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A dual approach to compatibilize PLA/ABS immiscible blends with epoxidized cardanol derivatives

Alan Rigoussen[a,b], Jean-Marie Raquez[b], Philippe Dubois[b], Pierre Verge[a,*]

[a] *Luxembourg Institute of Science and Technology (LIST), Esch-sur-Alzette L-4362, Luxembourg*
[b] *Centre d'Innovation et de Recherche en Matériaux Polymères(CIRMAP), Mons 7000, Belgium*

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ABSTRACT

With the aim to reinforce polylactide (PLA) mechanical properties, poly(acrylonitrile-butadienestyrene) (ABS) is considered as a polymer of choice. However, PLA and ABS are immiscible, leading to blends with weak properties. Cardanol is a lipid phenolic known to compatibilize these two polymers thanks to its reaction with ABS, but does not react with PLA and restricts its use to the modification of ABS. In this work, we investigated the effect of cardanol-based compatibilizers able to react by reactive extrusion with both PLA and ABS. In a first approach, cardanol unsaturations were epoxidized (CardE), hoping to react with PLA, while cardanol phenolic group would react with ABS. This compatibilizer was efficient as attested by ABS nodules size reduction and dispersion within PLA, in addition to the merging of the relaxation temperatures of both polymers at 69.5 °C when 5 wt% CardE was used. In addition, it led to a substantial improvement of PLA/ABS impact strength and elongation at break. In a second approach, we used of a mixture of compatibilizers, containing raw and epoxidized cardanol, both of them reacting either with PLA or with ABS. Here, a clear synergistic effect was observed, as attested by the exceptional increases of both impact strength (+172% compared to neat PLA) and elongation at break (+1000% compared to neat PLA). We assumed modified chains of both PLA and ABS with cardanol derivatives during reactive extrusion would intersperse between PLA and ABS, reducing the interfacial tension and improving the interfacial adhesion, leading to the outstanding compatibilization of the blend.

1. Introduction

Polylactide (PLA) has become one of the most promising bio-polymers according to its potential biodegradability and natural origin while presenting interesting intrinsic properties such as high strength, high stiffness, resistance to fats and oils in addition to a reasonable price [1–3]. However, despite undeniable advantages, PLA has major drawbacks that restricts its use in potential application areas: a low impact resistance and a short extensibility. The elongation at break is generally less than 10%, and the impact strength below 2.5 kJ m^{-2} [4,5].

Considerable efforts were made in this way by using several strategies such as plasticization [4], copolymerization [6,7], addition of fillers [8,9] or blending PLA with other polymers. In particular, direct blending of PLA with other polymers is considered as a straightforwardly and cost-effective strategy to obtain tougher materials [10–12].

Among toughening polymers for PLA, poly(acrylonitrile-butadienestyrene) (ABS) represents an interesting candidate to improve the impact resistance properties of PLA according to its high mechanical strength, good chemical resistance, and ease of extrusion and molding. Moreover, widely used as a toughening agent for many engineering plastics such as polycarbonate (PC) [13] or polyamide (PA) [14], ABS has also been reported to be a good candidate to toughen PLA [15–21].

However, since PLA and ABS are immiscible, their mixture leads to a hybrid material characterized by a lack of interactions between the phases resulting in weak mechanical properties as well as an unstable morphology [14,17,21]. To overcome this issue, a compatibilization is required.

The compatibilization of PLA and ABS can be achieved by adding a phenolic compound such as cardanol during the melt blending process [22,23]. Indeed, cardanol is grafting onto ABS, leading to the improvement of the miscibility of the two polymers. In this specific case, PLA was preserved from any reaction, limiting in consequence the efficiency of the compatibilizer to its interactions with ABS. The strategy of this work was to promote the functionalization of both PLA and ABS, to lead to a "third" polymer, miscible with the two constitutive polymers.

To promote cardanol reactivity toward PLA during reactive

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* Corresponding author.
E-mail address: pierre.verge@list.lu (P. Verge).

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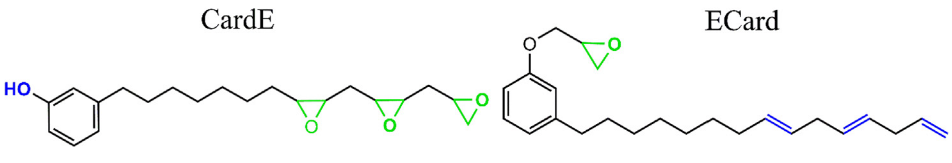


Fig. 1. Schematic representation of CardE (left) and Ecard (right).

extrusion, the addition of epoxy groups onto the cardanol structure was envisaged. Indeed, epoxy groups are known to be reactive with PLA end chains [24–26]. Two approaches were investigated:

- The first approach was to examine the effect of epoxidizing cardanol unsaturations (CardE, Fig. 1), assuming its phenolic group would react with ABS [22], while epoxidized unsaturations would react with PLA [24–26].
- In the second approach, a mixture consisting of raw cardanol and Ecard, a cardanol derivative which phenolic group is epoxidized (Fig. 1), was extruded with the two polymers.

2. Experimental

2.1. Materials

Polylactide (PLA - reference Ingeo™ 4043D, CAS number 26100-51-6) was supplied by NatureWorks (Minnetonka, MN, USA) and contained 4.2 mol% D-isomeric units (Mw = 219.6 kg/mol, Đ = 2.1). Poly(acrylonitrile-butadienestyrene) terpolymer (ABS - Terluran HI-10, CAS number 9003-56-9, Mw = 149 kg/mol, Đ = 2.59), an injection molding and extrusion grade, was purchased from Styrolution (Frankfurt, Germany). Cardanol (UltraLite2023, CAS number 8007-24-7, 100%), epoxidized cardanol (Ecard – NC 513, CAS number 68413-24-1, 99%) were kindly supplied by Cardolite Chemical Zhuhai Ltd (Zhuhai, Guangdong, China). Methanol (CAS number 67-56-1, 99%) and p-toluenesulfonic acid (CAS number 6192-52-5, 98%) were supplied by CarlRoth (Karlsruhe, Germany). Formic acid (CAS number 64-18-6, 88%), hydrogen peroxide (CAS number 7722-84-1, 30%), anhydrous sodium sulfate (CAS number 7757-82-6), sodium bicarbonate (CAS number 144-55-8), deuterated chloroform (CAS number 865-49-6) were purchased from Sigma Aldrich (Saint-Louis, MO, USA). Toluene (CAS number 2037-26-5), and butanone (CAS number 78-93-3) were provided by Fisher Scientific (Hampton, USA). All chemicals were used as received.

2.2. Synthesis of CardE

CardE was synthesized as described in [27]. To a 250 mL flask cardanol (5.00 g, 17 mmol), formic acid (0.78 g, 15 mmol), p-toluenesulfonic acid (0.1 g, 0.58 mmol), and toluene (5.00 g, 54 mmol) were charged. The mixture was slowly heated to 50 °C and 30% hydrogen peroxide (5.78 g, 51 mmol) was added dropwise, then heated at 65 °C for 3 h. Then the crude product was filtered and washed with a 5 wt% sodium bicarbonate and distilled water, respectively. The organic phase was dried with anhydrous sodium sulfate. Finally, toluene was removed by distillation under vacuum, and 4.30 g yellowish liquid was obtained (yield: 86% relative to cardanol), and 63% of cardanol unsaturations were epoxidized.

2.3. Processing

2.3.1. Reactive extrusion

Extrusions were performed on a twin-screw DSM XPlore 15 mL micro-compounder (Geleen, The Netherlands) at a temperature of 190 °C under a nitrogen purge flow. The screw speed was set to 100 rpm, and the overall residence time was 5 min. Batches of 10 g per batch were introduced into the micro-compounder. Prior any processing, PLA and ABS were dried at 50 °C under vacuum during 24 h. PLA and ABS were introduced, melted and blended in the micro-compounder with ratio of 70 wt% and 30 wt% respectively. Other chemicals were introduced simultaneously with polymers at the given ratio.

2.3.2. Injection moulding

The extruded strands were pelletized and molded using an injection-molding machine (Haake MiniJet Thermo Scientific). The temperature of the cylinder was set to 190 °C and the mold temperature to 65 °C. Injection was done at a pressure of 700 bar. Samples were annealed during 1 h at 100 °C. Dimensions of the samples were 60 mm × 10 mm × 3 mm.

2.4. Characterizations

2.4.1. Scanning electron microscopy (SEM)

The microstructure of PLA/ABS blends was determined by means of a pressure-controlled scanning electron microscope (SEM) model Quanta FEG 200 from FEI (Eindhoven, The Netherlands). The samples were immersed in butanone for 3 days under stirring to remove the ABS phase, and dried under reduced pressure for 48 h at 50 °C, and cryo-fractured after immersion in liquid nitrogen. The obtained surfaces were coated with gold using a high vacuum coating system Baltec med020 (60 mA during 15 s) in order to avoid PLA degradation during the analysis. Different magnifications (×2500, ×5000 and ×10,000) were achieved with the large field detector (LFD) at a pressure of 150 Pa with an accelerating voltage below 5 kV to avoid any sample degradation.

2.4.2. Dynamic mechanical analysis (DMA)

The viscoelastic properties of the blends were assessed by using a Netzsch DMA 42C equipment (Selb, Germany). Samples were sized (60 mm × 10 mm × 3 mm) by injection molding. Samples were tested in a 3-point bending mode in the temperature range from −120 °C to 140 °C with a heating rate of 3 °C/min,. The loading amplitude was 20 µm, the dynamic force was 6 N and the frequency of solicitation was 5 Hz.

2.4.3. Differential scanning calorimetry (DSC)

DSC thermograms were recorded by means of a Netzsch DSC 204 F1 Phoenix apparatus operating in inert atmosphere (nitrogen) with a succession of linear heating/cooling/heating ramps from 0 to 190 °C/190 to 0 °C/0 to 190 °C at a 10 °C/min rate.

2.4.4. NMR

Liquid state NMR spectra have been recorded on a Bruker Avance III HD 600 MHz spectrometer equipped with a 4 mm standard bore H-X probe. The delay between the scans was 10 s. Samples were prepared in deuterated chloroform $CDCl_3$ (containing 0.03% of tetramethylsilane) at a concentration of 20 mg/mL. NMR interpretations of cardanol-based spectra were performed following previous work [28].

2.4.5. NMR

Ecard ^1H NMR ($CDCl_3$, 600 MHz, 298 K) $\delta = 0.86–0.94$ ($-CH_3$ from the cardanol alkyl side chain (***11)***, exp 1.82 H, th 1.77 H), 1.23–1.43 ($-CH_2$ ***(7)*** from the cardanol alkyl side chain, exp 12.55 H, th 13.56 H), 1.54–1.64 ($-CH_2$ β from Ar ***(6)***, exp 2.64 H, th 2.1 H), 1.98–2.09 ($CH_2^*{=}CH$ ***(8)*** exp 3.20 H, th 3.10 H), 2.49–2.57 ($CH_2{-}Ar$ ***(5),*** aliphatic proton reference 2.00 H), 2.77–2.87 ($CH_2^*({=}CH)_2$ (***10′***), exp 1.43 H, th 1.34 H), 2.9 ($-CH$ from epoxy ring ***(a)***, exp 0.59 H, th 1.00

H), 3.35 (−CH(−CH_2)$_2$O− from epoxy ring ***(b)***, exp 0.53 H, th 1.00 H), 3.2–4.5 (−CH_2 α from epoxy ring ***(c)***, exp 3.41 H, th 2.00 H), 4.96–5.88 (CH= (***9, 9′, 9″, 9‴***), exp 4.24 H, th 4.47 H), 6.60–6.90 (H−Ar ***(2, 4),*** exp 2.81 H, th 2.00 H), 7, 18–7.23 (H−Ar ***(3)*** exp 0.93 H, th 1.00 H) (Fig. SI1).

CardE ^{1}H NMR ($CDCl_3$, 600 MHz, 298 K), δ = 0.86–0.94 (−CH_3 from the cardanol alkyl side chain (***11***), exp 1.82 H, th 1.68 H), 1.23–1.43 (−CH_2 ***(7)*** from the cardanol alkyl side chain, exp 12.60 H, th 13.56 H), 1.54–1.64 (−CH_2 β from Ar ***(6)***, exp 2.64 H, th 2.11 H), 1.71 (CH_2^*−CH α from the epoxy ring ***(8)***, exp 0.99 H, th 1.96 H), 2.49–2.57 (CH_2−Ar ***(5),*** aliphatic proton reference 2.00 H), 2.90–3.152 (−CH from epoxy rings ***(9, 9′, 9″, 9‴)***, exp 1.20 H, th 4.06 H), 6.60–7.18 (H−Ar ***(2–4),*** exp 3.99 H, th 4.00 H) (Fig. SI2).

2.4.6. *Impact testing*

The impact properties of PLA/ABS blends were assessed by the Izod impact testing method using an impact pendulum Instron Ceast 9050 (Norwood, MA, USA, 2.7 Joules) at room temperature. The size of the samples tested was 60 mm × 10 mm × 3. The specimens were notched with an Instron Ceast Motorized Notchvis machine (Norwood, MA, USA). At least 5 specimens were tested per reference.

2.4.7. *Tensile testing*

Tensile tests were performed at room temperature using an universal test machine Instron 5967 (Norwood, MA, USA) equipped with a load cell of 1 kN. The measurements were achieved at a speed of 5 mm/min. Before tests, samples were bone-shaped by injection-moulding and stored during 48 h in the environmental conditions of measurement. At least 5 specimens were tested per reference.

3. Results and discussions

3.1. *CardE as compatibilizer for PLA/ABS immiscible blends*

CardE was composed of a phenolic ring and epoxy groups, aiming at reacting with ABS and PLA, respectively. To delve into the mechanisms of reactions, PLA/CardE (5 wt%) and ABS/CardE (5 wt%) blends were prepared by extrusion and analysed by ^{1}H NMR before and after the removal of unreacted CardE by solid-liquid extractions (Fig. 2).

^{1}H NMR characterization of ABS/CardE blends revealed the presence of both components, as attested by the peaks at the chemical shifts between 2.0 and 2.5 (ABS aliphatic −CH_2), 2.49–2.57 (CH_2−Ar of CardE), 2.90–3.152 (−CH from epoxy rings of CardE) and between 6.35 and 7.22 ppm (H−Ar of ABS). After solid-liquid extraction, ABS/CardE blends were still composed of a few part of CardE (0.86–0.94, 2.49–2.57 and 2.90–3.152 ppm, corresponding to −CH_3 from the cardanol alkyl side chain, CH_2−Ar, and −CH from epoxy rings, respectively), presumably grafted onto ABS following a similar mechanism than described elsewhere [22,23]. The presence of Ecard was also confirmed by DSC analysis before and after solid-liquid extractions comparted to ABS/CardE blends (Fig. SI3). The T_g of the initial blend was reaching 87.3 °C while ABS alone is transiting at 109.5 °C (Table 1, entries 2 and 4).

After the solid-liquid extraction, ABS T_g remained shifted to 105.3 °C. Even in slight amounts, cardanol is known to act as a plasticizer of ABS leading to the reduction of its Tg [22,29]. In the current case, all free CardE has been removed after the solid liquid extraction. If ABS remains plasticized, it is an indirect evidence cardanol has been successfully grafted onto ABS, supporting our initial assumption.

On the contrary, in spite of the epoxy rings opening according to the ^{1}H NMR analysis of the blends, no traces of CardE were found in the NMR spectra of PLA/cardE after solid-liquid extractions, indicating the absence of reaction between the two components. It might be deducted that the reactivity of the oxirane rings was not enough to modify PLA end chains [19–21].

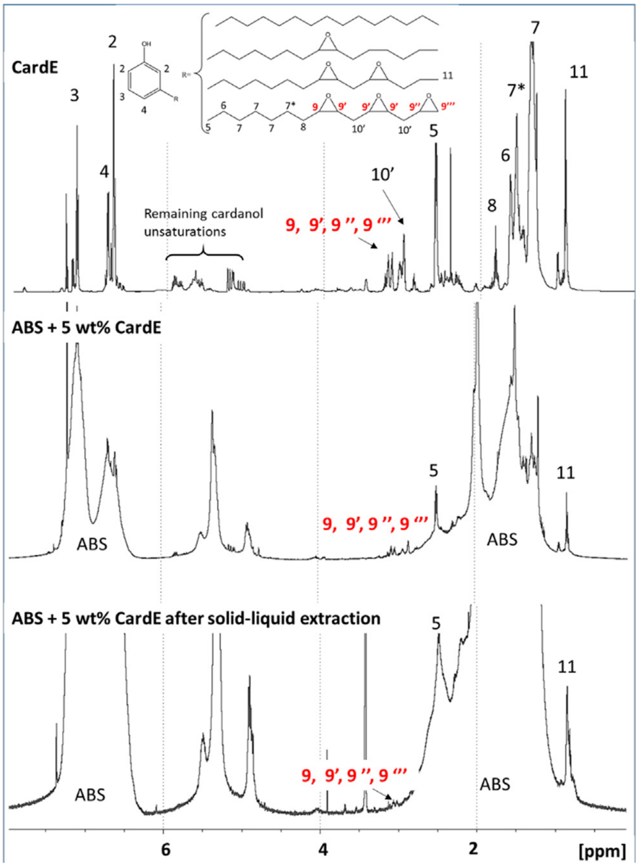


Fig. 2. ^{1}H NMR spectra of CardE, ABS + 5 wt% CardE and the solid fraction of ABS + 5 wt% CardE after solid-liquid extractions.

Table 1
Glass transition temperatures (T_g) of PLA, ABS, and their blend by extrusion with 5 wt% of Ecard, before and after solid-liquid extraction, measured by DSC.

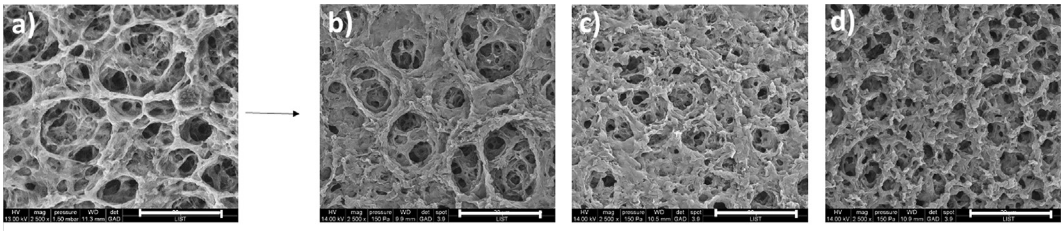
Composition	$T_{g\ \text{before solid-liquid extraction}}$ (°C)	$T_{g\ \text{after solid-liquid extraction}}$ (°C)
PLA	59.2 ± 0.1	59.2 ± 0.1
ABS	109.5 ± 0.2	109.5 ± 0.2
PLA + 5 wt% cardE	51.2 ± 0.1	60.1 ± 0.3
ABS + 5 wt% cardE	87.3 ± 0.3	105.3 ± 0.1

These elements highlighted the extrusion of PLA/ABS and CardE would not lead to a simultaneous reaction of the three components. At best, CardE might modify ABS chains as we reported before with cardanol [22], leading to a higher interaction toward PLA as the polarity of the alkyl side chain is higher for CardE than Cardanol alone. This assumption was supported by the preparation of the blends and their characterizations by morphological, DMA and mechanical techniques.

Mixtures of PLA and ABS with different contents of CardE were prepared by reactive extrusion. Morphological analyses were performed on cryo-fractured surfaces of the mixtures to appreciate the morphology changes of the blends. When ABS and PLA are melt-blended (Fig. 3), a typical morphology of immiscible blend was observed, characterized by irregularly sized ABS nodules dispersed in the PLA matrix.

A progressive decrease of ABS nodules size could be observed while adding cardE, (Fig. 3b, c and d) attesting its efficient compatibilization. While a too large amount of neat cardanol was detrimental, cardE promotes the dispersion of ABS within PLA even at content above 5 % wt, and the smallest nodules were reached with 10 wt% cardE.

Dynamic mechanical analyses (Fig. 4) were performed to confirm this trend. A compatibilization effect is demonstrated as attested by the shift of both PLA and ABS mechanical relaxation temperatures Tα to



PLA/ABS (70/30 wt%)   5 wt% cardE   7 wt% cardE   10 wt% cardE

Fig. 3. Scanning electron micrographs of PLA/ABS (70/30 wt%) blends without and with 5 wt%, 7 wt% and 10 wt% cardE. Scale bar corresponds to 20 µm.

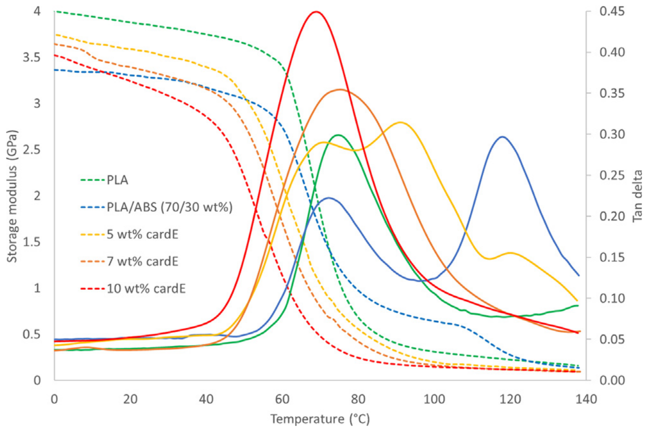


Fig. 4. Thermo-mechanical analyses of PLA/ABS (70/30 wt%) blends without and with 5 wt%, 7 wt% and 10 wt% cardE.

each other, with one unique relation peak above 5 wt% of cardE. Interestingly, with 5 wt% (3.6 GPa) and 7 wt% (3.4 GPa) an improvement of the PLA/ABS blend storage modulus (3.2 GPa) is observed at room temperature while a decrease would have been expected due to the plasticization effect of the compatibiliser,. The improvement of the properties of the immiscible blends is a key index of its successful compatibilization using CardE.

Stress-strain curves are reported on Fig. 5, and the data extracted from these measurements compiled in Table 1. PLA is a brittle polymer with a high Young's modulus (E) around 2.3 GPa, a high ultimate stress (σ) of 70.6 MPa and a low elongation at break (ε) around 4.6% (Table 1, entry 1). At the opposite, ABS has a ductile behaviour, characterized by a weak E of 1.5 GPa, σ 38 MPa and ε around 14.1% (Table 1, entry 2). Blending these two polymers results in a brittle material with values of E, σ and ε of 2.2 GPa, 51 MPa and 7.6%, respectively (Table 1, entry 3).

When adding cardE, a gradual improvement of ε was observed. Elongation at break increased from 7.6% to 11.0% (+145%), 22.8% (+300%) and 50.8% (+670%) with the addition of 5 wt%, 7 wt% and 10 wt% of cardE, respectively (Table 2, column 9). Moreover, the presence of cardE weakly affected the ultimate stress σ as attested by the slight decrease from 50.9 MPa to 44.9 MPa, 42.7 MPa and 37.1 MPa in the presence of 5 wt%, 7 wt% and 10 wt% of cardE, respectively MPa (Table 2, column 8).

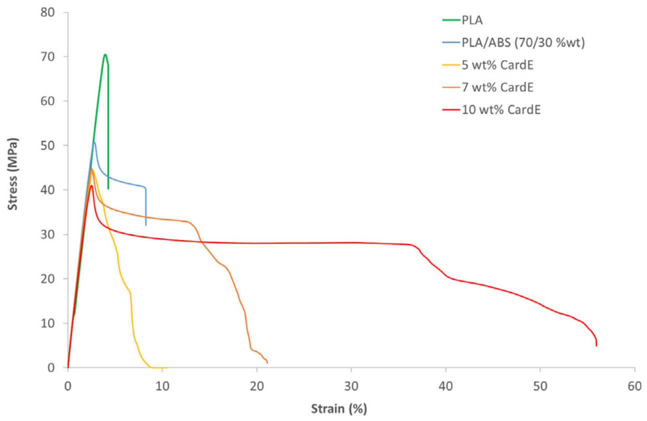


Fig. 5. Tensile curves of PLA/ABS (70/30 wt%) blends without and with cardE at different ratio.

The improvement of the impact resistance of PLA/ABS blends was also demonstrated with the addition of CardE (Table 2, column 6). Raw PLA/ABS blend led to a material with a low impact resistance (3.7 kJ m^{-2}) attesting the incompatibility between both polymers. With 5 wt% of cardE, a significant improvement of the impact resistance was appreciated (from 3.7 kJ.m^{-2} to 5.2 kJ m^{-2} (+41%)), highlighting the efficiency of the epoxidized biophenol to act as an interfacial compatibilizer. Above 7 wt%, the impact strength of the blend was decreasing, fitting to thermo-mechanical analyses.

In conclusion, CardE promoted the compatibilization of PLA and ABS as attested by DMA, tensile and impact tests and morphological analyses, with a higher efficiency than cardanol alone [22] (Table 2, entry 4). However, CardE exhibited secondary epoxy groups (oxirane type), not reactive to modify PLA end chains, while common primary epoxy groups did [24]. In light of these elements, the compatibilization might be the combination of cardE plasticization on either or both PLA and ABS as reported elsewhere [30–33], its higher polarity, and its reaction with ABS. The polarity of modified ABS chains might be enhanced enough to promote the compatibilization of the two immiscible polymers. However, PLA remained unaffected while a higher level of compatibilization might be reached in the case of a concomitant reaction of the compatibilizer with both PLA and ABS. To this aim, we investigated the effect of Ecard, a cardanol derivative which phenolic group was epoxidized, in combination with raw cardanol.

3.2. Mixtures of cardanol and Ecard as compatibilizer of PLA/ABS

The phenolic group of cardanol can be epoxidized by its reaction with epichloridrin [34], leading to the so-called Ecard, which might be more reactive toward PLA than CardE. ^{1}H spectrum of Ecard can be found on Fig. SI1. Ecard and PLA reaction during reactive extrusion was supported by ^{1}H NMR after solid-liquid extraction (Fig. 6).

Ecard epoxy groups were characterized by the peaks at the chemical shifts at 2.76 and 3.28 ppm corresponding respectively to protons (a) and (b). Before mixing (a) and (b) integrated for 0.69 and 0.54 respectively (Table 3, entry 2). After mixing, the same peaks integrated for 0.35 and 0.16, respectively. The drop of integrations was due to the epoxy ring opening during the extrusion process. After solvent extraction in methanol, traces of cardanol were found in the resulting material, as attested by the peaks corresponding to the protons (5), (8), (9′), (9″), (9‴), (10) and (10′) of the aliphatic chain of cardanol on Fig. 6. By comparing the integrations of peaks (a) and (b) to peak (5), it appears clearly that the peaks corresponding to the protons of the epoxy groups are substantially integrating less to 0.27 and 0.08 respectively (Table 3, entry 3), as expected in the case of opened epoxy rings. In addition, DSC measurements were performed on the extracted samples (Fig. SI4). After solid-liquid extraction, PLA T_g was shifted from 64.5 °C to 51.2 °C,

Table 2
Summary of the thermo-mechanical properties of PLA, ABS, and PLA/ABS (70/30 wt%) blends without or with cardE at different content.

Composition	T_α PLA (°C)[a]	T_α ABS (°C)[a]	ΔT (°C)[a]	E' at 20 °C (GPa)[a]	Notched Izod impact strength (kJ m^{-2})[b]	Young's modulus (GPa)[c]	Ultimate stress (MPa)[c]	Strain at break (%)[c]
PLA	74.7 ± 0.5	–	–	3.9 ± 0.2	2.9 ± 0.1	2.3 ± 0.2	70.6 ± 0.5	4.6 ± 0.3
ABS	–	113.2 ± 0.2	–	1.8 ± 0.1	31.6 ± 1.2	1.5 ± 0.1	38.3 ± 0.4	14.1 ± 3.5
PLA/ABS (70/30)	72.2 ± 0.3	117.9 ± 0.7	45.7	3.3 ± 0.1	3.7 ± 1.2	2.2 ± 0.1	50.9 ± 0.8	7.6 ± 2.5
10 wt% cardanol	65.0 ± 0.6	–	0	2.5 ± 0.2	4.1 ± 0.7	1.8 ± 0.1	25.2 ± 4.0	2.4 ± 0.3
5 wt% cardE	74.7 ± 0.4	95.6 ± 0.1	20.9	3.1 ± 0.1	5.2 ± 0.3	2.2 ± 0.1	44.9 ± 2.6	11.0 ± 7.6
7 wt% cardE	74.6 ± 0.2	75.4 ± 0.3	0.8	3.4 ± 0.1	5.1 ± 0.2	2.2 ± 0.1	42.7 ± 2.6	22.8 ± 6.7
10 wt% cardE	69.5 ± 0.1	–	–	3.1 ± 0.2	4.5 ± 0.2	2.0 ± 0.1	37.1 ± 2.9	50.8 ± 11

[a] Values obtained from DMA.
[b] Values obtained from Izod impact tests.
[c] Values obtained from tensile tests.

confirming the presence of cardanol species grafted to PLA in the material. The grafting mechanism may correspond to Fig. 7, according to previous work reported on the reaction of PLA end chains with epoxy groups [24].

Nevertheless, this approach had a drawback: the epoxidation of the cardanol phenolic group might reduce its antioxidant properties, decreasing in consequence its reactivity with ABS [23]. To provide a simultaneous reaction with PLA and ABS, we investigated the impact of mixtures of raw cardanol and Ecard. Raw cardanol would react with ABS, while Ecard with PLA. It was expected to promote the interfacial interactions between both modified ABS and/or PLA phases, by making closer their surface energies. The cardanol and epoxidized cardanol (respectively noted as c and Ec for the sake of clarity) mixtures were prepared with different ratios of 30/70 wt%, 50/50 wt% and 70/30 wt %, and introduced at 10 wt% within PLA and ABS blends by extrusion. A moderate addition of 10 wt% of compatibilizer was decided, essential to preserve the phase separation while promoting a finer phase dispersion. An improvement in the interphase adhesion and more importantly of the ultimate properties might be expected by following this strategy [35].

The incorporation of c/Ec to PLA/ABS led to a finer dispersion of ABS nodules within PLA, as attested by the morphological analyses by SEM reported on Fig. 8. Without compatibilization, ABS nodules sizes were around 10 µm. When a mixture of 50/50 C/Ec was used, a very fine dispersion of ABS was reached, with ABS nodules diameter decreasing between 2 and 3 µm in average. Mixtures of 70/30 and 30/70 of c/Ec (c and d) helped to reduce ABS nodules size to 5–6 µm. The finest dispersion of ABS within PLA attested an efficient compatibilization of the polymers, in particular when c/Ec 50/50 mixtures were employed.

Table 3
Summary of the integrations of the characteristic peaks of Ecard epoxy groups.

	Assignment	Chemical shift (ppm)	Experimental integration
Raw Ecard	$CH_2{-}\mathbf{CH_2}{-}Ar$ ***(5)***	2.48	2.00 H
	$CH{-}\mathbf{CH}{-}O$ ***(a)***	2.90	0.59 H
	$CH_2{-}\mathbf{CH}{-}O$ ***(b)***	3.28	0.53 H
PLA + 10 wt% Ecard	$CH_2{-}\mathbf{CH_2}{-}Ar$ ***(5)***	2.48	2.00 H
	$CH{-}\mathbf{CH}{-}O$ ***(a)***	2.90	0.35 H
	$CH_2{-}\mathbf{CH}{-}O$ ***(b)***	3.28	0.16 H
Solid fraction (PLA + 10 wt% Ecard)	$CH_2{-}\mathbf{CH_2}{-}Ar$ ***(5)***	2.48	2.00 H
	$CH{-}\mathbf{CH}{-}O$ ***(a)***	2.90	0.27 H
	$CH_2{-}\mathbf{CH}{-}O$ ***(b)***	3.28	0.08 H

Dynamic mechanical analyses led to similar conclusions, as attested

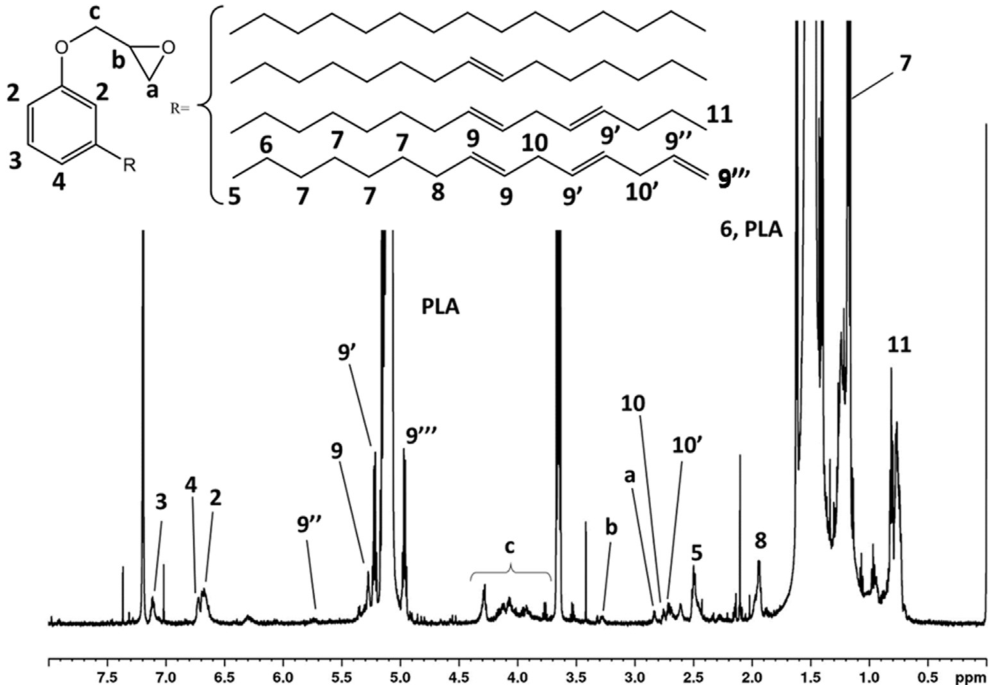


Fig. 6. ^{1}H NMR spectrum of the solid fraction of extruded PLA + 5 wt% Ecard.

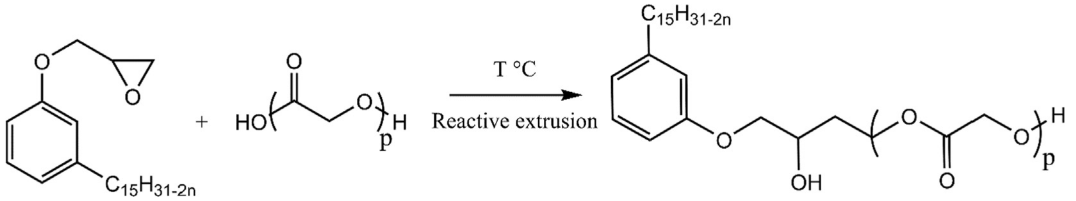


Fig. 7. Schematic representation of the mechanism of Ecard grafting onto PLA.

by the single Tα peak (Fig. 9). A slight decrease of the Tα was observed compared to the Tα of both PLA and ABS, due to the combination of the compatibilizing and plasticizing effects of cardanol [22,24,30–33]. The theoretical value of the blend Tα, assuming PLA and ABS would be miscible or fully compatibilized, can be estimated following the Fox equation:

$$1/T_{\alpha\ \ blend} = \frac{\phi_{ABS}}{T_{\alpha ABS}} + \frac{\phi_{PLA}}{T_{\alpha PLA}}$$

where $T_{\alpha\ ABS}$ and $T_{\alpha\ PLA}$ correspond to the Tα of ABS and PLA, respectively, and ϕ_{ABS} and ϕ_{PLA} are weight fractions of PLA and ABS respectively.

The calculation led to a theoretical value of 82.5 °C, while the experimental values are around 70 °C. It may be assumed the plasticizing effect of the mixture of cardanol and Ecard led to the significant decrease of the Tα of the blend, even at temperatures slightly below PLA Tα.

A highest level of compatibilization was evidenced by the evolution of the mechanical relaxation related to ABS domains around 120 °C. With cardanol or Ecard used separately, a small relaxation occurred around 120 °C, as attested by the small shoulder of the tan(δ) evolution, linked to domains of raw ABS. While using c/Ec, this relaxation peak disappeared, concomitantly with the increase of the maximum of the peak of the loss factor, indicating a full compatibilization state. Storage moduli in presence of 10 wt% of c/Ec were higher than separately for

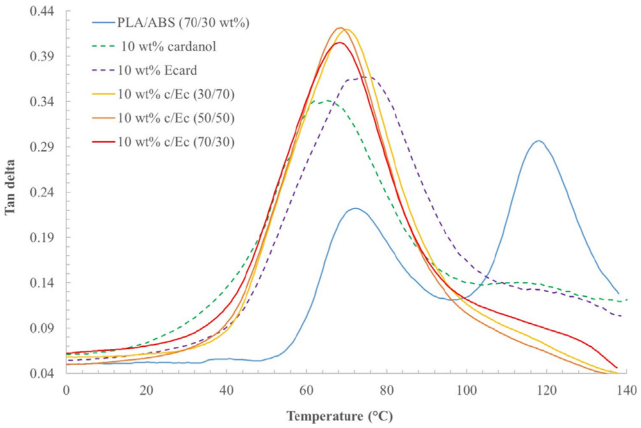


Fig. 9. Thermo-mechanical analyses of PLA/ABS (70/30 wt%) blends without and with 10 wt% c/Ec at different ratio.

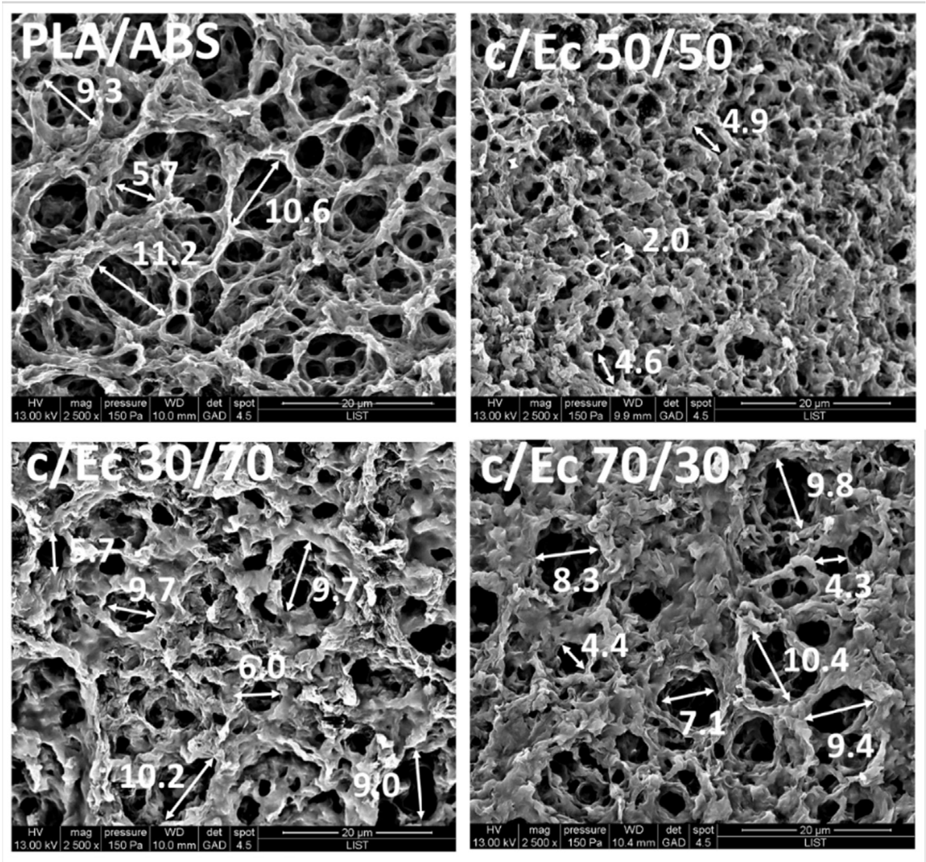


Fig. 8. Scanning electron micrographs of PLA/ABS (70/30 wt%) blends without and with 10 wt% of c/Ec mixtures. Scale bar corresponds to 20 µm.

Table 4
Summary of the thermo-mechanical properties of PLA, ABS, and PLA/ABS (70/30 wt%) blends without or with c/Ec at different composition.

Composition	Tα PLA (°C)[a]	Tα ABS (°C)[a]	ΔT (°C)[a]	E' at 20 °C (GPa)[a]	Notched Izod impact strength (kJ m^{-2})[b]	Young's modulus (GPa)[c]	Ultimate stress (MPa)[c]	Strain at break (%)[c]
PLA	74.7 ± 0.5	–	–	3.9 ± 0.2	2.9 ± 0.1	2.3 ± 0.2	70.6 ± 0.5	4.6 ± 0.3
ABS	–	113.2 ± 0.2	–	1.8 ± 0.1	31.6 ± 1.2	1.5 ± 0.1	38.3 ± 0.4	14.1 ± 3.5
PLA/ABS (70/30)	72.2 ± 0.3	117.9 ± 0.7	45.7	3.3 ± 0.1	3.7 ± 1.2	2.2 ± 0.1	50.9 ± 0.8	7.6 ± 2.5
10 wt% cardanol	65.0 ± 0.6	–	0	2.5 ± 0.2	4.1 ± 0.7	1.8 ± 0.1	25.2 ± 4.0	2.4 ± 0.3
10 wt% Ecard	74.1 ± 0.2	–	0	2.6 ± 0.1	3.6 ± 0.7	1.9 ± 0.1	29.7 ± 1.9	2.2 ± 0.4
10 wt% c/Ec (30/70)	70.0 ± 0.4	–	0	2.9 ± 0.1	7.2 ± 0.2	2.0 ± 0.1	30.4 ± 3.1	68.7 ± 13.2
10 wt% c/Ec (50/50)	68.6 ± 0.5	–	0	2.8 ± 0.1	7.9 ± 0.2	2.0 ± 0.1	29.3 ± 3.8	82.9 ± 14.9
10 wt% c/Ec (70/30)	67.6 ± 0.3	–	0	2.7 ± 0.1	5.9 ± 0.4	2.0 ± 0.1	26.0 ± 1.2	40.3 ± 16.1

[a] Values obtained from DMA.
[b] Values obtained from Izod impact tests.
[c] Values obtained from tensile tests.

each bio-phenol, attesting a synergistic effect (Table 4, entries 4, 5 and 6).

In particular, substantial resilience improvements were observed by adding 10 %wt c/Ec (50/50), the impact resistance reaching 7.9 kJ m^{-2} (+172%) from an initial value of 3.7 kJ m^{-2} for PLA/ABS (Table 4, column 6). With c/Ec (70/30) and c/Ec (30/70), the improvement was also consistent: +148% (7.2 kJ m^{-2}) and +103% (5.8 kJ m^{-2}), respectively.

In agreement with impact tests, tensile tests showed a similar and significant improvement of the elongation at break of PLA/ABS (Fig. 10). The most impressive results were also obtained when using 10 wt% of c/Ec (50/50) as indicated by the evolution of ε from 7.6% to 82.9%, *i.e.* an increase of almost 1000%. With c/Ec (70/30) and c/Ec (30/70), the improvement of the elongation at break was also significant: 430% (ε = 40.3%) and 800% (ε = 68.7%), respectively.

Cardanol and Ecard alone were able to modify either ABS or PLA. The compatibilization was enhanced for two reasons: the rapprochement of the surface energies of the two polymers and the plasticizing effect of the compatibilizer. When using c/Ec mixtures, the modified polymer chains would gather at the interface between the two polymers, providing stability to the interfacial structure. Modified chains of both PLA and ABS with cardanol derivatives would intersperse between PLA and ABS, reducing the interfacial tension and improving the interfacial adhesion. This behavior may be compared to the addition of a third polymer, miscible with the two constitutive polymers PLA and ABS [35]. A tentative description of the compatibilization mechanism is schematized on Fig. 11.

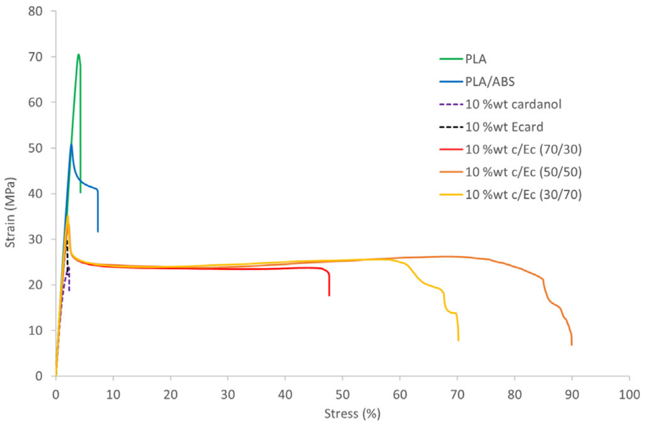


Fig. 10. Tensile curves of PLA/ABS (70/30 wt%) blends without and with 10 wt % c/Ec at different ratio.

4. Conclusions

In a previous paper, the compatibilization of immiscible PLA/ABS blends by reactive extrusion was exposed when using cardanol, thanks to its grafting onto ABS. The described mechanism was relying on the antioxidant properties of the bio-phenol. In the present study, epoxy groups were introduced on the cardanol structure to promote its reactivity toward PLA, aiming to improve the compatibilization of PLA/ABS.

As the phenolic ring of cardanol was aimed to react with ABS, a first approach was to epoxidized the unsaturations of the alkyl side chains of cardanol (cardE). The compatibilization of PLA and ABS was observed, as attested by morphological, DMA and mechanical characterizations. Nevertheless, no evidence of a reaction between PLA and cardE was found, while a bundle of presumptions (from ^{1}H NMR and DSC characterizations) highlighted a reaction between ABS and CardE, as previously published with cardanol. It is assumed a similar mechanism was occurring, enhanced by the increased polarity of the cardanol alkyl side chain compared to neat cardanol, leading to a higher affinity between modified ABS and PLA.

In a second approach was used a mixture of cardanol and its epoxidized form through its phenolic ring (Ecard), both of them able to react either with PLA or ABS. The reaction of PLA and Ecard was demonstrated by ^{1}H NMR. When using c/Ec mixtures, the modified polymer chains would gather at the interface between the two polymers, providing stability to the interfacial structure. Modified chains of both PLA and ABS with cardanol derivatives would intersperse between PLA and ABS, reducing the interfacial tension and improving the interfacial adhesion. The ratio 50/50 appeared to be ideal, for which the elongation at break and the impact resistance of the samples were as high as 82.9% and 7.9 kJ m^{-2} respectively. These results emphasized the importance of the co-reactivity to reach a high level of compatibilization of PLA and ABS.

The perspectives of this work are straightforward. All the components are already commercially available. Among them, cardanol is widely available and his low cost (around 1 €/kg at ton scale) is competitive. In addition, PLA and ABS are two polymers widely considered in the 3D printing industry. The next steps would be the transfer of these results to a larger and more applied scale. The question of the recyclability is not addressed in this paper. and at the actual state, it is not known if compatibilised PLA/ABS by reactive extrusion may be recycled or reused for the same application. The identification of the degradation mechanisms of such multiphase systems should be taken into account for the development of new plasticized materials that could endure the thermomechanical constraints of recycling. This approach is under investigation in our group.

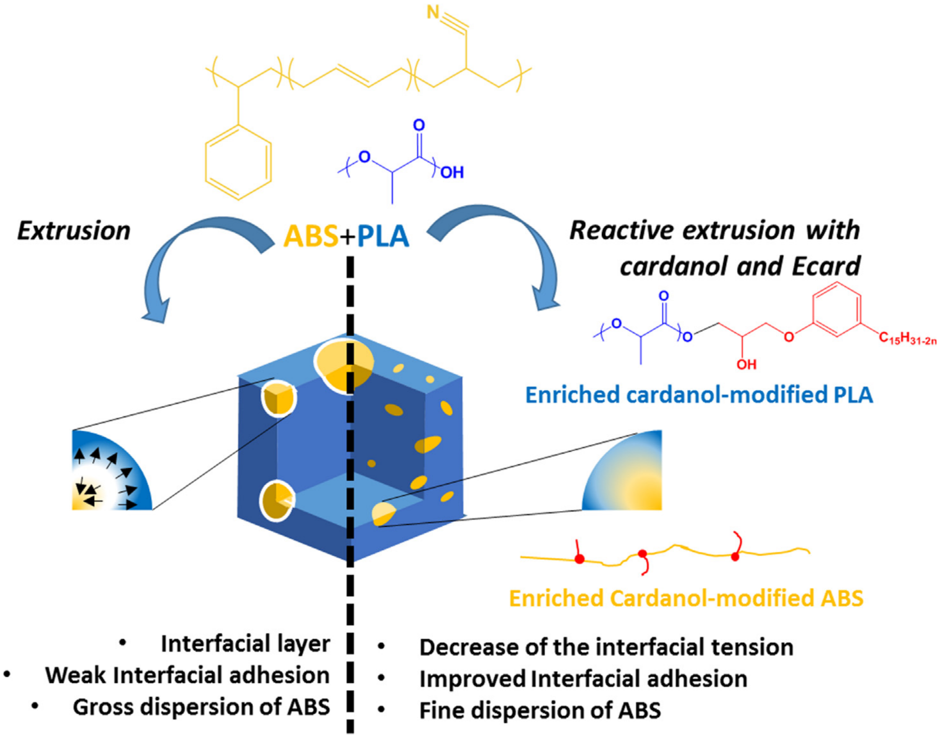


Fig. 11. Schematic representation of the compatibilization mechanism of PLA and ABS by using C/Ec.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.eurpolymj.2019.02.017.

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