Development and optimization of renewable vinyl plastisol/wood flour composites exposed to ultraviolet radiation

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Abstract. The application of vegetable oils as novel plasticizers for poly(vinyl chloride) (PVC) is currently in the spotlight of the polymer industry due to their ingrained sustainability. In this study, novel vinyl plastisol/wood flour composites based on epoxidized linseed oil (ELO) were evaluated. For this, PVC was first plasticized by 70 parts by weight of ELO per hundred parts of resin (phr) to form a vinyl plastisol. Wood flour, obtained by dry grinding from reed (Phragmite communis), was then incorporated at five different loadings (10, 15, 20, 25, and 30 wt.-%) and three particle sizes (100, 250, and 500 μm). The effect of ultraviolet (UV) radiation was explored to activate the surface of wood flour to increase its interfacial adhesion with the vinyl plastisol. Stereomicroscopy and scanning electron microscopy (SEM) were used to examine the composites fracture and determine the dispersion of wood flour in the vinyl matrix. As per the surface appearance and mechanical results, optimal materials were observed for vinyl plastisol composites at high contents of wood flour with the largest particles that were previously exposed to UV for 4 min. Resultant renewable vinyl plastisol composites show a great deal of potential as designed materials for wood replacement in building applications.

1. Introduction

Plasticizers are well-known additives employed to increase flexibility of thermoplastic materials that can facilitate processing by reducing the melt viscosity and lowering the glass transition temperature (T_g) [1]. The major demand for plasticizers can be found in a multitude of vinyl plastics, which are manufactured by the full spectrum of compounding and fabrication processes employed in the plastics industry. Dissimilar amounts of plasticizers are typically applied to make poly(vinyl chloride) (PVC) workable for a wide range of applications, such as building and construction, packaging, automotive, electrical and electronics, toys, agriculture, furniture, stationery, household, etc. [2]. The combination of a PVC resin with a large fraction of plasticizer forms a PVC paste or viscous liquid, called "vinyl plastisol", in which the plasticizer component in the formulation generously exceeds 50 wt.-% [3].

Vinyl plastisols are liquid suspensions of fine PVC particles and aggregates highly dispersed in the plasticizer media with other additives. In commercial practice, these typically undergo solidification by controlled heating in a chamber (e.g., an oven) at about 140–180 °C [4]. Since the plasticizer molecules are intimately associated with the PVC particles, the final properties of the plastisol significantly depend on the curing conditions, i.e., temperature and time [5]. As the plastisol is heated, the plasticizer starts diffusing into the PVC particles, solvating their non-crystalline regions, swelling the individual particles, and causing an intense rise in the paste viscosity [6]. With continued heating, solvation of crystalline parts of PVC drops the paste viscosity, allowing polymer molecules to flow more freely [7]. Typically it is necessary to reach temperatures above 190 °C to produce complete fusion of PVC microcrystallites to form a homogeneous matrix with absorbed plasticizer [8]. Once cooled, the plastisol acquires the gel structure and it becomes a solid material with very high particle cohesion and certain flexibility [9,10].

Among PVC plasticizers, general-purpose phthalate plasticizers have historically served as the preferred choice as they provide a desirable balance of cost vs. performance. However, these are usually not chemically bonded to the PVC matrix so that they can migrate while being used or after disposal [11]. This has risen considerable concerns, as some studies suggested that phthalate plasticizers for PVC can potentially bioconcentrate and/or bioaccumulate in some species of fish and amphibians, acting as carcinogenic and endocrine disruptors [12]. This has addressed the vinyl industry to produce alternative bio-based and nontoxic plasticizers, which can be still capable of achieving similar performance to that of traditional phthalate plasticizers [13,14].

Vegetable oils have attracted considerable attention in recent years as novel alternatives to phthalate plasticizers for PVC due to their low ecotoxicity, total or partial biodegradability, ready availability in large quantity, and competitive cost [15–17]. These naturally occurring additives are derived from plants and predominantly consist of triglycerides, i.e., the glycerol esters of fatty acids [18]. The amount and nature of fatty acids vary within different oils and even within the same plant oil that is, in turn, dependent on the plant species and, seasonally, on the growing conditions [19]. This determines the degree of unsaturation of the fatty acid, i.e., the number of double bonds, which is measured by the iodine value (IV) and it plays a significant role in the physico-chemical properties of the oil. In this sense, linseed oil extracted from oilseed flax (Linum usitatissimum L.) presents a relatively high IV, typically in the range of 168–204, by which it is catalogued as a drying oil (IV N 130) [20]. Such rich linolenic content, i.e., ca. 55% [21], makes linseed oil a good candidate for bio-based thermosetting polymers application in which high cross-link densities are preferred [22].

As the internal double bonds present in the fatty acids of linseed oil are relatively rich in electrons, they are susceptible to epoxidation process by which both carbons of the double bond become linked to an oxygen atom. Epoxidized linseed oil (ELO) is commonly prepared in the industry using peracids such as performic and peracetic acid [23]. ELO, together with epoxidized soybean oil (ESO), accounts for an annual industrial production N200,000 tons [24]. Similar to ESO, ELO holds many outstanding properties such as good lubricity, low volatility, low odor, and good solvency for being applied in the vinyl industry. However, ELO offers lower migration profiles for PVC than ESO due to its higher molecular weight (MW) and its remarkably higher oxirane oxygen content (OOC), i.e., ca. 8–9%, which leads to more intense interactions [25]. In this sense, some recent studies have showed the potential of ELO as a plasticizer in PVC and vinyl plastisol [25–28]. ELO does not only deliver flexibility due to an internal lubrication effect but also increases the polarity and the stability of PVC [22]. The stabilization effect is due to the presence of epoxide groups, which are capable to scavenge acid groups, resulting in a positive effect on the overall polymer stabilization [29].

Natural fillers can be additionally incorporated to increase the sustainable profile of PVC, resulting in renewable vinyl composites [30]. The incorporation of cellulosic materials is justified not only for their neutrality with the environment but also to improve their superficial aspect and reduce cost [31]. Wood flour obtained by conventional grinding is gaining increasing acceptance in vinyl plastics since it offers many advantages, including low density, renewability, high availability, triggered biodegradability, noise absorption, minimum damage during processing, etc. [32]. Resultant renewable filled vinyl plastisol composites show potential for wood substitute applications like door shutters, flooring tiles, roofing sheets, partitions, and decking boards [33]. However, these composites can present some important limitations in relation to their mechanical performance as the wood particles habitually present poor compatibility with the vinyl matrix. This effect is produced due to the hydrophilic nature of vegetable fillers, which are mainly composed of cellulose, hemicellulose, and lignin, and their relatively high moisture content, i.e., 8–12.6% [34]. The polar hydroxyl groups on the surface of the cellulosic particles then have difficulty in forming a tightly bonded interface with the nonpolar vinyl matrix. Furthermore, the incorporation of cellulosic fillers in the polymer matrix is often associated with insufficient dispersion, caused by the tendency of the fillers to form internal hydrogen bonds. This leads to some large discontinuities along the polymer matrix that may act as a stress concentrator, the so-called "notch effect", i.e., high concentrations of stress around the fiber perimeter that favors the initiation and spread of cracks. For instance, a brittletype fracture behavior was reported to PVC composites by Shah et al. [35], who related the low mechanical strength to a low interfacial adhesion between wood flour and the vinyl matrix.

Adhesion properties of polymer matrix-cellulosic filler can be improved by different surface treatments focused on cleaning and/or activating the filler surface in vinyl composite systems. Some smart strategies to increase the fillers interaction capacity include the use of oxidant substances (e.g., chromic and nitric acid, ozone, and hydrogen peroxide), alkali treatments, i.e., mercerization (e.g., NaOH), coupling agents (e.g., silane agents and maleic anhydride-grafted polymers), and physical methods (e.g., electric discharge, plasma, and radiation treatments) [34–40]. The most common radiation treatments comprise ultraviolet (UV), electron beam, and gamma radiation. Compared to the wet process of using chemicals, radiation treatments are able to modify the surface energy without changing the bulk mechanical properties of the fillers [38]. Among them, UV radiation is considered as a straightforward and cost-effective methodology for polymer composites. Kato et al. [39] were the first to oxidize cellulose by UV radiation at vacuum to introduce carbonyl and carboxylic acid groups onto the fillers surface. The efficiency of the UV method was comparable to chromic and nitric acid, whereas it was better than ozone and hydrogen peroxide. More

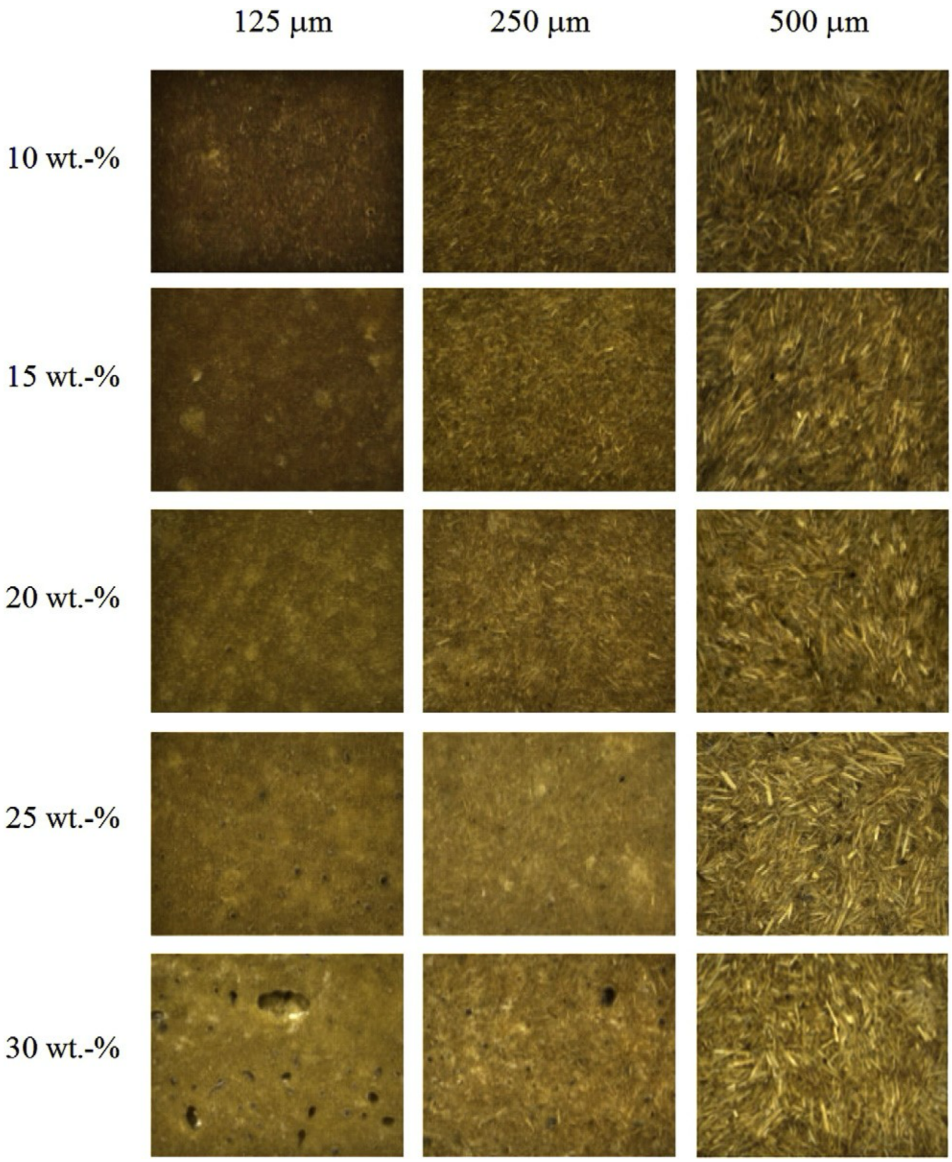

Fig. 1. Surface aspect of the vinyl plastisol composites as a function of the weight content (wt.-%) and particle size of untreated wood flour.

recently, Khan et al. [40] improved the wettability of jute fibers by UV radiation, which increased the composite strength.

The aim of this research work was to optimize the appearance and mechanical performance of ELO-based vinyl plastisol composites with reed wood flour. With the objective to increase their compatibility with the vinyl matrix, the wood flour particles were exposed to UV radiation in a previous stage. The renewable composites were characterized in terms of superficial aspect, mechanical properties, and morphology. Finally, the thermomechanical properties were also evaluated to ascertain their application at room conditions.

2. Experimental

2.1. Materials

Commercial Lacovyl PB 1172 H from Atofina (Midlands, UK) was used as the base resin for the study. This PVC is produced by microsuspension polymerization for the preparation of plastisols. According to the manufacturer, this grade is characterized by a viscosity index of 115 ml/g and kwert (k) value of 67 obtained by ISO 1628-2.

Renewable ELO with CAS number 8016-11-3 was supplied by Traquisa S.L. (Barcelona, Spain). This is characterized by a MW of 1037 g/mol, OOC of ca. 8%, and IV ≤ 5. The average fatty acid profile was: 3–5% stearic acid, 5–7% palmitic acid, 14–20% linoleic acid, 18– 26% oleic acid, and 51–56% linolenic acid.

Reed wood (Phragmite communis) was purchased from a local carpenter's workshop. This was subjected to dry grinding followed by sieving in a Sieve Shaker model RP09 from CISA Cedaceria Industrial S.L. (Barcelona, Spain) to produce wood flour at three different particle sizes: 100, 250, and 500 μm. Reed wood was constituted of 43% cellulose, 20% lignin, and 30.5% hemicellulose [41]. Prior to being used, it was dried at 45 °C for 12 h to remove moisture.

2.2. Ultraviolet radiation treatment

To increase their interfacial adhesion, wood flour was placed in a metal tray and UV irradiated in a cabinet of UVASPOT 1000RF2 from Honle UV Technology (Barcelona, Spain). A high pressure mercury lamp with a power of 1000 W and a wavelength at 350 nm was used. The treatment was applied at different times to select the optimal conditions.

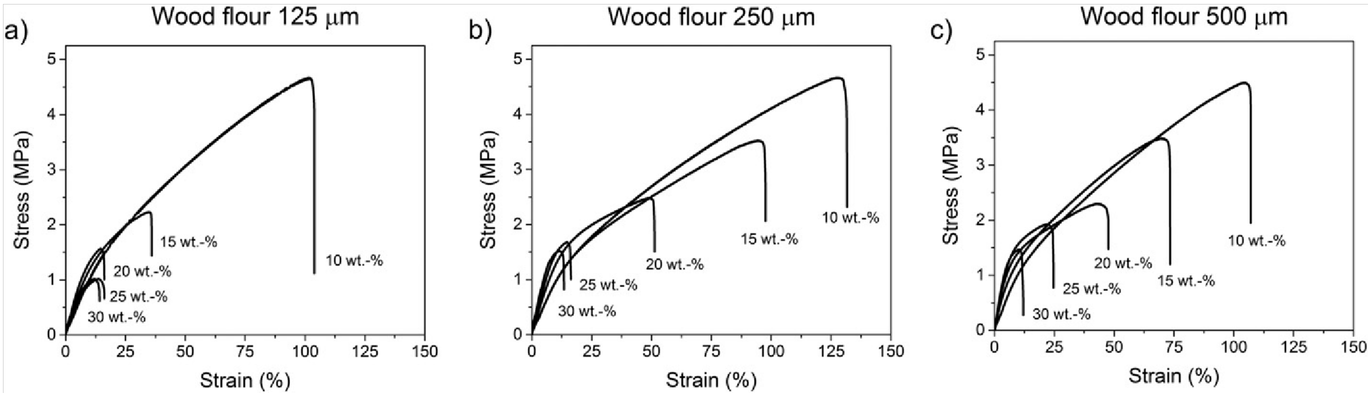

Fig. 2. Typical tensile stress-strain curves of the vinyl plastisol composites containing untreated wood flour of: a) 125 μm; b) 250 μm; c) 500 μm.

2.3. Plastisol composites preparation

A planetary professional stand mixer KAPL model 5KPM5 from KitchenAid (Michigan, USA) of 4.8 L was used to produce the vinyl plastisols. These were prepared by mixing 70 parts by weight of ELO per hundred parts of PVC resin (phr) at a rotating speed of 3 rpm for 5 min. This concentration was selected since it was previously optimized in terms of mechanical properties and behavior toward migration [25]. The following amount of wood flour was added to the mixture: 10, 15, 20, 25, and 30 wt.-%.

After the mixing process, to remove entrapped air, all pastes were subjected to a vacuum process for 30 min in a MCP Group vacuum chamber model 00ILC from HEK-GmbH (Lubeck, Germany). A maximum vacuum of −1 bar was applied. Once all air bubbles were removed, the mixtures were spread into an aluminum mold of 150 × 100 × 5 mm^3. Curing process was then performed in a ventilated oven Carbolite model 2416CG from Keison Products (Barcelona, Spain) at 200 °C for 10 min. These conditions were selected from optimization achieved during previous research work [42].

Once the curing process was completed, the samples were cut according to ISO 527 using a die on a hydraulic press model MEGA KCK15A from Melchor Gabilondo S.A. (Vizcaya, Spain) to obtain standardized composite parts for characterization.

2.4. Mechanical and thermomechanical testing

Tensile tests were carried out using a universal tensile test machine ELIB 30 from S.A.E. Ibertest (Madrid, Spain) according to ISO 527 with 20 mm/min crosshead speed. All specimens were tested in a controlled chamber at room conditions, i.e., 23 °C and 50% RH, and six samples were analyzed. Average values of the tensile modulus (E), tensile strength (σ_s), and strain at break (ε_b) were determined.

Dynamic mechanical thermal analysis (DMTA) was carried out using a AR-G2 equipment from TA Instruments (New Castle, USA) in tensile mode. Samples with gauge dimensions of 4 × 10 × 40 mm^3 were used. The storage modulus (G′), loss modulus (G″), and loss tangent (tan δ) were determined from −75 to 100 °C at a frequency of 1 Hz, a strain amplitude of 0.1%, and a heating rate of 2 °C/min.

2.5. Fracture surface analysis

Morphological images of the tensile fractures were performed with a stereomicroscope system SZX7 model from Olympus (Tokyo, Japan) with an ocular magnifying glass of 10×. Scanning electron microscopy (SEM) was carried out using a PHENOM model from FEI Company (Eindhoven, The Netherlands) with accelerating voltage of 5.0 kV. Samples were initially coated with a fine layer of gold–palladium alloy under vacuum conditions in a Sputter Coater EMITECH model SC7620 from Quorum Technologies Ltd. (East Sussex, UK).

3. Results and discussion

3.1. Characterization of vinyl plastisol composites with untreated wood flour

Fig. 1 shows the surface appearance of the vinyl plastisol composite parts obtained with untreated wood flour. It can be observed that both wood flour content and particle size had a noticeable influence on the appearance of the composite parts. In particular, the vinyl plastisol/ wood flour composites obtained with lower particle sizes presented a more homogenous and continuous aspect. In contrast, larger wood flour particles enhanced the wood-like visual aspect since the vinyl plastisol composites became more irregular, similar to the natural aspect of wood. Additionally, it can be seen that the color intensity was decreasing as the wood flour content was increased. It is also worthy to mention that for the lowest particle size, i.e., 125 μm, some irregularities and porosities could be observed on the parts of high wood flour contents, which was probably related to entrapped water in the wood flour. This points out that vinyl plastisol composites with medium or high

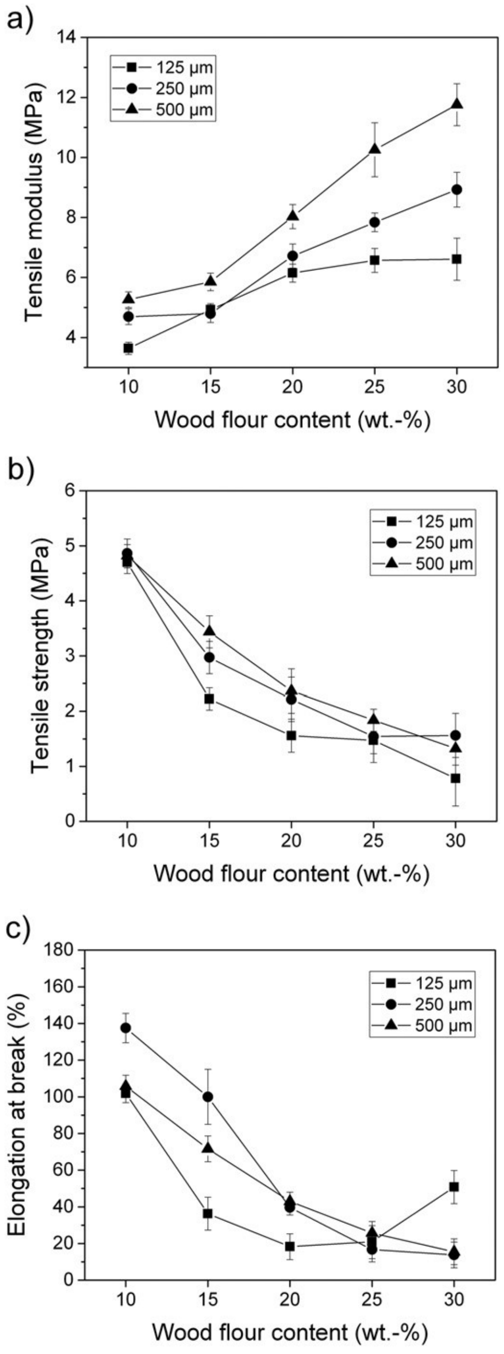

Fig. 3. Mechanical properties of the vinyl plastisol composites as a function of the weight content (wt.-%) and particle size of untreated wood flour: a) Tensile modulus; b) Tensile strength; c) Elongation at break.

wood flour contents composed of large particle sizes are more aesthetically suitable and attractive to replace solid wood parts.

Tensile properties were evaluated to ascertain the loading effect of wood flour on the mechanical properties. Fig. 2 presents the stress vs. strain curves for the vinyl plastisol composites in relation to the content and particle size of untreated wood flour. The trend of the mechanical values is summarized in Fig. 3. Fig. 3a shows that an increase of the tensile modulus was observed for all vinyl plastisol composites with content and particle size of wood flour. This points out that the cellulosic filler intensified the rigidity of the vinyl matrix. The highest increase was observed for the vinyl plastisol composites containing the longest wood flour particles, i.e., 500 μm. In particular, vinyl plastisol composites with wood flour contents of 25 and 30 wt.-% presented a tensile modulus of 10.3 and 11.7 MPa, respectively. However, as shown in Fig. 3b, tensile strength was found to decrease linearly as the amount of wood flour increased. This reduction was even more noticeable for composites with shortest particles, i.e., 125 μm. Tensile strength values particularly decreased from 4.7 to ca. 1 MPa in all composite samples, which could be possibly attributed to a heterogeneous phase distribution of the wood flour particles within the vinyl matrix. A sharp decrease in the ductility of the vinyl plastisol after wood flour incorporation can be seen in Fig. 3c, in particular for contents above 15 wt.-%. The lowest elongation-at-break values were also shown for the vinyl plastisol composites containing particles of lower sizes.

As shown in previous research [25], plasticization of PVC by 70 phr of ELO generated mechanical values of elastic modulus and stress fracture of 4.9 and 9.7 MPa, respectively. These vinyl plastisols were additionally characterized by an extraordinary flexibility, showing elongation-atbreak values above 200% for high ELO contents. This ductile behavior was produced by a decrease in the polar forces of attraction among PVC chains, which takes place when ELO fills the space between the chains and increases their separation. According to this, the above results indicate that the addition of unmodified wood flour increased the elastic modulus, i.e., stiffness. Nevertheless, it also drastically embrittled the vinyl plastisol as it decreased the tensile strength and elongation at break, which are properties related to the material cohesion. This suggested a poor load transfer from the wood particles to the vinyl matrix as a result of their low compatibility. A similar mechanical performance was reported for other vinyl composites [43,44]. The addition of cellulosic fillers in particle form gave increase of stiffness and hardness but also showed a negative effect on tensile strength and elongation at break.

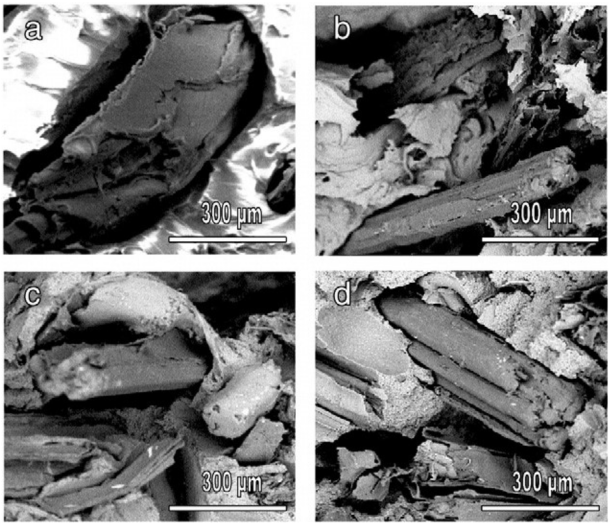

Fig. 5. Scanning electron microscopy (SEM) images corresponding to fractured surfaces of the vinyl plastisol composites containing untreated wood flour at: a) 10 wt.-% of 125 µm; b) 15 wt.-% of 250 µm; c) 20 wt.-% of 250 µm; d) 25 wt.-% of 500 µm. Scale markers of 300 µm in all cases.

In relation to the failure mechanism of the vinyl plastisol composites, particle debonding was evidenced using stereomicroscopy analysis at the fractured surfaces in Fig. 4. This can be observed by the presence of a rough morphology with large voids and cavities, produced after fracture during tensile tests, which corresponds to the pullout processes of the wood flour particles from the vinyl matrix. This confirmed the expected poor interfacial adhesion and low affinity of wood flour with the vinyl matrix. Additionally, it can be seen that the cellulosic particles were predominantly aggregated and poorly distributed within the vinyl matrix, which supports the poor mechanical behavior. In relation to the wood flour content, in general, the composites presented similar fractures. However, for the composites made of larger particles, i.e., 250 and 500 µm, the surfaces were more irregular and showed a higher degree of roughness. Some large particles could be also distinguished in the images.

The fractured surfaces of the vinyl plastisol composites were examined by SEM in Fig. 5, which ascertain the interaction between wood flour particle and vinyl matrix. The fracture surfaces of a 10 wt.-% composite (Fig. 5a) and a 15 wt.-% (Fig.

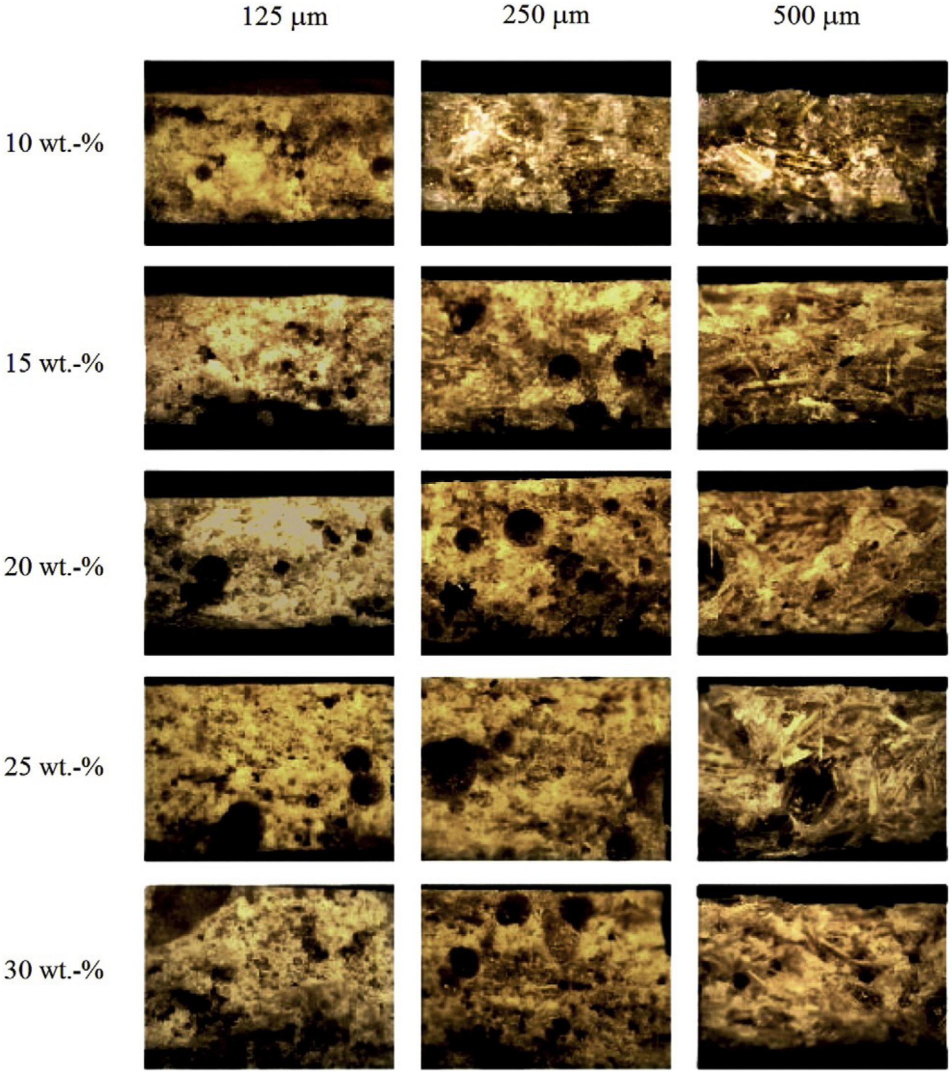

Fig. 4. Stereomicroscopy images corresponding to fractured sections of the vinyl plastisol composites as a function of the weight content (wt.-%) and particle size of untreated wood flour.

5b) clearly revealed the presence of material discontinuities between the wood flour particles and the vinyl plastisol. These gaps correspond to a phase material separation, which could be intensified during mechanical deformation, due to the lack of intimate adhesion between the cellulosic fillers and the surrounding polymer matrix. The micrographs for a 20 wt.-% composite (Fig. 5c) and a 25 wt.-% (Fig. 5d) correspond to composites made of wood flour particles of 250 and 500 µm, respectively. These also revealed that wood flour at these sizes present a fiber-like morphology. The presence of fillers of larger aspect ratios could explain the elastic improvement previously reported in the mechanical properties. This fiber morphology as well as the presence of particles with more surface defects offered higher mechanical interlocking to increase adhesion with the vinyl matrix [44]. In contrast, fractures were predominantly rough, for all composites. The poor interfacial adhesion certainly favored the brittle-type fracture described in the tensile results, in which the crack could propagate during fracture in the vinyl matrix at the surroundings of the wood flour. SEM images also corroborated the presence of large aggregates of particles, which was previously evidenced.

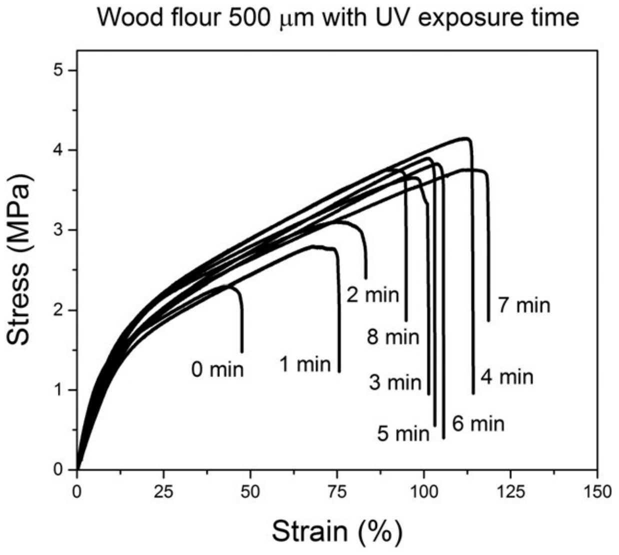

Fig. 6. Typical tensile stress-strain curves of the 20 wt.-% vinyl plastisol/wood flour composites of 500 µm in terms of exposure time to ultraviolet (UV) radiation.

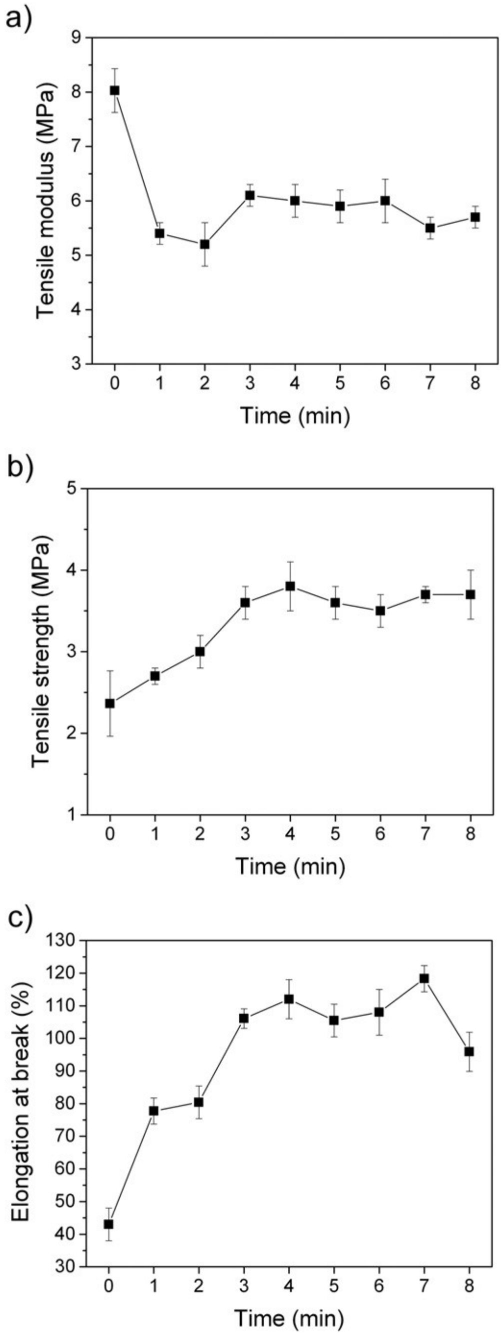

Fig. 7. Mechanical properties of the 20 wt.-% vinyl plastisol/wood flour composites of 500 µm in terms of exposure time to ultraviolet (UV) radiation: a) Tensile modulus; b) Tensile strength; c) Elongation at break.

3.2. Optimization of ultraviolet radiation on wood flour

From the previous results, the 20 wt.-% vinyl plastisol composite containing the largest particles, i.e., 500 µm, was selected to determine the optimal time of exposure during UV treatment. This particular composite contains the optimal particle size and an intermediate content of wood flour that highly resembled natural aspect of wood. Prior to be incorporated into the vinyl plastisols, the wood flour particles were exposed to UV radiation for different times, i.e., from 1 to 8 min.

Fig. 6 includes the stress vs. strain curves for the 20 wt.-% vinyl plastisol composite containing 500-μm wood flour exposed to UV radiation at different times. The trend of the mechanical properties in relation to the UV exposure time is represented in Fig. 7. Different times under UV radiation certainly changed the mechanical properties of the vinyl plastisol composite. However, the greatest changes were observed during the first minutes of exposition. Fig. 7a indicates that the tensile modulus decreased with UV exposure though it remained relatively constant with the exposure time, only showing a minor increase from 5.3 to 6.1 MPa in the range of 3–6 min. Interestingly, in Fig. 7b it can be seen that the tensile strength of the vinyl plastisol composite was increased after short times of UV radiation on wood flour. While the initial tensile strength of the 20 wt.-% vinyl plastisol composite with untreated 500μm wood flour was ca. 2.3 MPa, after 3 min of exposure time, this value reached 3.7 MPa, which represents a percentage increase of ca. 61%. As the exposure to UV radiation was further extended, the tensile strength remained nearly stabilized. A similar trend was observed in Fig. 7c in which the elongation-at-break values increased during the first 3 min, then reached a plateau from a span time of 3–7 min, and finally slightly decreased at 8 min. In particular, the elongation at break of the vinyl composites was seen to increase up to ca. 120%. This value is positively closer to the overall mechanical performance reported for unfilled vinyl plastisols based on high contents of ELO [25]. The elastic modulus remained nearly constant because it relates stress to strain in the elastic zone and both values increased during UV exposition. In any case, as there was not any significant improvement upon a prolonged exposure, a time of 4 min was selected to continue the optimization study of the vinyl plastisol composites.

From the improved mechanical results, it can be expected that interfacial adhesion of wood flour with the vinyl matrix increased after UV radiation. Two main critical aspects can explain this enhancement. On the one hand, UV oxidation could promote the generation of more hydroxyl groups (−OH) on the cellulosic surface of wood flour, which could create active sites able to form strong covalent interactions with the reactive epoxy groups of ELO. Fundamentals on the chemical reactivity of ELO with cellulosic fillers have been recently reported and it was particularly proposed that the hydroxyl groups could act as nucleophiles to attack and open the epoxide ring [45]. Therefore, as depicted in Fig. 8, surface bonding was effectively achieved due to the formation of an alkoxy alcohol between the epoxy groups of ELO and the hydroxyl groups of cellulose of wood flour. Additionally, the coupling effect of ELO was complemented by lower secondary linking forces between the PVC polymer chains [25] as well as by the presence of its long hydrocarbon chains that can retain certain chemical affinity for the aliphatic macromolecular polymer chains [46]. On the other hand, UV radiation could feasibly weaken the hydrogen bonds inherently presented in the surface of wood flour that may improve its wettability with the nonpolar groups from the vinyl matrix. In this sense, Wang et al. [47] concluded that UV radiation decrease the overall polarity of lignocellulosic fillers that favors good particle dispersion in hydrophobic (or low hydrophilic) polymeric matrices. For this reason, the UV process was also effective to displace entrapped water and remove impurities from the wood flour surface to uniformly expose chemically reactive functional groups.

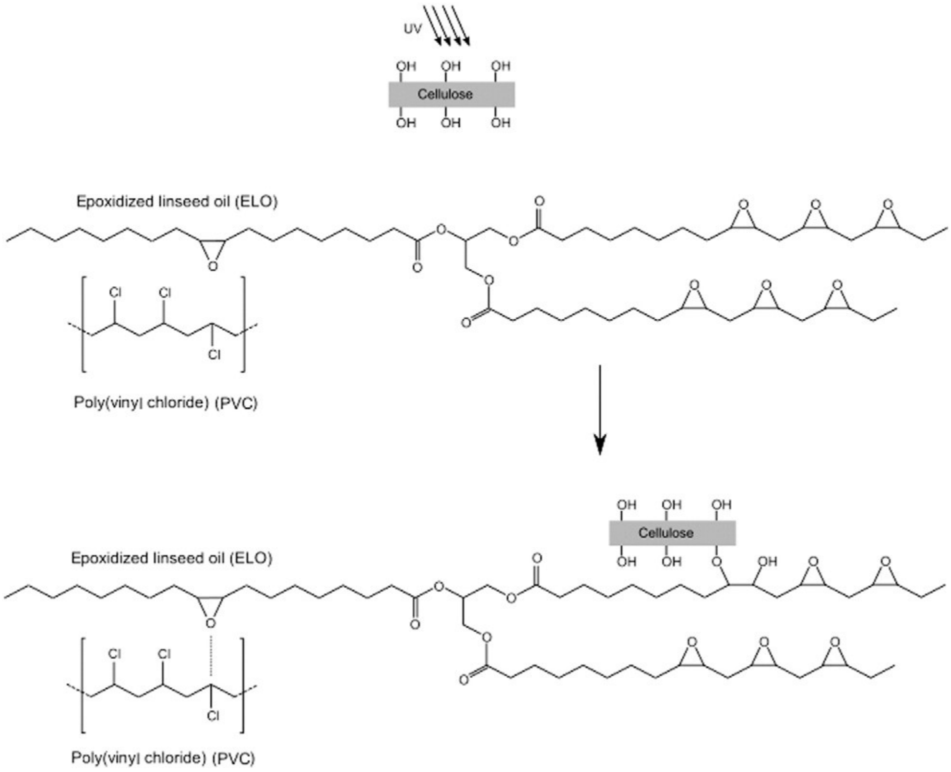

Fig. 8. Schematic representation of the proposed mechanism of adhesion between the poly(vinyl chloride) (PVC) plasticized by epoxidized linseed oil (ELO) and the ultraviolet (UV)activated surface of cellulose in wood flour.

3.3. Characterization of vinyl plastisol composites with UV-exposed wood flour

Fig. 9 shows the external appearance of the composites produced with wood flour treated with UV for 4 min. The 500-μm composite samples were selected to study the effect of UV treatment since these vinyl plastisol composites presented the optimal performance from both aesthetical and mechanical point of view. It can be seen that these composites presented a relatively similar wood-like aspect for all wood flour contents. Some heterogeneities were still observed for some zones in the composites related to large sizes of the cellulosic particles, mainly at high contents of wood flour. In general, the visual appearance of the composites was very similar to that previously observed for equivalent composites obtained with untreated wood flour. However, these vinyl plastisol composite parts did not clarify as the wood content was increased.

Fig. 10 presents the stress vs. strain curves for the vinyl plastisol composites containing 500-μm wood flour exposed to UV radiation for 4 min. Fig. 11 shows a complete comparison for the mechanical values between the equivalent composite obtained with untreated and UV-exposed wood flour at different contents. It can be observed in Fig. 11a that the tensile modulus decreased about 20–30% for all vinyl plastisol composites when the surface of wood flour was previously activated by UV radiation. On the contrary, Fig. 11b and c clearly show that the UV exposure improved both the tensile strength and elongation at break for all vinyl plastisol composites. This mechanical increase was particularly noticeable for high contents of wood flour, i.e., above 20 wt.-%. For instance, an increase of ca. 42% in the tensile strength for the 30 wt.-% vinyl plastisol composite obtained with UV-exposed wood flour was observed. This result was even more noticeable for the elongation at break in which the same composite increased the value from 15.5 to 53.4%, i.e., about 3.5 times higher. Therefore, the surface activation of wood flour by UV exposure decreased the stiffness of the vinyl plastisol composites and induced a significant improvement in their elongation at break. Similar to that explained above, as the composite samples produced with UV-exposed wood flour were mainly gaining flexibility, this produced a reduction in the elastic modulus. It is also worthy to mention that the mechanical properties of the vinyl composites followed the same tendency for untreated and UV-exposed wood flour, i.e., the tensile modulus increased and both the tensile strength and elongation at break decreased as the wood flour content was increased.

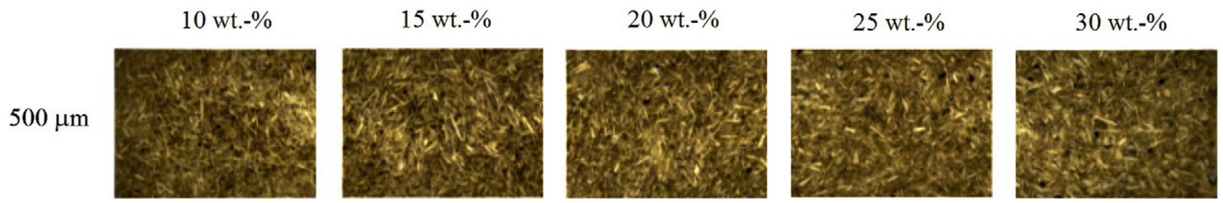

Fig. 9. Surface aspect of the vinyl plastisol composites as a function of the weight content (wt.-%) of 500-μm wood flour exposed to ultraviolet (UV) radiation for 4 min.

The above-observed enhancement in the ductile performance indicates that the UV exposure effectively exerted a positive effect on the interfacial adhesion between the wood flour particles and the vinyl matrix. Although, there is no previous literature explaining the use of UV radiation as surface modifying treatment of wood flour in PVC composites, some other research works have already reported the positive effect of coupling agents or chemical treatments. These methods have been typically based on blocking and/or minimizing the hydroxyl groups located on the wood flour surface. For instance, in the pioneering experiment carried out by Matuana et al. [48] the tensile strength of plasticized PVC/wood composites increased from 28.5 to 38.3 MPa by promoting adhesion with γ-aminopropyltriethoxysilane (APTES). Similarly, an increase of 40% in the tensile strength for PVC/wood flour composites was achieved by means of 10 wt.-% of this aminosilane [49]. In another study, the flexural modulus was 15% improved with the addition of 6.67 wt.-% chitin and 0.5 wt.-% chitosan, which effectively altered the acid–base interactions at the interface between wood flour and the vinyl polymer [35]. More recently, Nedjma et al. [50] reported an increase in the tensile strength from 16.6 to 20.1 MPa when the fillers were chemically modified with potassium permanganate ($KMnO_4$).

A similar morphological observation was followed to determine the compatibility of the UV-exposed wood flour with the vinyl matrix. In Fig. 12 it can be seen that the surface activation by UV exposure of the wood flour particles improved the fracture of the vinyl plastisol composites. Although the composite morphologies after fracture revealed a rough surface, which was produced due to the large particles embedded to the vinyl matrix, the wood flour particles were more homogeneously distributed. Importantly, the fractures clearly showed lower voids than equivalent composite samples obtained with untreated wood flour. This indicates that a more optimal bonding vinyl matrixwood flour was achieved after exposing the surface particles to UV radiation.

Fig. 13 shows the SEM micrographs of the fractured surfaces of the vinyl plastisol composites containing UV-exposed wood flour of 500 μm. These images clearly showed the remarkable decrease of the gap or material interphase between the dispersed cellulosic fillers and the surrounding vinyl matrix. In Fig. 13a it can be observed that a wood flour particle presenting a fiber-like morphology was perfectly embedded to the vinyl matrix in the 10 wt.-% composite. A similar improved vinyl matrix–wood flour particle interaction was also observed for the 20 wt.-% composite in Fig. 13b. Fiber pullout was less perceptible in these composites, in which a stronger adhesion between the natural filler and the polymer matrix is expected. Particle fracture instead of particle pullout as the failure mode for the 30 wt.-% composite was noticeable in Fig. 13c.

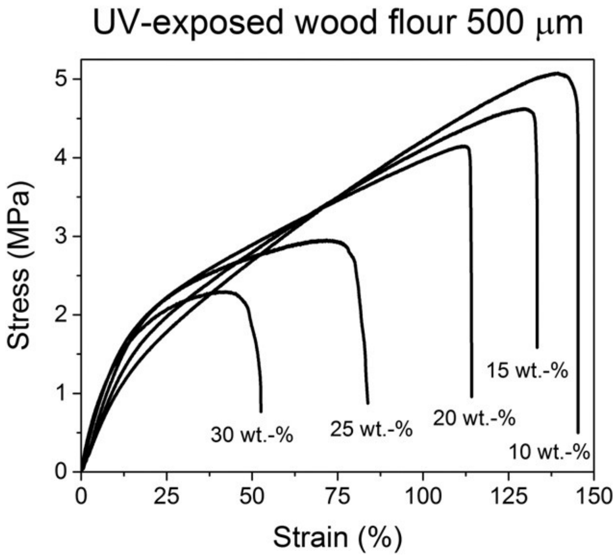

Fig. 10. Typical tensile stress-strain curves of the vinyl plastisol composites as a function of the weight content (wt.-%) of 500-μm wood flour exposed to ultraviolet (UV) radiation for 4 min.

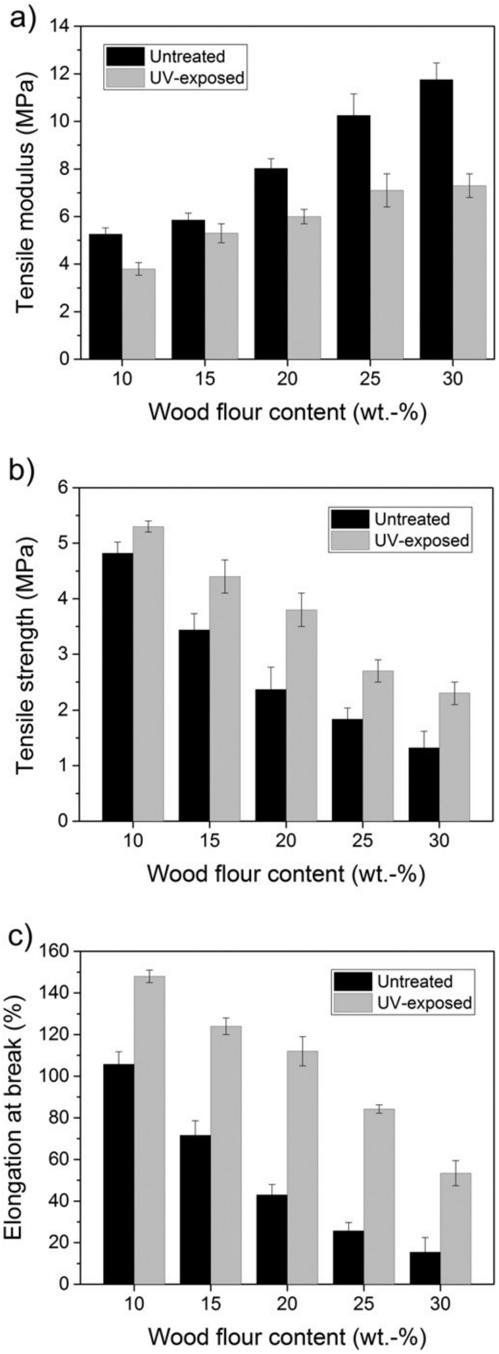

Fig. 11. Mechanical comparison between the vinyl plastisol composites obtained from untreated and 4-min ultraviolet (UV)-exposed 500-μm wood flour in terms of the weight content (wt.-%).

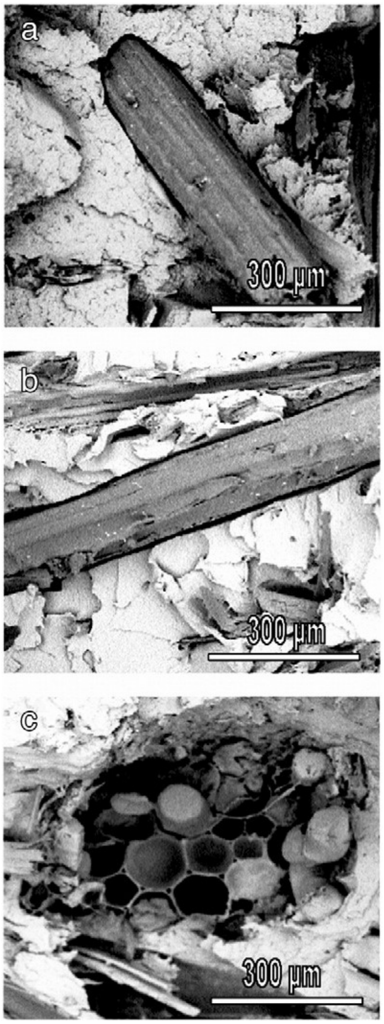

Fig. 13. Scanning electron microscopy (SEM) images corresponding to fractured surfaces of the vinyl plastisol composites containing 500-μm wood flour exposed to ultraviolet (UV) radiation for 4 min at: a) 10 wt.-%; b) 20 wt.-%; c) 30 wt.-%. Scale markers of 300 μm in all cases.

This means that adhesion strength of the wood flour particles on the vinyl matrix was greater than the inherent matrix strength. This image also revealed the peculiar internal structure of the reed wood particle that was based on a honeycomb-like morphology. Therefore, morphological studies confirmed the improved structure achieved in the vinyl plastisol composite after surface activation of wood flour by UV radiation. This supports the above-reported mechanical properties in which more efficient load transfer from dispersed wood flour particles to the vinyl matrix was achieved, leading to an improved ductile response, i.e., higher elongation at break.

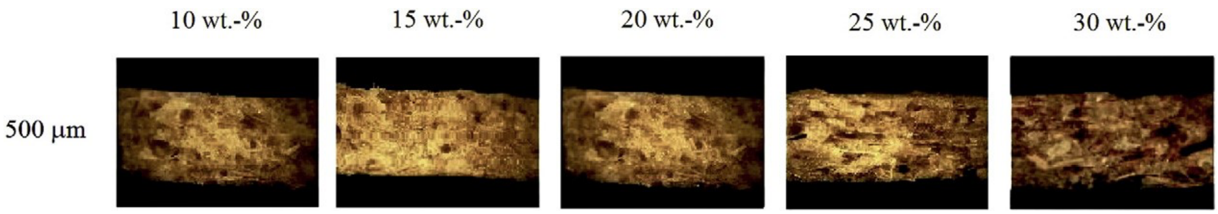

Fig. 12. Stereomicroscopy images corresponding to fractured sections of the vinyl plastisol composites as a function of the weight content (wt.-%) and particle size of 500-μm wood flour exposed to ultraviolet (UV) radiation for 4 min.

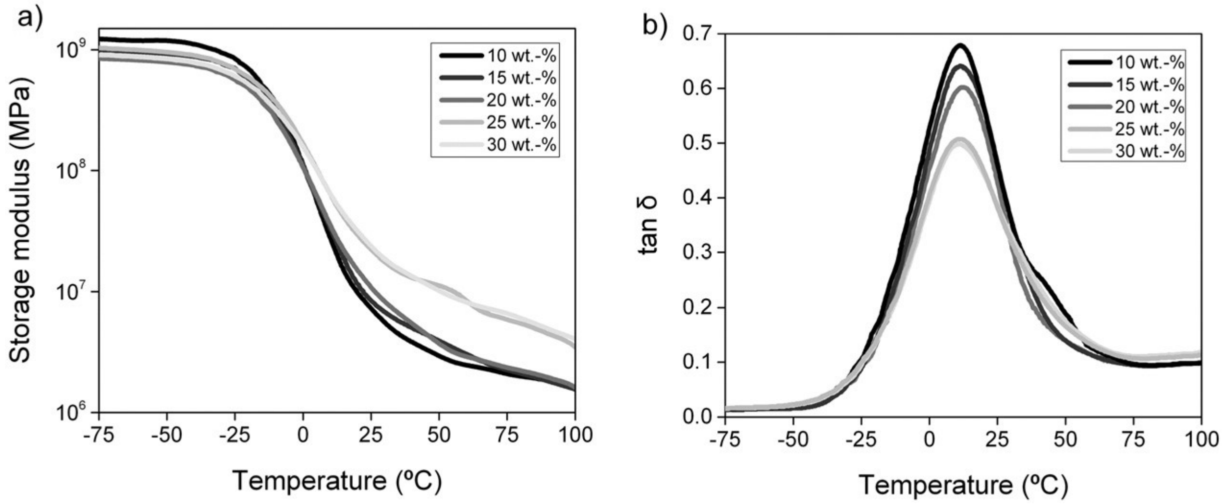

Fig. 14. Dynamic mechanical thermal analysis (DMTA) of the vinyl plastisol composites as a function of the weight content (wt.-%) of 500-μm wood flour exposed to ultraviolet (UV) radiation for 4 min: a) Storage modulus; b) Loss tangent (tan δ).

Finally, DMTA was used to ascertain the extent to which the vinyl plastisol composites containing UV-exposed wood flour of 500 μm can perform as wood substitute materials at different temperatures. Storage modulus and tan δ as function of temperature for the vinyl plastisol composites are shown in Fig. 14. In Fig. 14a it can be seen that all vinyl plastisol composites displayed a similar trend, i.e., the storage modulus was maintained at a high level below ca. −40 °C due to an elastic-vitreous behavior. The frozen segmental structure began to relax gradually with increasing temperature and the storage modulus decreased sharply from −25 °C due to an elastic-viscous behavior. The addition of UVexposed wood flour increased the storage modulus, in particular for the 25 and 30 wt.-% composites, which points out the reinforcing effect of the natural filler. This correlates well with the study of Shah et al. [35] who previously reported that the addition of wood flour into a vinyl matrix also increased the storage modulus, regardless of both the type of coupling agent used and the processing conditions.

With regard to the tan δ, i.e., the damping factor, Fig. 14b shows its evolution with temperature. All composites displayed a single peak in the curves with a maximum point at ca. 11.8 °C, which was related to the T_g of the vinyl plastisol. This reflects the change in behavior from elastic to viscous material. The low T_g observed suggests that the vinyl chains could slide more easily due to the plasticizing effect provided by ELO. As previously reported [45], the addition of ELO had the effect of lowering T_g and broadening the tan δ peak in polymer composites. A significant reduction in T_g of PVC from 78 to 12.7 °C was also reported by Bouchoul et al. [14] by adding 60 phr of di-(2-ethyl hexyl) phthalate (DEHP). The composites containing high contents of wood flour, i.e., 25 and 30 wt.-%, exhibited lower values of tan δ. This is related to the dampening of the vinyl chains due to an elastic stiffness and restriction for the molecular motion. In the tan δ curves, a wide relaxation peak dominated over the entire temperature of measurement from −50 to about 75 °C. The broadening of the tan δ peak can be attributed to the heterogeneity of the plastisol structure, which leads to a wider distribution of molecular interactions. These results indicated that all vinyl plastisol composites are flexible materials at room temperature due to the high content of ELO. Furthermore, the introduction of UV-exposed 500-μm wood flour increased their load-bearing capacity for practical applications.

4. Conclusions

Novel vinyl plastisol composites based on natural ELO plasticizer were successfully prepared by introducing reed wood flour at different contents and particle sizes. Tensile tests showed that the optimal mechanical performance was achieved for composites of high contents of wood flour with the largest particle sizes, i.e., 500 μm, although all composites presented poor mechanical response. Morphological analysis revealed that the wood flour presents low compatibility with the vinyl matrix by which it could not effectively transfer tensile stress. To overcome this, UV radiation was applied to the surface of wood flour as an adhesion promoting treatment. Mechanical results indicated that tensile strength and elongation at break were significantly increased for the composites containing wood flour particles previously exposed to UV for 4 min. Vinyl plastisol composites presented considerably higher dispersion and improved interfacial adhesion than equivalent untreated composites, which was supported by stereomicroscopic images and SEM micrographs on the fracture surfaces after tensile tests. In particular, it was proposed that UV functionalized the surface of wood flour by the formation of active hydroxyl groups that could open the epoxide rings of ELO and then link the cellulosic particles to the vinyl plastisol. Accounting for their optimal surface appearance and superior mechanical functioning, the resulting vinyl plastisol composites could be applied to obtain ductile parts as a cost effective and sustainable wood substitute in the design of new materials for building applications.

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