreased from 1.96 to 1.84 nm. In this case, apparently, triacetin was introduced into the galleries with either changing the modifier conformation to give a smaller lateral size or displacing some of the dimethyl-benzyl-hydrogenated tallow ammonium causing the same effect.

Compounding of CA with Dellite LVF and Dellite 43B resulted in XRD patterns similar to each other. Broad diffraction

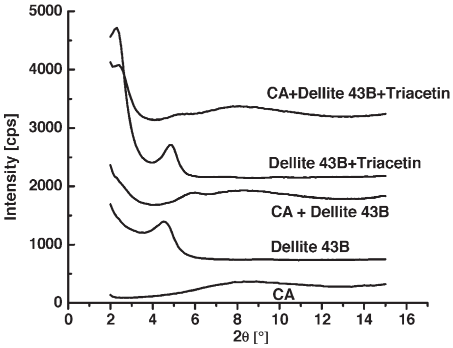


Figure 2.
Wide angle X-ray diffraction scans of compositions using modified clay.

peaks in both cases at 5.8° are visible, indicating a penetration of CA in between the silicate layers enlarging the LVF distance and reducing the 43B distance to roughly the same value.

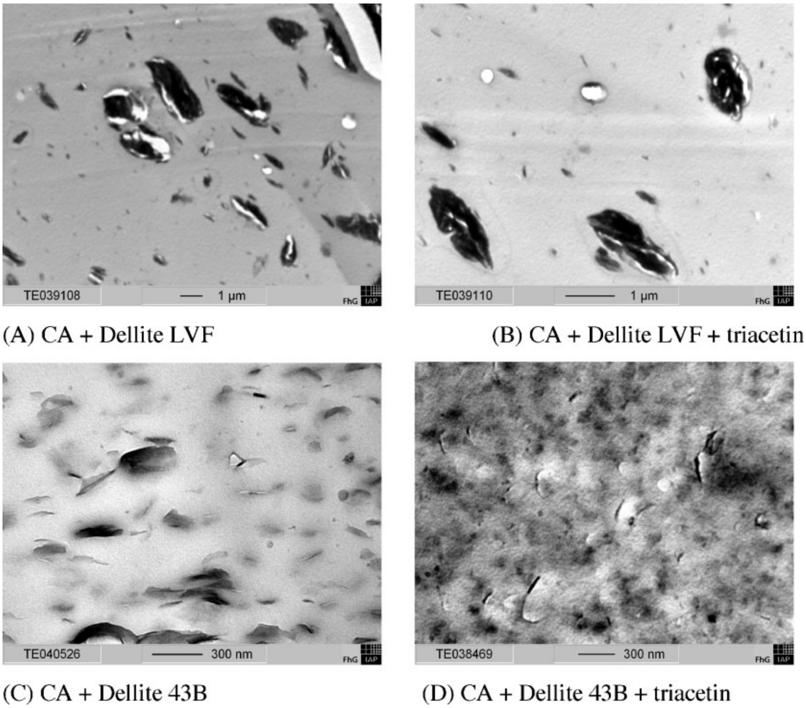
Composites with added triacetin no longer show distinct peaks in the measured range above 2°, i.e. for distances grater then 4.4 nm. Only a hint is visible for 43B at the position of the peak for the 43B clay immersed in triacetin. This could mean either exfoliation or a structure with irregular distances in a way that X-ray no longer detects interferences. This will be further discussed in view of the TEM results.

Transmission Electron Microscopy (TEM)

To study the morphology and, in combination with WAXS findings, the exfoliation in CA/nanoclay and CA/triacetin/nanoclay composites, TEM micrographs are presented in Figure 3.

Obviously, the dispersion of the clays is much better for the composites with modified clays (Figure 3 (C) and (D)), i.e. with Dellite 43B both in the plasticized and unplasticized systems. Nevertheless, it is clear from the X-ray investigations (Figure 1) that the agglomerates visible in the TEM pictures for unmodified clay (Figure 3 (A) and (B)) cannot be the original LVF clay particles. Cellulose acetate and triacetin must have penetrated into the clays in a way as to destroy the regular layer distances in the stacks leading to a disappearance of the distinct X-ray interferences. In any case, there is no exfoliation of the (unmodified) clay particles.

For the modified clay system the situation is different. At least partial exfoliation is visible in Figure 3 (C) and (D) in accord the WAXS findings. A similar behavior was reported for plasticized CA and organo-modified clays[3,5] and other polysaccharides and organo-modified clays.[9–12]



(A) CA + Dellite LVF

(B) CA + Dellite LVF + triacetin

(C) CA + Dellite 43B

(D) CA + Dellite 43B + triacetin

Figure 3.

TEM micrographs of nanocomposites: (A) CA/5 mass% Dellite LVF, (B) CA/10 mass% triacetin/5 mass% Dellite LVF, (C) CA/5 mass% Dellite 43B, (D) CA/10 mass% triacetin/5 mass% Dellie 43B.

Tensile Properties

Effect of Plasticizer

Figure 4 shows the tensile properties of the CA/triacetin compositions with different triacetin content up to 30 mass% of triacetin corresponding to the CA mass. The extruding temperatures for unplasticized CA and CA plasticized with 10, 20, and 30 mass% plasticizer were optimized to give 235, 200, 190, and 180 °C, respectively. It is clear that by incorporating the plasticizer into the CA processing is facilitated and optimal extruding temperature is reduced.

Processing and mechanical properties were considerably improved by the use of plasticizer. Adding just 10 mass% of plasticizer to CA increased the tensile strength by 177% and reached 113.3 MPa from 40.8 MPa. Young's modulus showed a little decrease and elongation with a big improvement jumped to 7% from 1%. By increasing the amount of plasticizer up to 20, 30 mass%, tensile and modulus decreased (80 MPa and 3.4 GPa for CA/triacetin = 80:20 and 34 MPa, 1.9 Gpa, for CA/triacetin = 70:30, respectively).

Plasticized CA with MMTs

Figure 5 shows the mechanical properties of plasticized CA with different mass% of triacetin up to 30 mass% and compounded with organo-modified and unmodified MMTs. Among the clays tested, Dellite 43B gave the best values with 10 mass% triacetin composition, increasing tensile strength and modulus to 119 MPa and 5 GPa, respectively. Adding 5 mass% Dellite LVF to this composition although, showed a little improvement in modulus but tensile strength and elongation at break reduced to 80.0 MPa and 2.2% respectively. CA and 20 mass% of triacetin compounded with 5% Dellite 43B showed a little improvement in tensile strength and modulus. Adding Dellite 67G and LVF to this composition not only did not show improvement but also reduced the properties.

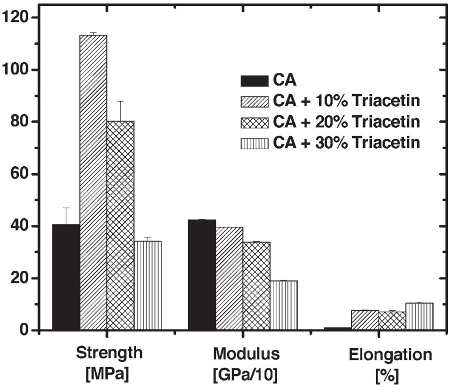


Figure 4.
Effect of triacetin concentration on tensile properties of CA.

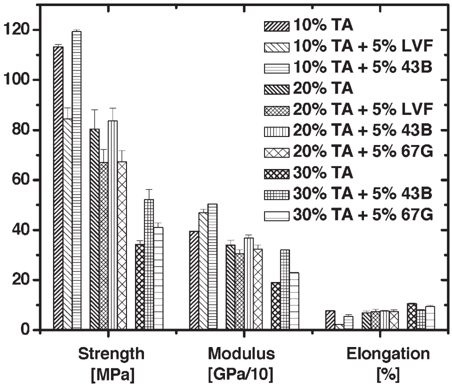


Figure 5.
Effect of different types of MMT on tensile properties of plasticized CA.

The highest improvement was obtained for 30% triacetin again with Dellite 43B, improving both strength and modulus by 52% and 68% to 52.2 MPa and 3.2 GPa respectively. Elongation at break did not show significant changes.

CA with MMTs

In this part, the tensile properties of compounded CA with organo-modified and unmodified clays without plasticizer are presented. Based on the authors' knowledge there is no publication about composition of CA and nano-clays without plasticizer. As presented here, this bio-nano-composite reveals a new structure with superior mechanical properties. Figure 6 shows the tensile properties of

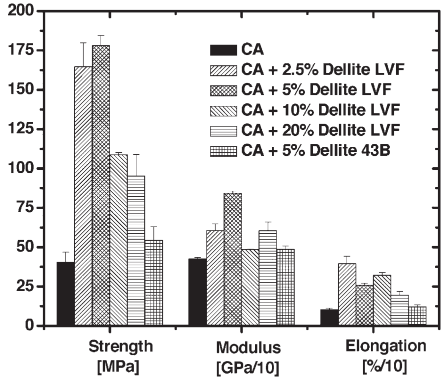


Figure 6.
Effect of different types of MMT on tensile properties of CA.

CA and 5 mass% Dellite 43 B and CA/Dellite LVF with different weight percentages of clay up to 20 mass%, corresponding to CA mass. The extrusion temperature for these compositions was optimized to 235 °C. As shown in the rightmost columns of Figure 6, adding 5 mass%, of Dellite 43 B, gives a little improvement in mechanical properties due to forming exfoliated nanocomposite and good dispersion of nano particles in the CA matrix.

The novel result was achieved when Dellite LVF was used as filler. Adding just 2.5 mass% of this unmodified clay showed significant improvements in mechanical properties of CA. So that, tensile strength and Young's modulus increased by 304% and 45% to 165 MPa and 6.1 GPa, respectively. Increasing the concentration of clay to 5 mass% again showed better properties. With this concentration, tensile strength reached 178 MPa (335% increase) and Young's modulus 100% improvement reaching 8.4 GPa. 5 mass% of Dellite LVF was the optimum percentage. Higher amounts of clay showed reduction in tensile properties. For example, with 20 mass% of Dellite LVF, tensile strength and young's modulus decreased to 95.0 MPa and 6.1 GPa, respectively.

These superior mechanical properties could not be caused by the usual process of intercalation, exfoliation and reinforcing by clay platelets. This process is not corroborated by the TEM results from Figure 3 (A). Rather, a new morphological structure of the injection moulded sample is formed as demonstrated in Figure 7. A core/shell structure was developed with this clay with high molecular orientation in the shell part. Moreover, temperature and temperature difference of cylinder and mould of the injection moulding machine played an important role for the orientation of the nano-composite that resulted in superior mechanical properties. When this difference is high and the mould has a lower temperature, the degree of orientation is high. By decreasing the difference of temperatures and increasing the mould temperature, the degree of orientation is reduced and so, the mechanical properties decrease as well.

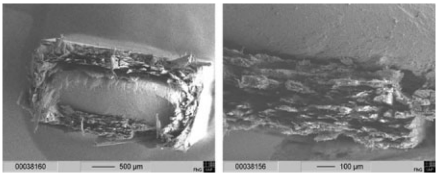


Figure 7.
SEM cryo fracture surfaces of CA with 5 mass% nanoclay Dellite LVF showing core/shell morphology (left) and shell structure (right).

Apparently, the shear forces acting during the moulding process lead in this case to an increased molecular orientation of the CA, as confirmed by X-ray measurements (unpublished results). As it is well known, the mould is filled from the surface to the interior with maximum shear gradients acting at the mould surface generating the highly oriented shell layer. The detailed mechanism and the role of non-exfoliating clay particles in this process is not clear yet and will be the subject of further investigations.

Conclusion

Bio-nanocomposites based on cellulose acetate (CA) with and without plasticizer were successfully fabricated using an extrusion technique followed by injection moulding. The morphology and mechanical properties of the resulting composites were studied. The procedure and processing conditions were optimized to achieve the best mechanical properties. The addition of triacetin as plasticizer, especially at a concentration of 10 mass%, showed the highest improvement in mechanical properties. Plasticized CA up to 30 mass% of plasticizer, compounded with organo-modified nanoclay, showed a slight increase in mechanical properties. On the other hand, unmodified clay in the plasticized systems caused a reduction in mechanical properties. The best mechanical properties were achieved by adding 5 mass% of unmodified clay to plasticizer-free CA leading to an increase in tensile strength and Young's modulus by 335% and 100%, respectively. This unusual behaviour is not caused by the usual intercalation/exfoliation mechanisms in nanocomposites. SEM micrographs showed a core/shell structure with high orientation in the shell part giving the superior mechanical properties. This novel bio-nano-composite might be suitable for replacing oil-based high performance plastics in applications where high strength and stiffness is essential.

Acknowledgements: The authors thank the Agency for Renewable Resources (FNR) for financial support within the project ''Novel Materials from Modified Polysaccharides'' (FKZ 22028705).

[1] T. Hatakeyama, H. Hatakeyama, ''*Thermal Properties of Green Polymers and Biocomposites*'', Kluwer Academic Publisher, **2004**, ISBN 978-1-4020-1907-4, Chapter 3, p. 1.

[2] H. M. Park, M. Misra, L. T. Drzal, A. K. Mohanty, *Biomacromolecules* **2004**, *5*, 2281.

[3] A. C. Wibowo, M. Misra, H. M. Park, L. T. Drzal, R. Schalek, A. K. Mohanty, *Composites Part A: Appl. Sci. Manuf.* **2006**, *37*, 1428.

[4] H. M. Park, A. K. Mohanty, L. T. Drzal, E. Lee, D. F. Mielewski, M. Misra, *J. Polym. Environ.* **2006**, *14*, 27.

[5] H. M. Park, X. Liang, A. K. Mohanty, M. Misra, L. T. Drzal, *Macromolecules* **2004**, *37*, 9076.

[6] R. B. Romero, C. A. P. Leite, M. C. Goncalves, *Polymer* **2009**, *50*, 161.

[7] Z. Shen, G. P. Simon, Y. B. Cheng, *Polymer* **2002**, *43*, 4251.

[8] Y. Li, H. Ishida, *Polymer* **2003**, *44*, 6571.

[9] H. M. Park, W. K. Lee, C. Y. Park, W. J. Cho, C. S. Ha, *J. Mater. Sci.* **2003**, *38*, 909.

[10] K. Dean, L. Yu, D. Y. Wu, *Composites Sci. Technol.* **2007**, *67*, 413.

[11] M. Huang, J. Yu, X. Ma, *Carbohydr. Polym.* **2006**, *63*, 393.

[12] B. S. Chiou, D. Wood, E. Yee, S. H. Imam, G. M. Glenn, W. J. Orts, *Polym. Eng. Sci.* **2007**, *47*, 1898.