"Green" Biocomposites Based on Cellulose Diacetate and Natural Resources - Cellulose Microfibers and Lignin

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Abstract

In the present study, a new process route was developed for cellulose diacetate (CDA) based biocomposites by melt processing. The new strategy developed in this work, makes use of two different plasticizers: a primary "external-type" or "non-reactive-type" plasticizer, Triacetin (TA), added prior to extrusion to enhance the "processing window" of the polymer and a secondary "internal-type" or "reactive-type", Glycerin Polyglycidyl Ether (GPE), added during the extrusion step to reduce the amount of potential volatiles or leachable products in the final product and to help in the reduction of viscosity and thus further improving processability. The thermo-mechanical properties and the morphology of biocomposites with Lyocell microfibres, other wood based fillers, which are typically considered as a reference to produce "green" biocomposites from natural resources, have been analyzed.

1 Introduction

The new field of biodegradable and bio-based polymers, which have some environmental friendly properties, has received growing consideration which has been so far focused specifically on starch based products, PLA (Polylactic acid), PHA (Poly hydroxyl alkanoates) in particular PHB (Poly hydroxyl butyrate), cellulose derived plastics [1], etc. The production of these materials is based on annually renewable agricultural and biomass feedstocks. Moreover biopolymers derived from natural sources can capture markets currently dominated by products based exclusively on petroleum feedstock [2-3].

However, biodegradable polyesters like PLA and PHA generally present some disadvantages over oil based plastics such as low fracture toughness, low glass transition temperature (Tg), high moisture absorption, difficult processing as well as limited applications. Cellulose diacetate (CDA), the most important cellulose derived biopolymer, from an industrial point of view, is a thermoplastic material produced through the esterification of cellulose. Cellulose acetate has been reported to be potentially biodegradable [4], so that new applications of CDA may be envisaged not only for packaging and automotive but also for medical and pharmaceutical applications, in the production of biocomposite materials and other bio-related fields. A variety of raw materials such as cotton, recycled paper, wood cellulose, and sugarcane are used in making cellulose esters in powder form [5-6]. CDA possesses high glass temperature (Tg), which results in limited processability compared with typical commodity plastics. In addition, it has low solubility in common solvents and is not suitable for melt processing as raw material because it starts to decompose before melting. Therefore,

the use of plasticizers to reduce the Tg and the melting temperature is crucial for CDA processing. The role of plasticizers is to decrease the intermolecular forces among the polymer chains, resulting in a softened and more flexible polymeric matrix. Traditionally plasticization of CDA has been accomplished using citrate, phthalates, glycerol derivatives, phosphates, triacetin, etc. Phthalate esters, historically the most common industrially used plasticizers for CDA, have been subjected to environmental scrutiny as a health threat and thus there is now a serious concern about their long-time use. In order to improve the processing of CDA, some studies explored new plasticizers such as poly(caprolacton triol) [7], polyethylene glycol, propylene glycol and dibutyl phthalate [8]. Others combined maleic anhydride, glycol and TA as multi-plasticizers [9]. Their research improved the processing of CDA based materials but at the expenses of their mechanical properties. On the basis of the examined literature, TA was chosen to improve CDA processing in this study, as an environmentally sustainable ("eco-friendly") plasticizer because of its low toxicity and fast biodegradability [10-11].

Moreover, the solubility of triacetin in CDA is high and triacetin is a highly effective plasticizer of CDA. The Gibbs energy of the mixing of the CDA/TA blend has a minimum corresponding to about 40 wt% TA, as a result of the fall in the entropy of the system following the formation of solvates between the functional groups of CDA and triacetin and increase in the entropy of the system as a result of disturbance of the interchain interaction in CDA on its solvation. Exceeding this amount, both Gibbs energy of the mixing increases and the main mechanical properties (modulus, tensile strength, and elongation at break) of materials became very low.

In order to improve mechanical properties, cellulose diacetate was blended with Poly (vinyl pyrrolidone), Poly (vinyl acetate), Poly (N-vinyl pyrolidone – co - vinyl acetate) [12-13], Poly(caprolactone monoacrylate) [14]. A number of trials were made to extend the cellulose diacetate chain through reaction with octadecenyl succinic anhydrides [15] and also with other biopolymer such as Polylactic acid and starch [16-17]. Most of the research related with cellulose diacetate used solvents to dissolve the materials and then proceed with processing. This induced a porous structure and reduced the toughness of the materials. A few researchers used a melt processing approach to improve the performance of cellulosic plastics [18]. Moreover, several studies have tried to develop biocomposite based on cellulose diacetate with natural fibers and fillers [19], while others used organically modified clay to produce "green" nanocomposites [20]. The suitability of cellulose fibers for thermoplastics in general and biopolymers in particular were investigated because of ecological advantages, high mechanical properties, low density and dimensional stability [19,21]. Glasser et al. reported the preparation of composites based on continuous rayon and lyocell fibers reinforced cellulose acetate butyrate (CAB) and other commercially-available thermoplastic cellulose esters by using solution impregnation. The fibers were also surface modified by acetylation to change the interfacial adhesion between the cellulose fiber and cellulose ester matrix, but no significant increase in strength of the composites was observed, leading the Authors to the conclusion that interfacial stress transfer is not a limitation in this system [22-24], although this result could be easily anticipated by anybody knowledgeable enough in the mechanics of continuous fiber reinforced composites. Until very recently, the properties of composites prepared with cellulose esters reinforced with short lyocell fibers have not been considered [25].

In summary, the mechanical properties of biocomposites based on CDA considered in the literature are still not satisfying, in view of their possible application, and use types of processing with are not economically viable on an industrial scale. In particular, the thermal characteristics of the materials developed and their matrix-filler interactions were not much investigated. So far, there are no publications about the effect of multi plasticizers on physical

properties, thermal stability and morphology of cellulose diacetate/cellulose fibers composites under melt processing [26].

Since both the cellulose diacetate and Lyocell fibers can be produced from renewable forest biomass, their manufacture does not imply any competition for land and water required for food production. The interest in the research on biocomposites based on CDA/Lyocell fibers is the development of high-performance, environmentally-friendly, sustainable, potentially biodegradable biomaterials.

2 Materials and testing methods

Materials

Cellulose diacetate (CDA, CAS # 9004-35-7) type LS/SS was kindly supplied by the Acetati Company – Italy, with a degree of substitution of 2.4. Triacetin (TA, also known as glycerin triacetate or 1,2,3-triacetoxypropane, CAS # 102-76-1) was purchased from Aldrich Chemicals as primary plasticizer, while a water soluble epoxy resin, polyglycidyl ether of glycerin (GPE), with an Epoxy Equivalent Weight, EEW = 135 ~ 155 g/eq, type EJ300, purchased by Joong-ang Special Industry Co – south Korea, was used as secondary plasticizer (scheme 1). Tencel® FCP-10/400 microfibers with a diameter of about 10.5 µm and an average fiber length of 390 µm, corresponding to an aspect ratio, ar = 37, were kindly provided by Lenzing AG, Lenzing, Austria. Lignin(Asian Lignin Company - India) were used as reinforcements

Processing

A cellulose diacetate (CDA) powder was mechanically mixed about 10 minutes with different ratios of primary plasticizer (TA) by means of a high speed mixer. After this mixing stage, the fillers and the secondary plasticizer (GPE) were added and mixed for extra 10 minutes, in the same equipment. The resulting mixtures were processed with a MiniLab II Haake Rheomex CTW 5 conical twin-screw extruder (Thermo Scientific Haake GmbH, Karlsruhe, Germany), at a screw rate of 80 rpm/min and a cycle time of 30 seconds, in the temperature range from 170 °C to 210 °C, depending on the material formulation. The processing temperature was chosen for each system at level below the onset of degradation phenomena, evidenced by the appearance of a dark coloring of the material, accompanied by a very brittle behavior. The content of Lyocell fibers was limited to a maximum 10 wt% (corresponding to 12 vol%) for physical limitation of the feeding system of the MiniLab extruder with a low apparent volume filler. After extrusion, the molten materials were transferred through a preheated cylinder to the Haake MiniJet II mini injection molder (Thermo Scientific Haake GmbH, Karlsruhe, Germany), to obtain ASTM D638 V dog-bone tensile bars used for measurements and analysis.

Characterization methods

Tensile tests were performed at room temperature, at a crosshead speed of 10 mm/min, by means of an Instron 4302 universal testing machine (Canton MA, USA) equipped with a 10 kN load cell and interfaced with a computer running the Testworks 4.0 software (MTS Systems Corporation, Eden Prairie MN, USA).

The morphology of the composites was studied, in the scanning electron microscope (JEOL JSM-5600LV, Tokyo, Japan), by analyzing the fracture surfaces of samples, broken in liquid nitrogen. Prior to SEM analysis all the surfaces were sputtered with gold.

The chemical bonding between Lyocell fibers and polymer matrix through GPE were analyzed by using a Nicolet 380 spectrometer with diffuse reflectance accessory (DRIFT). The composite was dissolved in acetone to remove the polymer matrix (CDA) and then the fibers were drying under vacuum at 100°C in 24 hours. Lyocell fibers were mixed with potassium bromide (KBr) in order to obtain the DRIFT spectra. During the DRIFT measurement, pure potassium bromide was chosen as background.

3. Results
Mechanical properties of CDA-based blends and composites

Samples name	CDA/TA (%)	GPE (%)	Lyocell (%)	Elastic Modulus (GPa)	Tensile Strength (MPa)	Strain at break (%)
CDA80TA20	80/20	0	0	4.54 ± 0.2	93.3 ± 2	6.85 ± 0.6
CDA70TA30	70/30	0	0	2.67 ± 0.1	49.3 ± 1.5	8.68 ± 0.5
CDA60TA40	60/40	0	0	0.96 ± 0.1	19.7 ± 1.3	9.35 ± 0.7
CDA80TA20-Ly10	80/20	0	10	5.57 ± 0.3	98.4 ± 3	6.8 ± 0.1%
CDA70TA30-Ly10	70/30	0	10	3.57 ± 0.1	54.6 ± 0.3	8.19 ± 0.8
CDA60TA40-Ly10	60/40	0	10	1.81 ± 0.1	27.2 ± 0.1	9.5% ± 0.4
CDA80TA20GPE5	80/20	5	0	3.67 ± 0.08	80.5 ± 1	9.04 ± 0.4
CDA70TA30GPE5	70/30	5	0	1.75 ± 0.03	33 ± 0.5	9.38 ± 0.2
CDA60TA40GPE5	60/40	5	0	0.34 ± 0.01	10.4 ± 0.4	8.55 ± 0.1
CDA80TA20GPE5-Ly10	80/20	5	10	4.78 ± 0.15	95.3 ± 4	7.21 ± 0.5
CDA70TA30GPE5-Ly10	70/30	5	10	2.48 ± 0.08	44.2 ± 0.3	10 ± 0.6
CDA60TA40GPE5-Ly10	60/40	5	10	1.4 ± 0.14	21.4 ± 0.6	9.8 ± 0.2
CDA80TA20GPE5-Ly10	80/20	5	Te -10%	4.78 ± 0.15	95.3 ± 4	7.21 ± 0.5

CDA80TA20GPE5-Re10	80/20	5	Re - 10%	5.1 ± 0.2	92 ± 3	4.73 ± 0.3
CDA80TA20GPE5-MC10	80/20	5	MC - 10%	4.58 ± 0.1	79.3 ± 3.7	6.91 ± 0.4
CDA80TA20GPE5-Li	80/20	5	Li-10%	4.58 ± 0.2	96.2 ± 4	7.17 ± 0.5

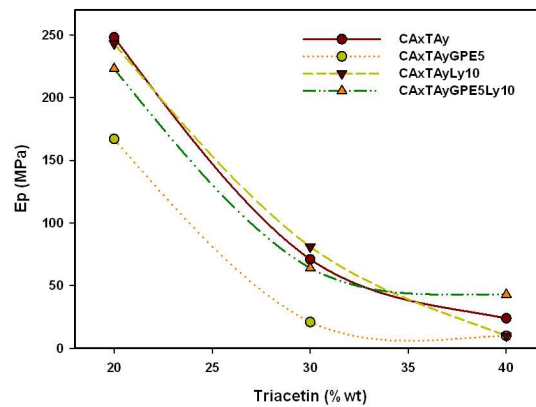Table 1. Mechanical properties of materials as modified plasticizers and different natural fibers

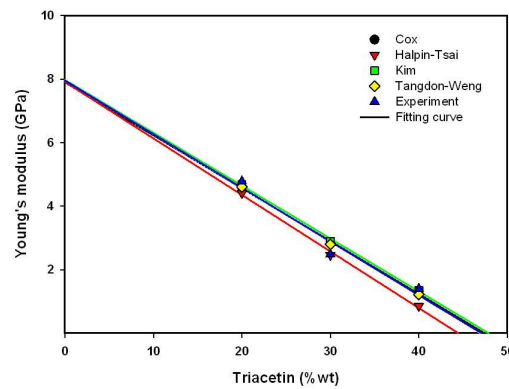Figure 1 Hardening modulus of materials with different plasticizers content

Figure 2 Young's modulus for (CDAxTAyGPE5)Ly10 at different TA content. Comparison between experimental data and theory prediction
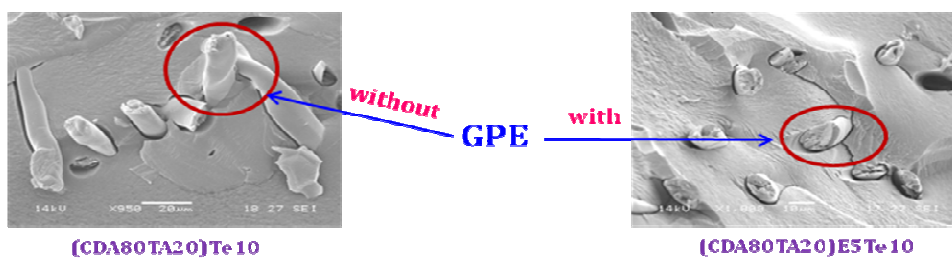
Morphology and FTiR
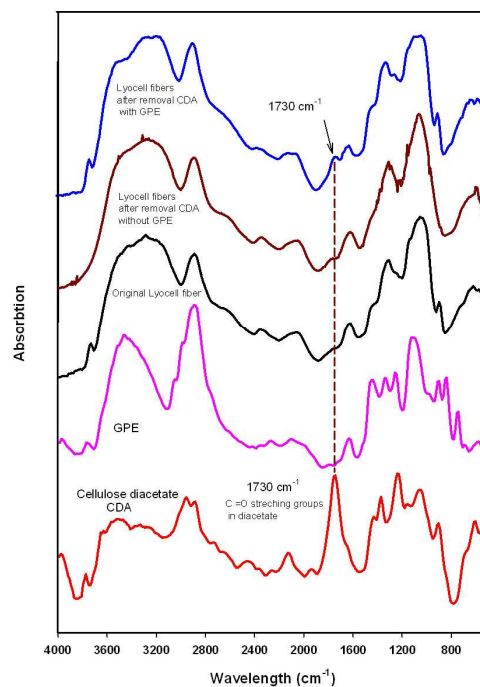

Figure 3 Morphology of composite with and without GPE

Figure 4 FITR spectra of materials

4. Discussion and conclusions

Although CDA is a long time known and used polymer, biocomposites based on CDA have not received recently as much attention in R&D as those based on other biopolymers such as polylactic acid, as attested by the limited recent literature on CDA based composites, despite the fact that cellulose is the most abundant biopolymer on our planet. One of the reasons is related to the difficult processability since the processing temperature for CDA is very close to the degradation temperature. Thus, there is the need for the addition of plasticizers such as phthalates which make the material not suitable for composting or biodegradation.

Thus, as mentioned above, some studies considered different plasticizers, more compatible with the envinronment like triethyl citrate or triacetin, blending with other biopolymers and producing biocomposites.

Triacetin is a relatively low viscosity liquid (at 20 °C = 23 mPa•s) that can easily diffuse into CDA molecules, leading to a rapid depression of its Tg, thus enabling a larger processing window for plasticized CDA. On the other hand, the GPE used in this study shows a much higher viscosity (at 25 °C about 250 mPa•s), thus higher temperatures and much longer times are required for its diffusion into CDA. Also GPE has shown to be capable of reacting with the matrix, thus acting more as an internal plasticizer. Thus, the new strategy developed in this work, which makes use of a system of two different plasticizers:

• a primary "external-type" or "non-reactive-type" plasticizer added prior to extrusion to enhance the "processing window" of the polymer.

• a secondary "internal-type" or "reactive-type", added during the extrusion step to reduce the amount of potential volatiles or leachable products in the final product and to help in the reduction of viscosity and thus further improving processability, may prove as an extremely useful approach in establishing a new process route for CDA based biocomposites.

On the other hand, many natural fibers used in composites possess a limited aspect ratios, and their non-homogeneity in both fiber diameter and fiber length and their size distribution, results in limited property enhancement, and little materials reproducibility.

Lyocell, also known as Tencel, is an artificial microfiber made from regenerated wood pulp cellulose. It is produced by spinning bleached wood pulp dissolved in a nontoxic ("green") organic solvent, N-Methylmorpholine-N-oxide or MMNO, which can recovered by washing the freshly spun cellulose microfibers in water, and later purified, and recycled. Both fiber diameter and fiber length can be accurately controlled during the production process.

In this study, we investigated Lyocell fibers reinforced CDA biocomposites and the effect of the content of two plasticizers (TA and GPE). In first instance it was considered the performance of the system, with and without regenerated cellulose microfibers, varying the TA amount from 20% to 40% by weight. Then GPE was evaluated as not only as a second plasticizer but also to improve the interactions between the fibers and the polymer matrix and consequently to target an increase in stiffness. The resulting materials showed excellent mechanical properties, much better than those reported in the literature for CDA composites prepared with traditional plasticizers and fillers. A comparison with other eco-friendly fillers like wood flour and microcrystalline cellulose, tested in this paper, showed that cellulose diacetate composites with Lyocell fibers showed superior dispersion in the polymer matrix, and higher mechanical properties, related to the higher aspect ratio of these fibers and to the good bonding with the polymeric matrix.

Without overlooking the difficulty of scaling-up a process from lab-scale to industrial-scale, this new approach enables to envisage potential innovative biocomposites, based on a readily available natural resource.

Acknowledgment

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