European Polymer Journal 57 (2014) 30–36

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Grafted D/L-lactide to cellulose acetate by reactive melt processing: Its role as CA/PLA blend compatibilizer

Robert Quintana [a,b,c], Olivier Persenaire [a,b], Yahia Lemmouchi [d], Leïla Bonnaud [a,b], Philippe Dubois [a,b,*]

[a] Materia Nova asbl, Parc Initialis, Avenue N. Copernic 1, 7000 Mons, Belgium
[b] University of Mons UMONS, Place du Parc 20, 7000 Mons, Belgium
[c] Institute of Materials Research and Engineering (IMRE), A*STAR, 3 Research Link, Singapore 117602, Singapore
[d] Group R&D Centre, British American Tobacco, Regents Park Road, Millbrook, Southampton SO15 8TL, UK

ARTICLE INFO

Article history:
Received 22 September 2012
Received in revised form 25 April 2014
Accepted 8 May 2014
Available online 16 May 2014

Keywords:
Cellulose acetate
Polylactic acid
Grafting
Plasticization
Blend
Biodegradation

ABSTRACT

Cellulose acetate (CA) with a degree of substitution (DS) of 2.5 and polylactic acid (PLLA) were plasticized by melt extrusion using triacetin. Blends of resulting thermoplastic materials were then prepared and characterized by their tensile strength and differential scanning calorimetry (DSC). Thermal analysis revealed the invariability of the PLLA glass transition temperature in all blends, indicating that the compounds were immiscible. Grafted D/L lactide to CA copolymers were prepared by reactive melt processing using CA with different degree of substitution i.e. 2.1 and 2.5 and evaluated as CA/PLLA blend compatibilizer. The compatibility of the blends was investigated by scanning electron microscopy (SEM). Results showed that blend compatibility was improved evidencing the best performance of grafted copolymers with long grafted chains as blend compatibilizer of CA/PLLA blends. Finally, compatibilized blends compositions with enhanced ultimate elongation were achieved by using plasticized PLLA instead of neat PLLA.

1. Introduction

One of the most important organic esters is cellulose acetate (CA), which is widely used for many industrial applications in the form of film and fiber [1]. CA is derived from cellulose using the acetylation process and its main properties are its hardness, good resistance to impact, high shine, transparency, pleasing texture, lack of static electricity and resistance to hydrocarbons [2]. Furthermore, CA has recently been reported to be potentially biodegradable [3,4], and that the biodegradation rate depends on its degree of acetyl-group substitution (DS). As DS of CA decreases, biodegradation rate increases. However, for some applications, a faster degradation rate is desirable in minimizing the impact of CA products in the environment.

Direct plasticization of cellulose acetate, i.e. mixing CA with one or more plasticizers, have long been known for their effectiveness in producing flexible plastics for applications ranging from the automotive industry to medical and consumer products. Since by definition plasticizers will be released into the environment during product common use, health and safety issues have determine the recent research in biodegradable cellulose acetate materials, focusing on developing compatible plasticizers that also biodegrade. Citrate-based plasticizers are derived from naturally occurring citric acid and are non-toxic. Triethyl citrate, acetyl triethyl citrate and glycerol triacetate or triacetin, which has properties of both glycerol and acetate, have been proved to be suitable environmental friendly plasticizers for CA [5–7]. Triacetin is one of the best plasticizer for cellulose acetate as its high boiling

---

[*] Corresponding author at: University of Mons UMONS, Place du Parc 20, 7000 Mons, Belgium. Fax: +32 65 373484.
E-mail address: philippe.dubois@umons.ac.be (P. Dubois).

http://dx.doi.org/10.1016/j.eurpolymj.2014.05.003
0014-3057/© 2014 Elsevier Ltd. All rights reserved.

point reduces the amount of plasticizer loss occurring during melt-processing. Polyols as glycerol, which its lower miscibility in acetone limited its use in solution mixing, have also been utilized for plasticize CA by melt processing. Indeed, one of the most useful advantages of melt processing is its independence of finding a suitable solvent for mixing blend components. This advantage has been largely exploited on the preparation of polymer blends, avoiding searching a common solvent for the involved polymers and suitable plasticizers.

Biodegradable polymer blends with CA and starch, poly(ethylene glycol), poly(ε-caprolactone), poly(L-lactide) and other aliphatic polyesters have shown to be suitable systems to study [7–13]. Poly(ethylene glycol) (PEG) is a flexible and water-soluble polymer. Although poly(ε-caprolactone) (PCL), which is readily available, sufficiently cheap and biodegradable and has good biocompatibility [14], would be one of the most obvious compounds for the modification of CA, their blends are immiscible and generally incompatible [15,16]. On the other hand, poly(L-lactide) (PLLA), which is obtained from renewable resources, also biodegradable, biocompatible with human tissues and its melting point (T_m) higher than poly(ε-caprolactone) wide its thermal application range [14,17]. Ogata et al. prepared CA/PLLA blends by solvent casting in chloroform, observing that a macrophase separation took place without a compatibilizer. However, they could obtain homogeneous blend films with the addition of tetraisopropyl titanate (TP) as a compatibilizer to the blend. Grafted copolymers are gaining special interest as blend compatibilizers [18]. Cellulose acetate grafting is a process aimed at the introduction of some branches of synthetic polymers into the main polysaccharide chain to confer specific additional properties to the substrate itself without destroying its intrinsic characteristics [5]. Extensive research on the grafting of CA has been conducted by several authors [19–28]. The free hydroxy groups in cellulose acetate offer possibility of grafting the backbone with cyclic monomers like lactones and lactides by ring opening polymerization (ROP). Up to our knowledge, the reactive processing approach to produce CA grafted PLA copolymers has not been previously described.

The present study focused on the preparation of CA-g-PLA copolymers by reactive processing and to evaluate their role as blend compatibilizer of thermoplastic CA blends with PLLA.

2. Experimental

2.1. Materials

Cellulose acetates (CA) with a degree of substitution of 2.5 (flakes, $M_n = 65.400$ and polydispersity index of 3.4) and 2.1 (flakes, $M_n = 28.000$ and polydispersity index of 2.3) were kindly supplied by British American Tobacco. Poly(L-lactide) (PLLA) was obtained from NatureWorks (grade 4032D), USA. Characteristics of PLLA are as follows: number average molecular weight (equivalent polystyrene), $M_n(PS) = 133500$, polydispersity index, PDI = 1.9, melt flow rate (190 °C, 2.16 kg) = 7.7 g/10 min). Triacetin (TA) was purchased from Acros and L-Lactide from Boehringer Ingelheim. These chemicals and solvents used in this study were all guaranteed reagent grade and used without further purification. D-Lactide was purchased from Purac and was purified by recrystallization from hot toluene before being used.

2.2. Measurements

The number average molecular weights and molecular weight distributions of the polymers were determined in THF at 23 °C using a Agilent size exclusion chromatograph equipped with a Knauer 2320 refractometer index detector and two PLGel columns (MIXED-D and 103A). Samples were dissolved in THF (5 mg/1 ml), 20 μL of the solutions were injected into the columns using a flow rate of 1 mL/min. Monodisperse polystyrene standards (Polymer Laboratories Ltd.) were used for the primary calibration.

Differential scanning calorimetry (DSC) measurements were performed by using a DSC 2920 from TA Instruments calibrated with indium under nitrogen flow (50 mL/min). The following procedure was used: first heating at 20 °C/min from room temperature to 150 °C, keeping at this temperature for 60 s to eliminate the dehydration, which occurs around 120 °C [3,14]. Then the temperature was reduced to −50 °C at 10 °C/min and finally a heating scan at 10 °C/min to 270 °C.

Modulated DSC spectra were obtained using a MDSC 2920CE from TA Instruments calibrated with indium under nitrogen flow (50 mL/min). The samples was heated at 20 °C/min from room temperature to 150 °C and held there for 60 s. Then the temperature was reduced to −50 °C at 10 °C/min and finally the sample was heated to 270 °C at 5 °C/min while applying a temperature oscillation of 1 °C/min.

The blend morphology was studied by scanning electron microscopy (SEM). SEM analysis was performed using a JEOL JSM 6100 apparatus at 10 kV. Cryo-fractured surfaces were covered by an aluminum thin-layer in order to make them conductive.

Films of uncompatibilized and compatibilized CA-based blends were prepared by hot-pressing molding at 235 °C using an Agila PE20 hydraulic press (low pressure for 120 s without degassing cycle, followed by a high-pressure cycle at 150 bars for 180 s and cooling by tap water at 50 bars for 120 s). Tensile testing measurements were performed by using a Lloyd LR 10 K tensile bench in accordance with ASTM D 882 “Standard Test Method for Tensile Properties of Thin Plastic Sheeting”, standard” at room temperature using a crosshead speed of 20 mm/min and a distance of 25.4 mm between grips. Rectangular test specimens (64 × 10 mm) were cut from melt-pressed films and were previously conditioned for at least 48 h at 20 ± 1 °C under relative humidity of 45 ± 5% and values were averaged over five measurements.

2.3. Procedures

2.3.1. Synthesis of P(L/D)LA-g-CA graft copolymer

CA2.5 or CA2.1 was dried at 105 °C at least 24 h before use. Ring-opening graft copolymerization was carried out in the Brabender internal mixer (model 50 EHT, 80 cm^3

free volume). The content of L or D-lactide or a mixture of both was 22.5 or 45 wt% and 0.1 wt% tin-bis(2-ethylhexanoate) catalyst was added to the reaction medium. The reaction was conducted at 235 °C for 45 min. Speed of the rotors in the internal mixer was kept constant at 50 rpm. Crude reaction product was purified by dissolving in chloroform and precipitation from methanol/toluene (70/30) mixture, in order to remove unreacted lactide and the polylactic homopolymer possibly formed in the reaction. The resulting precipitate was filtered off, washed and dried at 60 °C under vacuum.

2.3.2. Polymer plasticization

CA2.5 and PLLA were plasticized in a Leistritz ZSE 18HPe twin-screw extruder ($L = 40D$) equipped with a liquid feeder for plasticizer addition. Polymers were dried overnight at 80 °C in a ventilated oven before being introduced into polymer feeder. Extrusion speed was fixed at 200 rpm and the barrel temperature profile was set-up in function of the material to be processed. Extruded material was cold down in a water bath and pelletized.

2.3.3. Blend preparation

Prior processing, polymers were dried overnight at 80 °C in a ventilated oven. CA-based compositions were obtained by melt-compounding polymer pellets and compatibilizers at 190 °C using the same internal mixer equipped with cam blades for 3 min at 30 rpm, followed by 6 min at 60 rpm.

3. Results and discussion

3.1. Polymer plasticization

As cellulose, cellulose derivatives undergo thermooxidative degradation at high temperatures [11]. The decomposition temperature of CA2.5 is close to its softening point and it is thus necessary to blend this material with plasticizers in order to obtain cellulose acetate materials of suitable flow properties. Plasticization also permits to process this material at slightly lower temperatures which dismisses coloration due to degradation phenomena. Although PLA processing does not present this drawback, usually it is plasticized to reduce its inherent brittleness. Plasticization of CA2.5 and PLLA was carried out by twin screw extrusion using triacetin 30 and 20 wt%, respectively. Plasticizer was introduced through the second barrel zone and feeding controlled by a liquid feeder. In Table 1 are summarized extruder temperature profiles utilized for plasticization.

The effect of the plasticization on the tensile strength and modulus of the polymers is illustrated in Table 2. The unplasticized CA sample used as reference in Table 2 was prepared by solvent casting from a solution in acetone. As expected, plasticized materials are more ductile and flexible. The presence of triacetin in the matrix increases the free volume which favors chain mobility. According to this, DSC data (Table 2) reflected a reduction of the T_g on plasticized polymers.

3.2. Blend preparation

Mixing of two or more different polymers together makes it possible to achieve various property combinations of the final material. Cellulose acetate and PLLA are considered as biodegradable polymers and therefore their blends are likely expected to be also biodegradable. Furthermore, it is reasonable to consider that biodegradation rates will be different and will probably vary in function of blend composition. Although, this study is definitely outside the scope of this paper, the potential tuneable biodegradation rate of these blends it is of great interest for its composting. Indeed, this work is focused on the physical modification of thermoplastic CA (pCA) via blending with neat PLLA. Several blends were prepared by direct melt blending in an internal mixer, where PLLA composition was varied from 30 to 70 wt%. As a first hypothesis, plasticizer is considered to rest entangled on CA structure during processing. Film samples were produced from prepared blends by melt-compression and then characterized by MDSC measurements and tensile testing.

Table 3 reports PLLA glass transition temperature data and tensile strength, elongation at break and Young's modulus parameters for the parent polymers and their blends, respectively. As evidenced by the values of PLLA T_g, PLLA and CA are immiscible polymers. No variation of T_g is observed whatever the thermoplastic CA content. Tensile strength data sustained this incompatibility between this pair of polymers. The values of the blends 30/70 and 50/50 were lower than the neat PLLA value, with a reduction up to 48% in relation to PLLA. These results indicated the absence of strong chemical interaction between these polymers. Thermoplastic CA which has a degree of substitution of 2.5 contains a low concentration of hydroxyls which act as proton acceptors and are involved in hydrogen bonds with the carbonyl groups of PLLA. Polymers, such as CA, which have ester groups generally favor phase separation and produce immiscible blends [29].

3.3. Graft copolymerization of cellulose acetate with D/L-lactide

Reactive modification of CA2.5 and CA2.1 was conducted in bulk, in absence of any solvent, by ring-opening

Table 1
Extruder temperatures for CA and PLLA plasticization with triacetin.

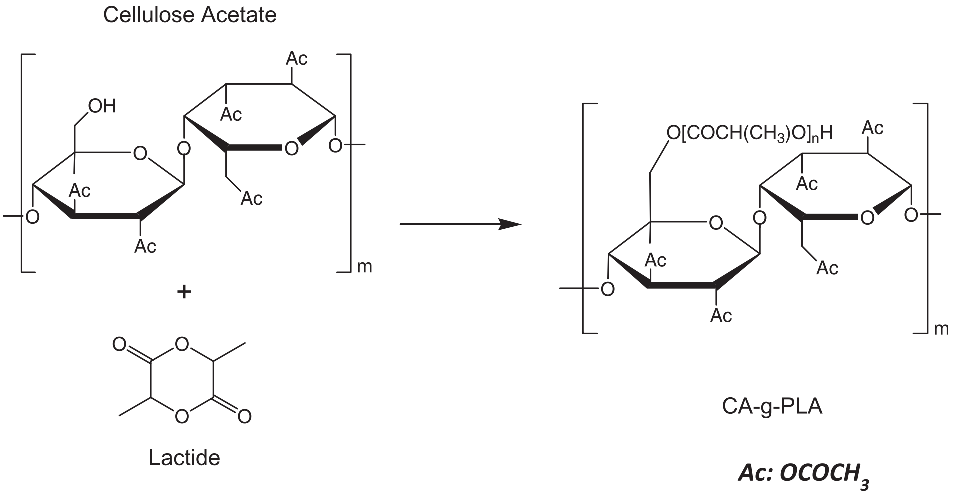
Polymer	Extruder temperatures (°C)								
	Barrel zones							Die	Melt
	1	2	3	4	5	6	7		
CA2.5	200	220	230	230	220	210	200	190	173
PLLA	170	190	210	210	210	210	200	200	168

Table 2
Tensile parameters and glass transition temperature of neat and plasticized CA2.5 and PLLA.

Polymer	Triacetin (wt%)	T_g (°C)	Young modulus (MPa)	Stress at break (MPa)	Strain at break (%)
CA2.5	0	192	2073 ± 81	75.4 ± 3.5	10 ± 2
CA2.5	30	96	1387 ± 21	36.6 ± 0.1	56 ± 6
PLLA	0	58	2364 ± 99	65.6 ± 3.7	5 ± 1
PLLA	20	29	259 ± 82	20.6 ± 2.2	353 ± 30

Table 3
Composition, glass transition temperature and tensile parameters of pCA/PLLA blends.

Polymer (wt%)		T_{gPLLA} (°C)	Young modulus (MPa)	Stress at break (MPa)	Strain at break (%)
pCA	PLLA				
70	30	58	1158 ± 28	27.0 ± 1.5	10 ± 2
50	50	59	1788 ± 52	30.7 ± 2.4	3 ± 1
40	60	58	2054 ± 132	38.9 ± 5.5	5 ± 1
30	70	59	2133 ± 67	42.3 ± 2.7	3 ± 1



Scheme 1. *In situ* graft polymerization of lactide to cellulose acetate.

polymerization of lactide. Residual hydroxyl groups of CA were used to initiate the polymerization. Grafting was conducted in the same internal mixer used previously for blend preparation. Up to our knowledge, the reactive processing approach to produce these CA-g-PLA grafted copolymers has not been previously described. The grafting of lactide to cellulose acetate is shown by Scheme 1. The two lactide stereoisomers, L and D, and certain mixtures of both were polymerized into grafted chains. Table 4 summarized the compositions prepared and the

Table 4
Feed composition and composition parameters of CA-g-P(D/L)A copolymers.

Code	Feed			Composition (by ^{1}H NMR)				
	Acetyl DS	[Lactide] (wt%)	D/L	gPLA (wt%)	MS[a]	Lactyl DS[b]	DP[c]	T_g
gc1	2.5	22.5	100/0	14.9	0.65	0.23 (45)	2.89	155
gc2	2.5	22.5	50/50	18.7	0.85	0.25 (50)	3.40	160
gc3	2.5	22.5	0/100	21.7	1.03	0.33 (65)	3.15	153
gc4	2.5	45	100/0	35.3	1.90	0.26 (52)	4.75	119
gc5	2.5	45	50/50	36.2	2.10	0.33 (65)	6.46	116
gc6	2.5	45	0/100	41.7	2.65	0.45 (90)	5.89	105
gc7	2.1	45	100/0	23.8	1.16	0.32 (36)	3.67	120
gc8	2.1	45	50/50	28.2	1.12	0.26 (29)	3.26	124
gc9	2.1	45	0/100	30.1	1.61	0.34 (38)	4.75	110

[a] Molar substitution.
[b] Grafting efficiency (%) in brackets.
[c] Average degree of polymerization of PLA grafted chain.

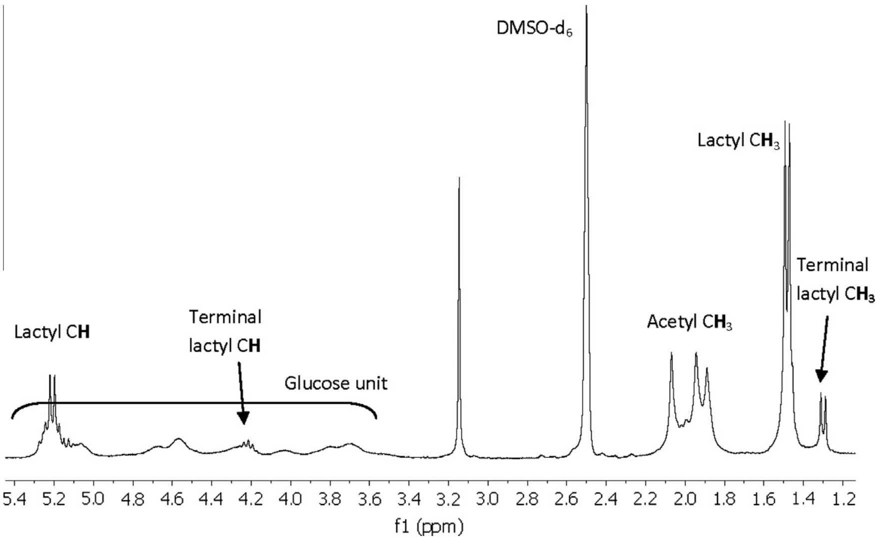


Fig. 1. ^{1}H NMR spectra of CA-g-PLLA copolymer recorded in DMSO-d$_6$.

composition parameters of resulting grafted copolymers after purification. The chemical constitution and composition of CA-g-PLLA grafted copolymers were assessed by ^{1}H NMR spectroscopy. For illustration, in Fig. 1 is shown the spectra recorded from grafted copolymer gc6 (Table 4). Spectrums were recorded in DMSO-d$_6$ instead of other usually used solvents for CA like $CDCl_3$ because this solvent splits the signals from lactyl CH_3 (B) and terminal lactyl CH_3 protons (C), making easier integration of these peaks. Then, estimates of the average length of the grafted chains (DPs), the molar substitution (MS) and the degree of lactyl substitution (lactyl DS) were estimated as previously reported [21]:

$$MS = DS_{CA}(B + C)/A$$

$$\text{lactyl DS} = DS_{CA}C/A$$

$$DPs = MS/(\text{lactyl DS})$$

where DS_{CA} is the degree of substitution of CA; 2.5 or 2.1, and A is the area of the methyl protons of CA acetyl groups. Estimates have been based on previous assumptions that degree of substitution of CA remained invariable during the reactive process [20–22].

Composition parameters indicates that the effect of increasing the concentration of L-lactide in feed mainly affect the length of the grafted chain as the number of hydroxyls substituted for oxyalkanoyls per anhydroglucose residue of CA are similar. Furthermore, this effect seems to be proportional to L-lactide feed concentration. The grafting efficiency is represented by the lactyl DS, defined as average number of hydroxyls substituted for lactyl per anhydroglucose residue of CA was estimated as lactyl DS/(3-DS_{CA}) * 100. A lactyl DS of 0.5 and 0.9 will correspond to the complete substitution of hydroxyls groups on CA2.5 and CA2.1, respectively. Grafting efficiency seems to decrease slightly with lactide composition on feed. However, as it could be expected for this type of reactions, grafting efficiencies are considerably high. Conversion of lactide into grafted PLA is affected by the content on D-lactide, which leads to low conversions. As a different reactivity is not expected, purity of D-lactide should explain this observation. Actually, D- and L-lactide were provided by different supplier. As mentioned in the experimental part, efforts were carried out to further purify the D-lactide. Nevertheless, the degree of purity achieved appeared not to be sufficient to allow similar polymerization efficiency. Composition parameters of grafted copolymers prepared from CA2.1 pointed out that grafting seems to be easier in CA2.5, in spite of the smaller number of active –OH groups present. This experimental result it was also observed for other CA grafted copolymers prepared by melt processing [19]. Thermal properties were investigated by DSC and in Table 4 are reported glass transition temperatures. The effect of the internal plasticization, provoked by the grafting of short chains of PLA on CA backbone, is clearly observed with the systematic reduction of T_g.

In this work, the use of mixture of stereoisomers was addressed mainly to prevent the crystallization of PLA side chains on grafted copolymers, which has been reported to occur when molar substitution is above 14 [21]. It was reasonable to consider that disrupting the regularity of grafted chains will make difficult the formation of crystallinity. Clearly, the development of this high order arrangement will limit and have a drawback on performance of these copolymers as compatibilizer of CA/PLA blends. However, finally, seeing that molar substitution indexes of the prepared grafted copolymers were much lower than 14, the crystallization studies were not performed. Furthermore, these grafted materials produced from mixtures of L and D lactide were not considered on next section.

3.4. Blend compatibilization

With the aim of evaluating the use of CA-g-PLLA grafted copolymers as compatibilizer of the CA/PLLA blends,

Table 5
Composition, plasticizer content and tensile parameters of uncompatibilized and compatibilized CA/PLLA blends prepared using neat or plasticized PLLA.

Polymer (wt%)			Compatibilizer [a]	Plast.[b](wt%)	Young modulus (MPa)	Stress at break (MPa)	Strain at break (%)
pCA	PLLA	pPLLA					
50	50	–	–	15.0	1521 ± 73	27.9 ± 1.0	5 ± 1
50	50	–	gc3	13.6	2154 ± 108	23.4 ± 6.4	2 ± 1
50	50	–	gc9	13.6	2266 ± 34	38.9 ± 4.4	3 ± 1
50	50	–	gc6	13.6	2149 ± 57	36.2 ± 6.7	3 ± 1
50	–	50	–	25.0	627 ± 56	14.7 ± 1.7	11 ± 2
50	–	50	gc6	23.6	498 ± 50	13.8 ± 0.8	25 ± 5

[a] Grafted copolymer content fixed at 10 phr.
[b] Plasticizer content on the blend.

various compositions were produced using plasticized CA, PLLA and three selected CA-grafted copolymers. Compatibilizer content was fixed at 10 phr (parts per hundred parts of resin) of grafted copolymer. Blends were produced as described previously in absence of compatibilizer. The mechanical properties of the so-obtained compositions are reported in Table 5.

The potentially effect of the small reduction (1.4%) of plasticizer content in the compatibilized blends, which is consequence of the blend preparation method, in tensile parameters could be considered negligible. Therefore, the observed increment of toughness in the CA/PLLA blends prepared with the addition of the graft copolymers were attributed to the improvement on the quality of the interface adhesion, evidencing the compatibilizer role of these grafted copolymers. This effect was subsequently investigated through electron microscopy. Cryofractured surfaces of these blends were analysed by means of SEM. The morphology of uncompatibilized blends and compatibilized compositions were observed. As evidenced in Fig. 2, compatibilized blends using CA 2.5-based graft copolymer (Fig. 2c and d) showed a finer morphology and an increase of adhesion between blend components. More precisely, Fig. 2c exhibited the formation of fine polymer strands as a result of the blend compatibilization. Further enhanced compatibilization was illustrated in Fig. 2d which clearly evidenced refined microstructuration. These observations pointed out that the best compatibilization performances were achieved by using graft copolymers with the largest grafted chains and higher grafting efficiency. Indeed, when the CA 2.1-based graft copolymer is considered as compatibilizer, no blend compatibilization occurred as shown in Fig. 2b. Actually, these copolymers are characterized by the lowest grafting efficiency (Table 4). These morphological observations supported the results obtained by tensile testing.

For some potential applications, the remaining brittle behavior of these compatibilized blends will limit its

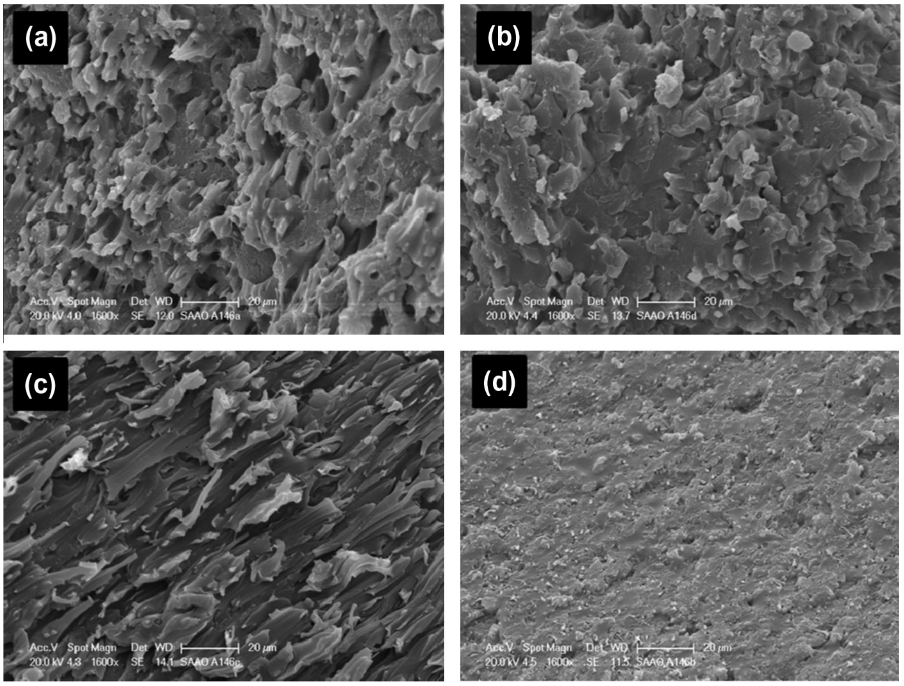


Fig. 2. SEM microphotographs of cryofractured surfaces CA/PLLA 50/50 (w/w) blends: (a) uncompatibilized; (b) compatibilized with gc9 (CA2.1); (c) compatibilized with gc3 (CA2.5) and (d) compatibilized with gc6 (CA2.5).

end-use as occurs with their parent polymers, PLLA and CA. Then, CA/PLLA blends with improved toughness were prepared by using plasticized PLLA (pPLLA), with 20 wt% of triacetin. Tensile parameters of the prepared compositions using thermoplastic CA2.5 and plasticized PLLA are reported in Table 5. As it was expected, the new blends were more ductile and showed an enhanced ultimate elongation up to three-fold. More interesting mechanical properties were obtained when grafted copolymer gc6 was used as compatibilizer. In this case, the elongation at break was doubled without affecting significantly the other parameters, obtaining a ductile composition with improved toughness. It is reasonable to expect that the ultimate mechanical properties of these plasticized and compatibilized CA/PLLA blends would widen their potential applications.

4. Conclusions

Blends of cellulose acetate and polylactic acid, two well-known biodegradable biopolymers, have been prepared by melt processing. For that propose, thermoplastic cellulose was obtained by direct plasticization with triacetin in a twin-screw extruder. Tensile properties and glass transition temperature measurements of CA/PLLA blends evidenced the immiscibility of this pair of polymers. In order to improve blend compatibility and phase cohesion, PLA grafted CA copolymers were prepared by ring opening polymerization of L or D lactide or mixtures of both by reactive processing and their chemical structure were determined. High grafting efficiencies have been observed were L-lactide was used. In addition, grafting polymerization has been found to take place in more extension on CA2.5 than CA2.1. As referrer to the role of CA-g-PLA copolymers as compatibilizer, their efficiency has been discussed in the light of the blend morphology and tensile results. As demonstrated by both studies, grafted copolymers increased the adhesion between CA and PLA phases, leading to finer morphologies and materials with enhanced toughness. Largest grafted chains and higher molar substitution are required to improve the quality of the interface. Blends prepared with both plasticized PLA and CA in combination with CA-g-PLA copolymers allowed making a step forward on tailoring of the mechanical properties of these interesting biodegradable blends. The improvement reached and the potential application of these blends as compostable materials, have encourage us to study their biodegradability. This study will be the topic of a forthcoming paper.

Acknowledgements

LPCM is very much indebted to the *Région Wallonne* and *European Community* for financial support (FSE-FEDER) in the frame of Objectif 1, Phasing-out: Materia Nova and Plan de convergence. LPCM thanks the *Belgian Federal Government Office Policy of Science* for general support in the frame of the PAI 6/27. British American Tobacco financial support is acknowledged.

References

[1] Ach A. J Macromol Sci Part A: Pure Appl Chem 1993;30:733–40.

[2] Bhattacharya BNMA. Progr Polym Sci 2004;29:767–814.

[3] Buchanan CM, Gardner RM, Komarek RJ. J Appl Polym Sci 1993;47:1709–19.

[4] Komarek RJ, Gardner RM, Buchanan CM, Gedon S. J Appl Polym Sci 1993;50:1739–46.

[5] Rahman M, Brazel CS. Progr Polym Sci 2004;29:1223–48.

[6] Nadia Ljungberg BW. J Appl Polym Sci 2002;86:1227–34.

[7] Kovačić T, Klarić I, Erceg M. Polym Degrad Stab 2005;90:313–8.

[8] Labrecque LV, Kumar RA, Davé V, Gross RA, McCarthy SP. J Appl Polym Sci 1997;66:1507–13.

[9] Mohanty AK, Wibowo A, Misra M, Drzal LT. Polym Eng Sci 2003;43:1151–61.

[10] Ghiya VP, Dave V, Gross RA, Mccarthy SP. J Macromol Sci Part A 1996;33:627–38.

[11] Teufel E, Sexauer W, Willmund R, U.S. Patent 6,154,511, November 14; 2000.

[12] Carvalho AJF, Zambon MD, Curvelo AAS, Gandini A. Polym Degrad Stab 2003;79:133–8.

[13] Rosa DS, Guedes CGF, Casarin F, Bragança FC. Polym Test 2005;24:542–8.

[14] Bragança FC, Rosa DS. Polym Adv Technol 2003;14:669–75.

[15] Buchanan CM, Pearcy BG, White AW, Wood MD. J Environ Polym Degrad 1997;5:209–23.

[16] Yamashita Y, Endo T. J Appl Polym Sci 2006;100:1816–23.

[17] Rosa DS, Guedes CGF, Bardi MAG. Polym Test 2007;26:209–15.

[18] Ogata N, Tatsushima T, Nakane K, Sasaki K, Ogihara T. J Appl Polym Sci 2002;85:1219–26.

[19] Szamel G, Domjan A, Klebert S, Pukanszky B. Eur Polym J 2008;44:357–65.

[20] Teramoto Y, Ama S, Higeshiro T, Nishio Y. Macromol Chem Phys 2004;205:1904–15.

[21] Teramoto Y, Nishio Y. Polymer 2003;44:2701–9.

[22] Teramoto Y, Yoshioka M, Shiraishi N, Nishio Y. J Appl Polym Sci 2002;84:2621–8.

[23] Videki B, Klebert S, Pukanszky B. Eur Polym J 2005;41:1699–707.

[24] Videki B, Klebert S, Pukanszky B. J Polym Sci Part B – Polym Phys 2007;45:873–83.

[25] Vlcek P, Janata M, Látalová P, Dybal J, Spírková M, Toman L. J Polym Sci Part A: Polym Chem 2008;46:564–73.

[26] Warth H, Mulhaupt R, Schatzle J. J Appl Polym Sci 1997;64:231–42.

[27] Yoshioka M, Hagiwara N, Shiraishi N. Cellulose 1999;6:193–212.

[28] Yoshioka M, Miyazaki T, Shiraishi N. Mokuzai Gakkaishi 1996;42:406–16.

[29] Müller R-J, Kleeberg I, Decker W-D. J Biotechnol 2001;86:87–95.