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In-depth investigation on the effect and role of cardanol in the compatibilization of PLA/ABS immiscible blends by reactive extrusion

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ABSTRACT

In this work, a sustainable approach was developed to melt-blend and enhance the compatibility of the immiscible blend of polylactide (PLA) and poly(acrylonitrile–butadiene–styrene) (ABS). Cardanol, a bio-based phenolic compound, was used as an interfacial (reactive) compatibilizer. The blending was conducted by a solvent-free reactive extrusion. The incorporation of cardanol resulted in an enhancement of the compatibility evidenced by the decrease of ABS nodules size within PLA from few micrometres to several tens of nanometres and the convergence of both polymers $T\alpha$ around 68.5 °C. In-depth investigation evidenced that cardanol grafted onto ABS during the reactive extrusion via its phenolic ring, leading to a substantial plasticizing effect and a significant decrease of the surface energy of ABS, similar to those of PLA. This work paves the way to a multitude of new compatibilization strategies based on the reaction of phenolic compounds during the extrusion of PLA and ABS.

1. Introduction

Polylactide (PLA) has attracted increasing attention in recent years due to its renewability and (bio)degradability. It has been widely used for biomedical applications such as sutures and drug delivery devices, but also in packaging industry [1]. PLA has also become an alternative to traditional commodity plastics for everyday applications as an environmentally friendly polymer due to its reasonable price and unique properties such as high strength, high stiffness, resistance to fats and oils. However, its toughness and heat distortion temperature are not satisfactory to extend its applications range. To overcome these drawbacks, direct blending of PLA with other polymers is considered as a straightforwardly and cost-effective strategy allowing the obtention of tougher materials. Among the wide range of examples reported in the literature, polymers with low glass transition temperature (Tg) such as poly(ε-caprolactone) (PCL) [2,3], poly(ethylene oxide) (PEO) [4,5], poly(carbonate) (PC) [6], poly(butylene succinate) (PBS) [7,8], poly(ethylene succinate) (PES) [9], poly(tetramethylene adipate-*co*-terephathalate) (PTAT) [10], poly(butylene adipate-*co*-terephthalate) (PBAT) [11], polyurethane [12,13], poly(vinyl acetate-*co*-vinyl alcohol) (PVA) [14] or polyisoprene [15] were successfully used as toughening agents for PLA. However, a drop of both the storage modulus and tensile strength of the resulting blends is generally observed in most cases.

As long as immiscible blends with PLA are concerned, a wide range of chemical reactions were explored to enhance the interfacial

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compatibility. These chemical reactions rely on the reactivity of PLA terminal hydroxyl (−OH) or carboxyl (−COOH) reactive groups. Compatibilized PLA/PBS blends were obtained by reacting both PLA −OH/−COOH and PBS −OH end groups with di-isocyanates (methylene diphenyl diisocyanate MDI). The so-compatibilized PLA/PBS (weight ratio 70/30 wt%) blend exhibited an increased elongation at break from 24.7% to 285% with a slight decrease of the tensile strength and tensile modulus [16]. Another approach was proposed by Al-Itry et al. [17] as well as by Dong, Zou et al. [18], by producing biodegradable PLA/PBAT blends from the reaction of PLA and PBAT with chain-extenders bearing epoxy groups (Joncryl™ and 1,6-hexanediol diglycidyl ether). The authors reported that the compatibility between PLA and PBAT was significantly improved by the *in situ* formation of PLA-*co*-PBAT copolymers, resulting in a significant increase of the elongation at break to 500% without any decrease of the tensile strength when 20 wt % PBAT was used. Compatibilized blends of PLA and glycidyl methacrylate-grafted-poly(ethylene octene) (GMA-*g*-POE) were obtained by reacting the epoxy groups of the GMA-*g*-POE with the carboxylic end-groups of PLA [19]. It resulted in a significant increase of both the elongation at break (from 21% to 282%) and impact strength (from 4 kJ/m^2 to 54.7 kJ/m^2) by adding 45 wt% of GMA-*g*-POE to neat PLA.

Outstanding impact resistance, high mechanical strength, good chemical resistance, and ease of extrusion and molding are characteristics that makes poly(acrylonitrile-butadienestyrene) (ABS) widely used as a toughening agent for many engineering plastics such as polycarbonate (PC) [20] or polyamide (PA) [21]. ABS has been reported to be a good candidate to toughen PLA as well [22–28]. In particular, the most significant results were obtained by using core shell particles of ABS, where the core is composed of the polybutadiene (PB) rubber phase while the shell contains the poly(styrene-*co*-acrylonitrile) counterpart (PSAN) [25]. This innovative approach clearly promoted the elongation at break of poly(L-lactide) (PLLA) up to 28 folds with only 6 wt% of ABS core shell particles. Moreover, the core shell particles proved to act as nucleating agents increasing also the crystallinity of PLLA from 0.6% to 20.2% with only 2 wt% of ABS. The strong interactions between the ester groups of PLLA and the nitrile groups of the PSAN shell layer promoted the interfacial adhesion between ABS particles and PLLA matrix. Thus, reactive compatibilizers rose interest since they could enhance the interfacial adhesion of PLA with another polymer. This approach was further developed in the work published by Li and Shimizu [22] in which the authors described the efficiency of a reactive compatibilizer composed of styrene-acrylonitrile and glycidyl methacrylate (SAN-GMA) to compatibilize PLA and ABS. The authors demonstrated that SAN-GMA epoxy groups were able to react with PLA end-groups during melt-blending to form a copolymer at the interface of PLA and ABS. When 5 wt % SAN-GMA were used, a clear improvement of the mechanical properties of the PLA/ABS (70/30 wt%) blends was observed: a two-fold increase was reported for the impact strength while the elongation at break increased from 3.1% to 23.8% and the tensile strength was preserved. A comparable enhancement of the mechanical properties was also observed for a PLA/ABS (39/61 wt%) blend prepared by reactive extrusion as attested by an improvement of the notched Izod impact strength of PLA/ABS blend when 20 wt% SAN-GMA was used [24].

Almost all strategies for reactive compatibilization involving PLA/ABS immiscible blends target the reactivity of PLA, while the occurrence of chemical reactions on ABS could also be of interest. For instance, it has been shown that cardanol, a bio-phenol issued from the cashew nutshell industry, was able to react with natural rubber (NR) through a radical pathway. This reaction involved the unsaturations of the cardanol alkyl side chain and the C=C of NR [29–31]. Likewise, cardanol was shown to react with ABS following a similar mechanism [32]. The starting point of our study was to check if a similar reaction can occur when cardanol is incorporated during the reactive extrusion of ABS with PLA, with an ultimate goal to develop a new chemical approach for the compatibilization of PLA/ABS blends. Indeed, it could be expected that cardanol could compatibilize this immiscible blend likewise PP/PS blends, for instance [33]. Interestingly, unexpected results, detailed hereby, showed that raw cardanol was effectively able to efficiently compatibilize PLA and ABS by reactive extrusion but via another reactivity pathway and without any additional chemical modification of the bio-phenol. This work attempts to shed light on the chemical mechanisms of this unexpected reactive compatibilization.

2. Experimental

2.1. Materials

Polylactide (PLA - reference Ingeo™ 4043D) was supplied by NatureWorks (Minnetonka, MN, USA) and contained 4.2 mol% D-isomeric units. Poly(acrylonitrile-butadienestyrene) terpolymer (ABS - Terluran HI-10), an injection molding and extrusion grade, was purchased from Styrolution (Frankfurt, Germany). Cardanol (UltraLite2023) was kindly supplied by Cardolite Chemical Zhuhai Ltd (Zhuhai, Guangdong, China). 3-Pentadecylphenol (PDP) was supplied by Sigma-Aldrich (Saint-Louis, USA). 3-pentadecylbenzene (PDB) and 4-amylcyclohexanol (cis- and trans-mixture) (ACC) were obtained from TCI (Portland, USA). Methanol was supplied by CarlRoth. All chemicals were used as received.

2.2. Processing

2.2.1. Reactive extrusion

Extrusions were performed using a twin-screw DSM XPlore 15 mL micro-compounder (Geleen, The Netherlands) at 190 °C under a nitrogen purge flow to avoid any oxygen presence in the extruder barrel. The screw speed was set to 100 rpm, while the overall residence time was 5 min. A total of 10 g per batch was introduced into the micro-compounder. Prior to processing, PLA and ABS pellets were dried at 50 °C under vacuum for 24 h. PLA and ABS were introduced, melted and blended in the micro-compounder. The ratio PLA/ABS was fixed to 70/30 wt% to get a good balance between toughening and the use of a petrochemical product. Other chemicals were introduced simultaneously with polymers at the given ratio.

2.2.2. Injection moulding

The extruded strands were pelletized and molded using an injection-molding machine (Haake MiniJet Thermo Scientific). The cylinder temperature was set to 190 °C and the mold temperature to 65 °C. Pellets were poured in the cylinder, melted for 5 min and injected at a pressure of 700 bar. For tensile testing and DMA measurements, the mold and Haake MiniJet 60 mm × 10 mm × 3 mm (reference 557-2296) was used. Samples were annealed at 100 °C for 1 h.

2.3. Characterizations

2.3.1. Scanning electron microscopy (SEM)

The microstructure of PLA/ABS blends was studied by means of a pressure-controlled scanning electron microscope (SEM) model Quanta FEG 200 from FEI (Eindhoven, The Netherlands). The samples were soaked in butanone for 3 days under stirring to selectively remove ABS domains, then dried under vacuum at 50 °C for 48 h, and cryo-fractured after immersion in liquid nitrogen. The obtained surfaces were observed at different magnifications (2500×, 5000× and 10,000×) with the large field detector (LFD) at a pressure of 150 Pa with an accelerating voltage ≤ 5 kV in order to avoid any sample degradation.

2.3.2. Dynamic mechanical analysis (DMA)

The viscoelastic properties of the blends were assessed by using a Netzsch DMA 42 C 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, with a loading amplitude of 20 μm, a dynamic force of 6 N at 5 Hz.

2.3.3 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.

2.3.4. Solvent extraction in methanol

Solvent extractions were carried out in methanol for 24 h to quantify the grafting efficiency of compatibilizers during extrusion. Recovered solid fractions were dried at 50 °C for 8 h under vacuum to remove residual methanol. Each extraction was repeated in quadruplicate.

2.3.5. NMR

^{1}H and ^{13}C NMR spectra were recorded using a BRUKER AMX-300 spectrometer working at a frequency of 300 MHz in a magnetic field of 7 T. 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.

2.3.6. Contact angle measurement

Contact angles were measured with a contact angle system OCA 15 from Dataphysics using the sessile drop technique. A sessile water droplet of 2 μL was deposited at the surface of the prepared sample by means of a syringe pump and the value of the contact angle was extracted from the recorded image of the droplet using a software based on the Laplace-Young model. Five droplets were deposited at different locations on the sample in order to obtain an average value. The surface energy of the tested sample was assessed by measuring the contact angle of distilled water and diiodomethane, then applying the Owens–Wendt method for the calculation of the polar and dispersive components of the surface energy.

2.3.7. Impact testing

The impact properties of elaborated PLA/ABS blends were assessed by the Izod impact testing method using an impact pendulum Instron Ceast 9050 (Norwood, MA, USA) at room temperature. The size of the samples tested was 60 mm × 10 mm × 3 mm (obtained by injection molding as aforementioned). The specimens were notched with an Instron Ceast Motorized Notch vis machine (Norwood, MA, USA). The impact energy was calculated by the integrated software of the pendulum machine. At least 5 specimens were tested per reference.

3. Results and discussions

3.1. Compatibilization of PLA/ABS blends with cardanol

As aforementioned, PLA and ABS are immiscible, and their blend (70/30 wt%) exhibits two distinct mechanical relaxation temperatures (Tα) as shown on the DMA curves depicted on Fig. 1. The Tα of PLA remains similar (74.7 °C) while the Tα of ABS increases from 113.2 °C to 119.6 °C after extrusion of the blend (Table 1), as already reported elsewhere [34]. As expected, the incorporation of ABS within PLA results in a decrease of the storage modulus of the blend at 20 °C from 3.9 GPa to 3.2 GPa due the relatively low storage modulus of ABS (1.8 GPa at 20 °C).

The addition of 1 wt% of cardanol in PLA/ABS blend leads to a decrease of the Tα of both PLA (from 74.6 °C to 71.8 °C) and ABS (from 119.6 °C to 112.2 °C). Interestingly, ABS seems to be more impacted by the addition of cardanol even if the bio-plasticizer seems to be located in both phases as both Tα are decreased. When increasing cardanol content, the Tα of both polymers are getting

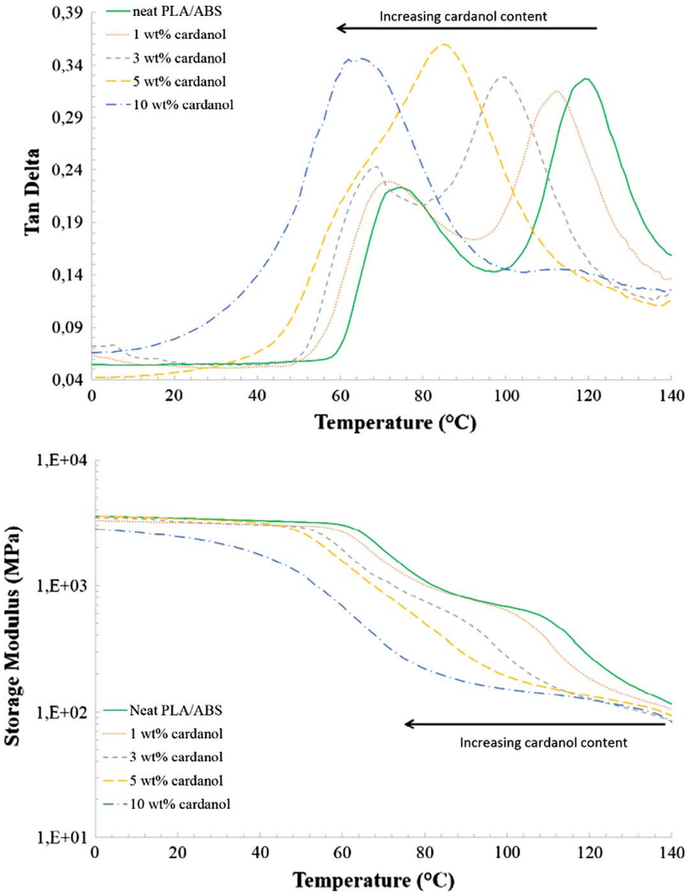


Fig. 1. Thermo-mechanical analyses of PLA/ABS (70/30 wt%) blends with 0 wt%, 1 wt%, 3 wt%, 5 wt% and 10 wt% cardanol.

closer and the ΔTα, defined as the temperature difference between the Tα's of PLA and ABS, is decreasing from 45.0 °C to 40.4 °C and 31.0 °C respectively when 1 wt% and 3 wt% cardanol are added. More particularly, both Tα's have merged in one unique tan(δ) peak when 5 wt% and 10 wt% of cardanol are introduced during the extrusion, even if a weak shoulder remains on the tan(δ) at 70 °C when using 5 wt% cardanol. In this last case, this shoulder could be an indication of the presence of some PLA-enriched domains.

The effect of cardanol on ABS is remarkably more pronounced as its Tα in non compatibilizerd PLA/ABS blend shifts from 119.6 °C to 65 °C when 10 wt% cardanol is used. At this particular loading, the storage modulus is also decreased from 3.2 GPa to 2.5 GPa, while it remains relatively constant, *c.a.* 3.3 ± 0.1 GPa, at lower content of the bio-plasticizer. Although cardanol is known to be an efficient plasticizer [35], the present observations from DMA analyses are clearly beyond a traditional plasticization effect, and are more likely to correspond to the result of a compatibilization between the two polymeric phases.

Morphological analyses were performed on cryo-fractured surfaces of extruded samples of PLA/ABS blends prepared in the presence or not of cardanol. When ABS and PLA are melt-blended (Fig. 2a), the resulting material displays a typical morphology of immiscible blend with irregular ABS nodules of about 1–2 μm diameter dispersed within the PLA matrix. When 5 wt% cardanol is added (Fig. 2b), the morphology of the blend is greatly affected as attested by the clear decrease of the size of ABS nodules to several tens of nanometres confirming the compatibilizing role of cardanol.

The impact resistance of PLA/ABS blends in presence or not of cardanol was then measured and the results are gathered in

Table 1
Summary of the thermo-mechanical properties of PLA, ABS, and PLA/ABS (70/30 wt%) blends without or with cardanol at different content.

Denomination	$T\alpha_{PLA}$ (°C)	$T\alpha_{ABS}$ (°C)	ΔTα (°C)	Storage modulus at 20 °C (GPa)
Extruded PLA	74.7	–	–	3.9
Extruded ABS	–	113.2	–	1.8
PLA/ABS	74.6	119.6	45.0	3.2
PLA/ABS + 1 wt% cardanol	71.8	112.2	40.4	3.2
PLA/ABS + 3 wt% cardanol	68.5	99.5	31.0	3.2
PLA/ABS + 5 wt% cardanol	86.7	86.7	0	3.4
PLA/ABS + 10 wt% cardanol	65.0	65.0	0	2.5

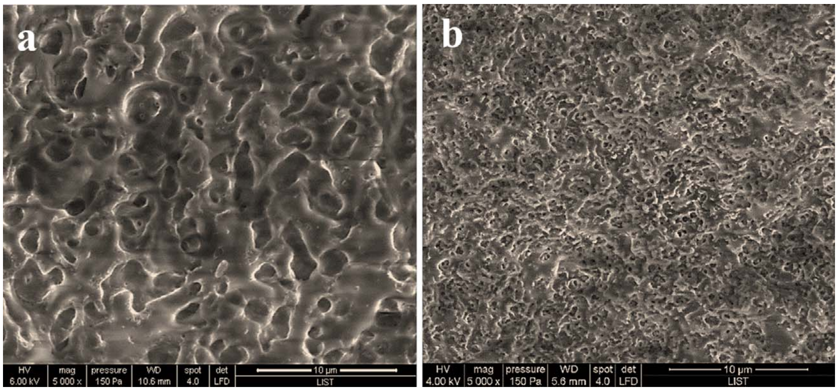


Fig. 2. Scanning electron micrographs of PLA/ABS (70/30 wt%) blends without (a) and (b) with 5 wt% cardanol.

Table 2. As expected, PLA presents a brittle behaviour (3.2 kJ/m^2) contrastingly to ABS (29.5 kJ/m^2) that shows good impact performances. The immiscible PLA/ABS blend shows an impact resistance as weak as neat PLA (3.7 kJ/m^2). However, the addition of cardanol induces a significant improvement of the impact resistance of the blend of 84% (from 3.7 kJ/m^2 to 5.9 kJ/m^2) when 3 wt% of cardanol is used, highlighting the efficiency of cardanol as interfacial compatibilizer. These observations are in accordance with the thermo-mechanical and morphological observations reported above.

As discussed in the introduction, cardanol is able to react with the unsaturations of natural rubber [29–31]. The formation of free-radicals due to ABS thermo-degradation during the reactive extrusion could lead to such reaction between the unsaturations of cardanol and the polybutadiene segments of ABS. Such a reactivity could mean that cardanol is essentially located within the ABS phase as suggested by the very pronounced decrease of the Tα in PLA/ABS blends. To get more insights on the mechanism of this compatibilization, the interactions between cardanol and ABS were characterized and the results are reported in the following part.

3.2. *Cardanol grafting onto ABS: Experimental evidence and consequences*

Methanol Soxhlet-extractions on blends after their extrusion were performed in order to evidence the affinity between ABS and cardanol (see Section 2). The extractions were performed on PLA/ABS samples prepared with 5 wt% cardanol using methanol for 24 h (corresponding to around 50 Soxhlet cycles). It was observed that 16 ± 10 wt% of the initially added cardanol was not removed (Table 3). Similar extractions were also performed on binary blends composed of either PLA added with 5 wt% cardanol or ABS added with 5 wt% cardanol. Interestingly, cardanol was fully removed from PLA samples while about 10% of the cardanol initially incorporated in ABS was not recovered after methanol extraction from the samples.

Despite these extractions were performed at least four times, the error on the measurement remained high. Thus, these results were confronted to DSC characterizations on ABS/cardanol binary blends before and after being extracted with methanol (Fig. 3). The presence of cardanol on non-extracted ABS is evidenced by its plasticizing effect as the Tg decreased from 109.5 °C to 88.4 °C. After methanol extraction and drying during one night at 50 °C under vacuum, ABS remains slightly plasticized as evidenced by its lower Tg of 103.8 °C confirming that a part of cardanol remained within ABS, certainly chemically grafted on the basis of the observations described in the literature [29–31]. It is worth noting that similar experiments were performed onto PLA/cardanol samples after solvent extraction and drying (not reported here). After extraction, the Tg of PLA remained unchanged compared to neat PLA attesting the complete removal of cardanol and evidencing that no chemical grafting between PLA and cardanol occurred in the conditions of the experiments.

The surface energy of PLA and ABS, in the presence of cardanol or not, was measured by contact angle measurements to check the surface energy of each component after the extrusion. To this aim, extruded ABS and ABS/cardanol samples were solubilized in chloroform and spin coated onto a glass substrate to get thin films of about 200 µm thickness. PLA and PLA/cardanol were similarly spin-coated as references. Pictures of the contact angle measurements against water or diiodomethane of neat ABS or ABS + 5 wt% cardanol are reported on Fig. 4.

Contact angles for neat ABS against water and diiodomethane are 97.1° and 22.2° respectively, corresponding to the behaviour of

Table 2
Summary of the impact properties of PLA/ABS (70/30 wt%) blends with or without cardanol at different contents.

Denomination	Notched Izod impact strength (kJ/m^2)	PLA impact strength improvement (expressed in %)
Extruded PLA	3.2	–
Extruded ABS	29.5	–
PLA/ABS	3.7	16
PLA/ABS + 1 wt% cardanol	5.0	57
PLA/ABS + 3 wt% cardanol	5.9	84
PLA/ABS + 5 wt% cardanol	5.4	69

Table 3
Summary of the methanol Soxhlet-extractions onto polymers (PLA, ABS and 70/30 wt% blends) extruded in presence of 5 wt% cardanol.

Composition	Non-extracted cardanol (wt%)
PLA/ABS + 5 wt% cardanol	16 ± 10
PLA + 5 wt% cardanol	0
ABS + 5 wt% cardanol	10 ± 4

a hydrophobic coating. The surface energy calculated from the Owens–Wendt method is equal to 48.7 mN/m and is composed exclusively of a dispersive part (Table 4). The addition of 5 wt% cardanol to ABS by melt-blending has a strong impact on these values. When using water, the contact angle drops from 97.1° to 68.1° indicating a clear reverse of the hydrophobic nature of ABS. With diiodomethane, the contact angle shifts from 22.2° to 45.8° corroborating the previous conclusion. The surface energy of ABS is clearly decreased from 48.7 mN/m for neat ABS to 41.7 mN/m when 5 wt% cardanol is incorporated. Interestingly, the polar component of the surface energy is highly improved from 0 mN/m to 12.7 mN/m. These results tend to indicate that ABS becomes more hydrophilic in the presence of cardanol despite that cardanol is an oily material. To the light of these results, it is reasonable to consider that the polar moiety of cardanol, *i.e.* the phenolic group, is pointing outward from the surface of the film. The effect of cardanol on the surface energies of PLA and PLA + 5 wt% cardanol are also reported in Table 4. The surface energy of PLA is only slightly affected by cardanol (36.8 mN/m and 38.2 mN/m for neat and cardanol-plasticized PLA, respectively). More importantly, the surface energies of PLA/cardanol (38.2 mN/m) and ABS/cardanol (41.7 mN/m) are very close to each other, likely explaining the compatibilization triggered by this naturally occurring phenolic compound within blends of PLA and ABS.

3.3. Insights into the cardanol grafting mechanism

As aforementioned, some studies reported the occurrence of chemical reactions between the C=C double bonds of the alkyl side chain of cardanol and those of the polybutadiene segments of ABS [29–31]. To confirm if this mechanism also take place in our system, a saturated derivative of cardanol, namely 3-pentadecylphenol (PDP), was extruded with PLA and ABS under similar experimental conditions. PDP has the same chemical structure as cardanol excepting its fully saturated alkyl side chain. Clearly, if just the unsaturations available along the alkyl chain of cardanol are involved in a chemical reaction with ABS during extrusion, PDP should not react at all. PLA/ABS blends were extruded with 5 wt% PDP using exactly the same conditions as for the blend added with cardanol. The thermo-mechanical properties of this blend are reported on Fig. 5. PLA/ABS + 5 wt% cardanol are also reported for sake of comparison.

Apple-to-apple comparison of the thermo-mechanical behaviours of PLA/ABS blends in the presence of 5 wt% cardanol or PDP is particularly confusing, since they are very close to each other. The mechanical relaxation temperatures of ABS and PLA are shifted in the same magnitude and merged similarly when PDP or cardanol are used. At 20 °C, the storage moduli of both blends are also very similar (3.2 GPa), evidencing that PDP acts alike cardanol within the blends.

Solvent Soxhlet-extractions were also performed to check if PDP is grafted onto ABS to confirm that the observed compatibilization is not the only result of a plasticization phenomenon. The results of these extractions are gathered in Table 5. DSC characterizations of PLA/ABS blends with PDP before and after methanol extraction have also been measured and are reported in Fig. 6.

Similar results are obtained when using PDP instead of cardanol. Around 17 ± 6 wt% of PDP was not recovered after the methanol Soxhlet-extraction of methanol from ABS/PDP blend, while all PDP is removed from samples prepared with PLA, indicating - as surprising as it may be – that PDP is grafted onto ABS similarly to cardanol. DSC measurements performed before and after

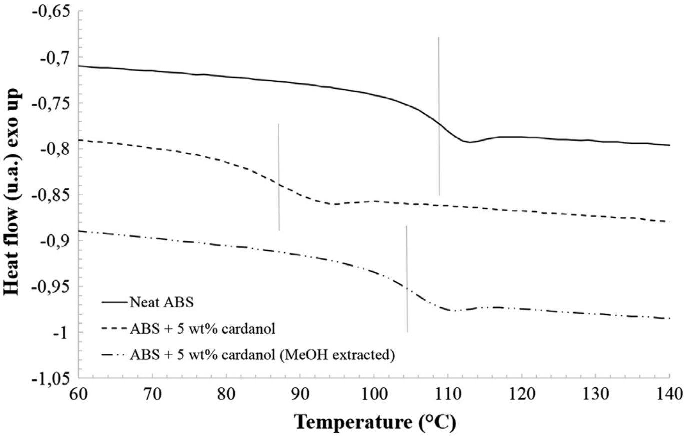
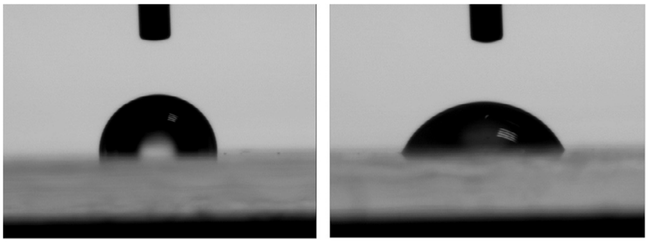
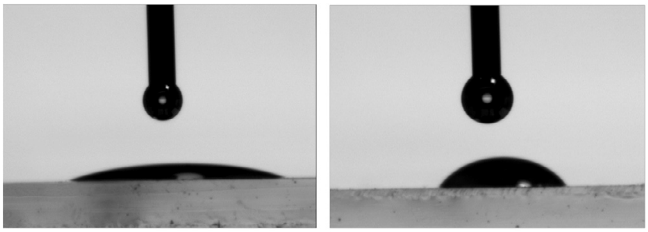


Fig. 3. DSC thermograms of neat ABS, ABS extruded with 5 wt% cardanol before and after methanol Soxhlet-extraction.



ABS - water *ABS/cardanol 5 wt% - water*



ABS - diiodomethane *ABS/cardanol 5 wt% - diiodomethane*

Fig. 4. Contact angle measurements on films of ABS (pictures on the left), or ABS + 5 wt% cardanol (pictures on the right) against water (top pictures) or diiodomethane (bottom pictures).

Table 4
Summary of the contact angle measurements on PLA, ABS and binary blends with cardanol.

Composition	Contact angle $\theta^\circ_{\text{water}}$	Contact angle $\theta^\circ_{\text{diiodomethane}}$	Surface energy (mN/m)	Dispersive component (mN/m)	Polar component (mN/m)
PLA	80.3 ± 1	46.3 ± 1.1	36.8	31.2	5.7
PLA + 5 wt% cardanol	78.6 ± 0.3	44.1 ± 0.2	38.2	32.0	6.2
ABS	97.1 ± 0.7	22.2 ± 1.1	48.7	48.7	0.0
ABS + 5 wt% cardanol	68.1 ± 1.8	45.8 ± 0.8	41.7	28.4	12.7

methanol extractions confirm these observations (Fig. 6). ABS is still plasticized after the treatment as attested by the shift of Tg from 109.3 °C for neat ABS to 104.5 °C for ABS/PDP after methanol extraction.

These results indicate that the compatibilization mechanism is similar for PDP and cardanol, while on the basis of literature data it was expected that a grafting should occur between the C═C of the alkyl chain of cardanol and the polybutadiene segments of ABS.

The recovered fraction after methanol Soxhlet-extraction from the blend ABS/cardanol was analysed by FTIR and ^{1}H NMR to identify any alterations of its chemical structure. This fraction contains only cardanol as attested by the spectra (not reported here) that were similar to those of raw cardanol. In a previous paper, Some of us used MALDI-Tof mass spectrometry to record the consumption of the unsaturations of cardanol during an UV exposure [36]. Similar experiments were performed on the recovered fraction but no modification of the characteristic pattern of cardanol was observed, which confirms once again the absence of reaction of the unsaturations of cardanol side chain.

Molecular characterizations of the residual solid fraction of ABS/cardanol samples after methanol extraction were performed both by ^{1}H NMR (please refer to the supporting information SI.1) and ^{13}C NMR. The comparison of the ^{1}H NMR spectra of ABS, cardanol and the solid fraction of extracted ABS/cardanol samples reveals the presence of the characteristic peaks of ABS (aliphatic protons between 1 and 3 ppm, aromatic protons between 6.50 and 7.50 ppm, and protons of the carbon double bonds of the butadiene repeating units at 5.47 and 4.97 ppm) and those of the alkyl side chain of cardanol located at 0.92 ppm, 1.31 ppm, 2.55 ppm, 2.80 ppm.

Interesting information can be extracted from the ^{13}C NMR spectrum of the solid ABS/cardanol fraction (Fig. 7). This NMR spectrum is mainly dominated by the contribution of ABS, with the contribution of the aliphatic carbons between 24 and 50 ppm, and of the aromatic carbons between 125 and 135 ppm. The atom of carbon bearing the nitrile group is found at 121.57 ppm. The contribution of cardanol is still confirmed by ^{13}C NMR, as evidenced by the peaks at 112.48 ppm, 115.31 ppm, 120.87 ppm and 144.85 ppm corresponding respectively to the carbon atoms in position 2, 4, 6 and 5, respectively (for the sake of clarity, neat ABS and cardanol ^{13}C NMR spectra are not reported here but they can be consulted in SI.2). As expected, the peaks corresponding to the unsaturations of cardanol (114.22 ppm, 130.01 ppm and 137.40 ppm for the carbon annotated c1, b4 and b1, respectively) are not altered as their chemical shift and relative intensity remain similar. The other peaks of the alkyl chain of cardanol at 14.11 ppm, 22.66 ppm, 29.22 ppm, 31.26 ppm and 35.83 ppm corresponding to the carbon atoms in position c, b, d, b2 and b3, respectively, are also present (Fig. 7b). Surprisingly, there is no trace of the carbon atom bearing the −OH group at 156 ppm attesting of a change in its chemical structure and/or surrounding.

This analysis suggests that the grafting of cardanol onto ABS is not involving its unsaturations, but more likely its phenolic moiety.

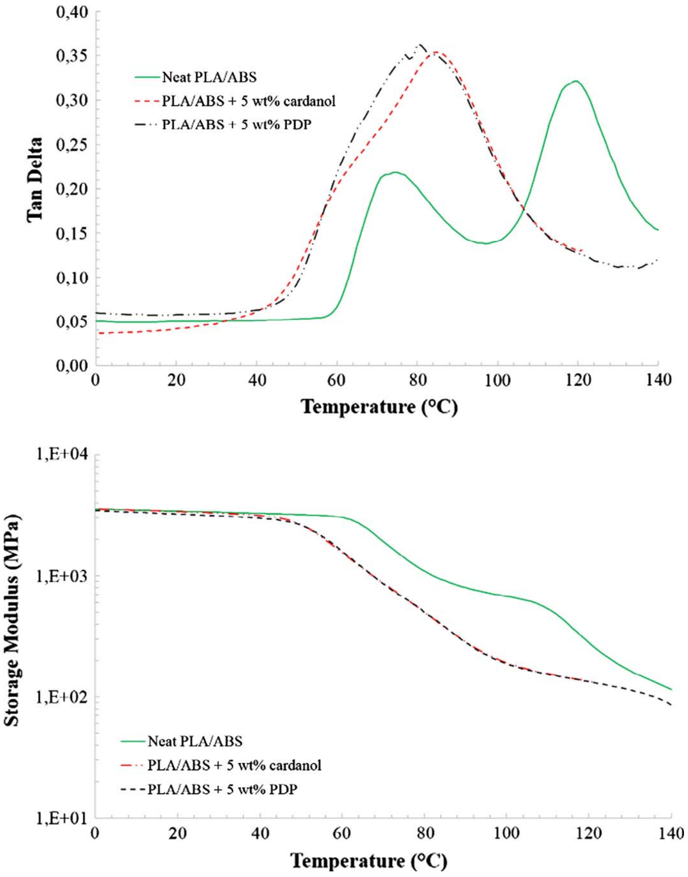


Fig. 5. Thermo-mechanical properties of neat PLA/ABS (70/30 wt%) blends, with 5 wt% of either cardanol or 3-pentadecylphenol.

Table 5
Summary of the methanol Soxhlet-extractions onto PLA and ABS prepared with 5 wt% PDP by extrusion.

Composition	Non-extracted PDP (wt%)
PLA + 5 wt% PDP	0
ABS + 5 wt% PDP	17 ± 6

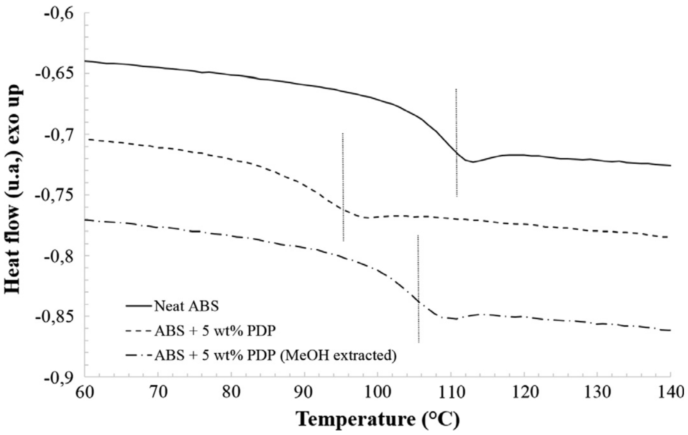


Fig. 6. Thermograms of neat ABS, ABS extruded with 5 wt% PDP before and after methanol Soxhlet-extraction.

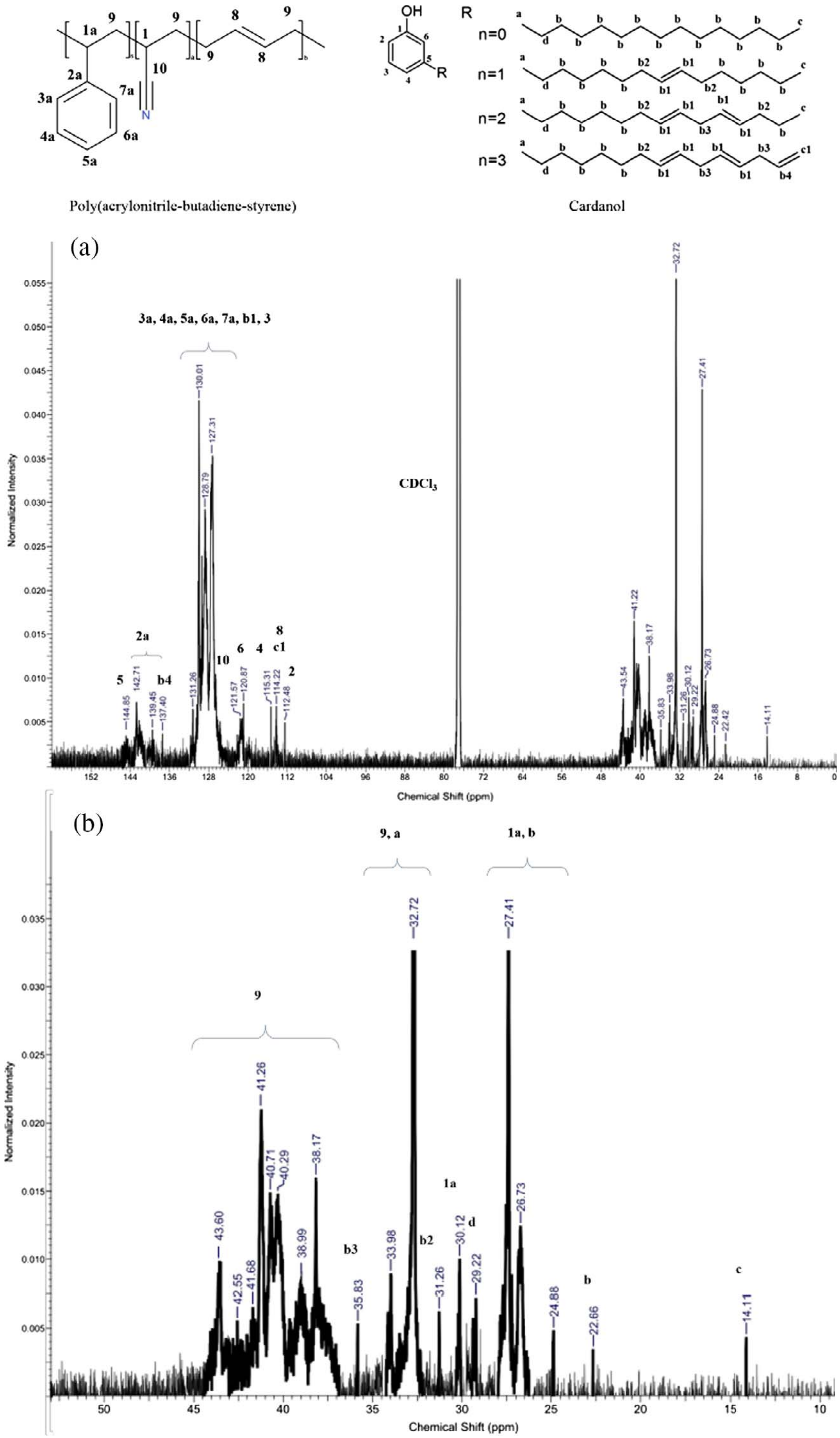
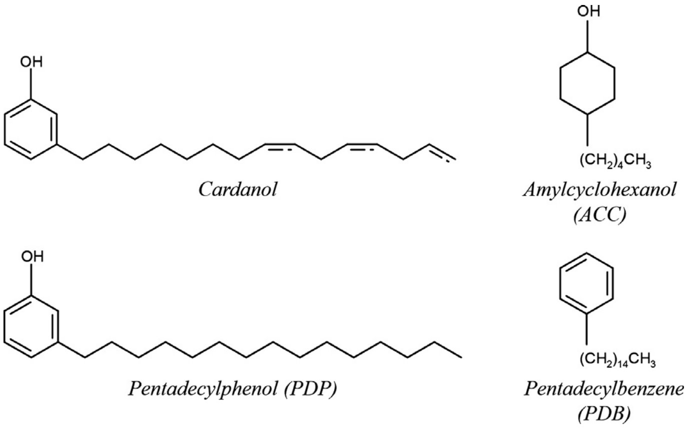
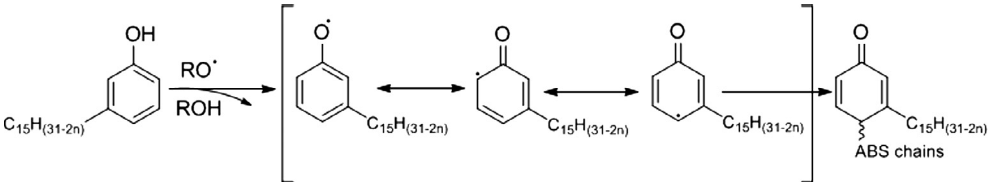


Fig. 7. ^{13}C NMR spectra of the solid fraction (after methanol extraction) of ABS + 5 wt% cardanol blends (a) from 0 ppm to 160 ppm and (b) from 10 ppm to 52 ppm.

A similar observation was done by Bova et al. [37] on lignin and nitrile-butadiene rubber (NBR) blends. The authors affirmed that NBR chains were grafted onto lignin during reactive mixing involving the generation of free radicals due to NBR thermo-mechanical degradation. The generated free radicals were trapped by the phenols of lignin, *via* a typical anti-oxidant mechanism. It resulted in a radical grafting of the NBR chains onto the lignin particles. These results corroborate with our observations suggesting the occurrence of a similar grafting mechanism within ABS/cardanol blends. Indeed, it could be expected that a chemical grafting occurs on the *para* position of cardanol after a mesomeric rearrangement due to the trapping of a free radical by the phenol. An attempt to schematically represents the mechanism is reported in scheme 1, inspired from the study of Bova et al. [37]. In light of this configuration, the



Scheme 1. Schematic representation of the possible grafting of cardanol onto ABS.



Scheme 2. Chemical structure of additives ACC, PDB, cardanol and PDP.

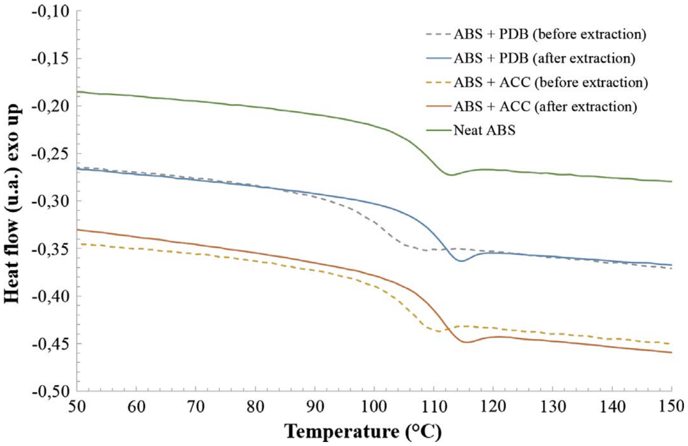


Fig. 8. Thermograms of samples of ABS blended with PDB (5 wt%) or ACC (5 wt%) before and after methanol extractions.

disappearance of the peak at 156 ppm would then be explained by longer relaxation times due to a steric hindrance brought by the ABS chains on which cardanol would be grafted, while the C═O peak expected around 187 ppm is not visible.

Finally, to confirm that the mechanism involves the phenolic group of cardanol, ABS was blended, in similar experimental conditions, with two additives very similar to cardanol but unable to trap any free radicals according to their chemical structure: 4-amylcyclohexanol (ACC) – a cycloaliphatic alcohol – or 3-pentadecylbenzene (PDB) – an aromatic ring bearing a C15 alkyl side chain. ACC is not aromatic and no mesomeric rearrangements are possible in the molecule if the alcohol is oxidized by free radicals. PDB is aromatic, but does not have any hydroxyl group on its benzene ring: its primary antioxidant properties are thus inhibited. The chemical structure of both products are depicted in Scheme 2. The chemical structure of cardanol and PDP are also depicted for the sake of comparison. The characterization by DSC of the blends of ABS with ACC and PDB (5 wt%) is given on Fig. 8.

As-extruded ABS is plasticized by ACC or PDB, as attested by the decrease of the Tg from 109.3 °C to 104.6 °C and 104.7 °C respectively. After methanol extraction, the initial Tg of ABS is recovered. Clearly, the solvent extraction fully remove the non-reactive plasticizers (*i.e.* PDB and ACC). As the chemical structures of these molecules do not provide any free radical scavenging properties, their grafting onto ABS is avoided. These last results corroborate our assumption: cardanol grafting onto ABS chains occurs, in our experimental conditions, from the aromatic cycle of the phenolic moiety of the bio-plasticizer without involving unsaturations of the alkyl side chain.

4. Conclusions

Sustainable compatibilization of immiscible PLA/ABS blends was successfully achieved through a solvent-free reactive extrusion process by the simple addition of raw cardanol, a naturally occurring phenolic compound, without the need of any prior chemical modification. During the melt-blending, cardanol proved to graft onto ABS through a free-radical pathway. While it was expected that this radical mechanism may involve the unsaturations available along the alkyl chain of the biomolecule, similar results were obtained by using 3-pentadecylphenol (PDP), the alkyl chain saturated homologue of cardanol. Surprisingly, PDP was also able to graft onto ABS and its use led also to a similar compatibilization of PLA/ABS blends by reactive extrusion, therefore confirming the non occurrence of the grafting through the unsaturations along the alkyl chain of cardanol, at least in our experimentail conditions. 13C NMR characterization evidenced the disappearance of the peak characteristic of the carbon atom bearing the −OH group of cardanol, leading to the assumption that the phenolic moiety of this bio-plasticizer was involved in the free-radical grafting mechanism. This assumption was further confirmed by the absence of any compatibilization effect of PLA/ABS blends melt-processed with either 4-amylcyclohexanol or 3-pentadecylbenzene, both unable to be involved in such a free-radical mechanism. In sum, cardanol grafting onto ABS allows the compatibilization between PLA and ABS following two ways: an outstanding plasticizing effect and a significant decrease of the surface energy of ABS, which gets similar to the one of PLA. Such finding paves the way to a multitude of strategies to tailor the properties of compatibilized PLA/ABS blends, since the carbon-carbon double bonds available along the alkyl side chain can be readily functionalized, for instance *via* epoxidation reaction to still promote additional reaction with PLA hydroxyl and carboxylic end-groups.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.eurpolymj.2017.06.004.

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