Recycling of organic fraction of municipal solid waste as an innovative precursor for the production of bio-based epoxy monomers

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ABSTRACT

This paper reports the preparation of newly synthesized bio-epoxy monomers, suitable for replacing petrochemical-derived epoxy resins. An original green method able to produce epoxy monomers starting from neat carbohydrates, waste flours, and even from the organic fraction of municipal solid waste (OFMSW), was here proposed. Hence, for the first time, the epoxidation of carbohydrates was attained only through the exposition to UV and ozone radiation, without using any organic solvent to carry out the reaction. Besides the innovation in the epoxidation method, this work explored the possibility of valorizing waste materials, by recycling carbohydrate scraps; in particular, the exposition of waste flours and municipal solid waste to UV and ozone and their consequent epoxidation allowed obtaining green precursors for the production of a bio-based epoxy resin.

Applicability and suitability of the synthesized compounds for epoxy monomers were investigated by curing experiments with a selected amount of a model cycloaliphatic amine-type hardener, i.e. isophoro-diamine (IPDA).

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1. Introduction

In recent years, growing economic and environmental concerns, as well as the uncertainty related to finite petrochemical resources, determined a huge increase in the research and development of new bio-based polymers (Baroncini et al., 2016). In the latest decades, polymers obtained from renewable resources became, hence, increasingly important as highly sustainable, eco-efficient, and biodegradable products (Rapi et al., 2015). The idea is to replace, at least partially, certain petroleum-based monomers (Belgacem and Gandini, 2008; Gandini, 2011; Pascault and Williams, 2010; Graedel and Howard-Grenville, 2005; Kaplan, 1998; Pillai, 2010; Wool and Sun, 2005), such as diglycidyl ether of bisphenol A (DGEBA). The latter is formed from the reaction of bisphenol A (BPA) and epichlorohydrin in the presence of a basic catalyst (Jin et al., 2015) and it is extensively used as epoxy component of thermo-setting polymers and in particular of epoxy resins, which are industrially common pre-polymers that contain oxirane groups (Baroncini et al., 2016).

Studies carried out on BPA revealed its toxicity for the living organisms (Chapin et al., 2008). Moreover, BPA was classified as a reprotoxic and therefore prohibited for use in children's bottles and glasses in Canada, in the European Union as well as in more than ten states of United States of America. Many scientists are, hence, now trying to produce bio-based epoxy resins which show comparable mechanical response to that of the DGEBA epoxy-based commercial products. Recent results on this topic are already reported in the literature (Auvergne et al., 2014). Synthesis methods for bio-based polymers have been starting from different natural materials (Baroncini et al., 2016), such as vegetable oil (Kadam et al., 2015; Lu et al., 2005; Miao et al., 2013; Park et al., 2004; Pin et al., 2015; Wang and Schuman 2013; Samanta et al., 2016; Omonov and Curtis, 2014; Tsujimoto et al., 2015), fatty acids (Pan et al., 2011) rosin (Mantzaridis, et al., 2013; Liu et al., 2012), wood biomass (Asada, et al., 2015; Koike, 2012), industrial lignin (Koike, 2012; Fache et al., 2014) and starch (Huijbrechts et al., 2007; Huijbrechts et al., 2010). From a life-cycle point of view, sugar can potentially replace the petroleum-based polymers, with the important advantage of being a natural renewable resource (Rapi et al., 2015). In particular, due to the presence of a highly reactive hydroxyl group, the monomers of carbohydrates can be suitable for the production of different polymers (Varma et al., 2004; Galbis and García-Martín, 2010; Kricheldorf, 1997; Okada, 2001; Varela and Orgueira, 2000). Also, natural polysaccharides have the potential to replace DGEBA for the synthesis of epoxy monomers. In particular, dianhydrohexitols, such as isosorbide,

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isomannide, isoidide, derived from D-glucose, D-mannose, and L-fructose, are good sugar-derivative candidate as raw material for epoxy monomers production.

On the other hand, synthesis of the bio-resins starting from the neat carbohydrates precursors required the use of organic solvents. (Feng et al., 2011; Hong et al., 2014; Chrysanthos et al., 2011).

To the extent of our knowledge, starch is an inexpensive, easily available and renewable starting material, which has not yet been applied, as it is, as a precursor of epoxy monomers avoiding the use of chemical solvents. Several attempts were carried-out by exploiting the sugar-derivatives, i.e. Rapi et al. (2015) prepared several functional epoxy components from d-glucose. Gandini (2010) reported on all the epoxy polymers based on renewable resources among which gelatinized cassava starch mixed with an epoxidized natural rubber. Conversely, the organic fraction of municipal solid waste contains a significant fraction of paper, food waste, wood, that are rich in carbohydrates. In addition, in the last decade, municipal solid waste management has grown as one of the main challenges of modern smart cities in the world. The amount of municipal solid waste, globally collected per year, is approximately 1.3×10^{12} t and it is expected to rise up to 2.2×10^{12} t per year by 2025 (EPA – United States Environmental Protection Agency, 2017). Any solution to improve the environmental sustainability represents a welcome candidate that can improve the quality of life for the population (Esposito Corcione et al., 2019a, 2019b). Because of the high amounts of organic municipal solid waste produced worldwide and the consequent negative environmental impact, hence, the possibility to convert them in a bio-resin represents an ambitus and important goal for all the scientific community that has not yet been investigated and therefore obtained. This work is thus aimed at the development of a new green method that avoids chemical solvents, to produce bio-based epoxy structures with good mechanical performances and high glass transition temperature. Furthermore, the developed approach was tested not only on neat natural polysaccharides, such as starch, but also on organic waste flours as well as on the organic fraction of municipal solid waste (OFMSW). This represents a further important innovation of this paper that, for the first time, proposes an innovative method to re-use waste materials, by producing high valorized bio-based polymeric products.

2. Experimental

2.1. Materials

Commercial maize starch (labeled as CMS) was purchased by Sigma Aldrich (CAS Number 9005-25-8) and, in this work, it was used as a control material for comparison purposes. Commercial maize starch consists of 27% of amylose (linear glucose polymer) and 73% of amylopectin (highly branched glucose polymer) (Sigma Aldrich, 2020). Waste flour (labeled as WF) was obtained from the processing waste of the pasta factory Benedetto Cavalieri Srl. The organic fraction of municipal solid waste (labeled as OFMSW) is made of unsorted food wastes collected according to the Italian standard regulation; in particular, the OFMSW was collected from a local restaurant and, apart from food wastes, it contains small amounts (less than 0.5% in weight) of different soft wastes, such as tissues or napkins.

The suitability of the synthesized compounds as epoxy monomers was investigated by curing probes with a model cycloaliphatic amine-type hardener, i.e. Isophorone diamine (IPDA), supplied by Sigma Aldrich and used as curing agent for the bio-epoxy monomers obtained from the neat starch and the wastes. The compositions of all the formulations produced are reported in Table 1 and further detailed in the patent application (Esposito Corcione et al., 2019c).

Table 1
Compositions of UV/ozone-epoxidized blends: epoxidized Commercial Maize Starch (eCMS), epoxidized Waste Flour (eWF) and epoxidized Organic Fraction of Municipal Solid Waste (eOFMSW).

Formulation Code	Bio-resin precursors (wt%)	IPDA (wt%)	WATER (wt%)
eCMS$_{70}$	70	30	0
eCMS$_{65}$	65	35	0
eCMS$_{60}$	60	40	0
eCMS$_{55}$	55	33	12
eCMS$_{52}$	52	32	16
eCMS$_{50}$	50	30	20
eWF$_{50}$	50	30	20
eOFMSW$_{70}$	70	30	0
eOFMSW$_{65}$	65	35	0
eOFMSW$_{60}$	60	40	0
eOFMSW$_{55}$	55	25	20

2.2. Methods

2.2.1. Waste carbohydrates bio-resins precursors characterizations

X-ray diffraction spectra were acquired by XRD-Ultima+ (by Rigaku) in order to study the crystallinity degree of the control system, i.e., Maize starch, and waste flour samples. The measurements were carried out by using Cu Kα radiation in reflection mode (λ = 0. 154 nm). All the samples were step-scanned at room temperature from 2θ values in the range 5–60°. The degree of crystallinity of starch/waste flours powders and relative films was calculated through the formula proposed by Hermans and Weidinger:

$$\%Cristallinity = \frac{Qst - Qam}{Qst} * 100 \qquad (1)$$

where Qst and Qam are the areas calculated under the X-ray spectra from the semicrystalline and amorphous samples, respectively (Hermans and Weidinger, 1961).

2.2.2. Waste bio-resins precursors epoxidation and characterization

In order to obtain the epoxidation of the bio-resin precursors (CMS, WF and OFMSW), a thin layer of CMS, WF, OFMSW and of the selected biomolecules present in the OFMSW (i.e. lipids, proteins and simple carbohydrates) was exposed to UV radiations by using a medium pressure Hg UV lamp (UV HG 200 ULTRA), with radiation intensity on the surface of the samples of 9.60 W/mm^2, working in air atmosphere. The photochemical ozone production from the interaction between UV rays and the oxygen present in the air atmosphere was also exploited. The research work predicted three steps for studying the epoxidation reaction due to UV/ozone exposure. Firstly, CMS, WF, and OFSMW samples were exposed to Hg UV lamp from 1 h to 5 h in the air in order to assess the epoxidation status; this process is labeled hereinafter as UV/ozone exposure. Then, the study of the epoxidation reaction was performed only on CMS samples, as a control material, by exposing it to UV exposure for 5 h by isolating the pattern from ozone with a transparent UV crystal window.

The FTIR analyses were performed with FT-IR Jasco 6300 Spectrometer. Infrared spectra were recorded in the wavelength range between 400 and 4000 cm^{-1}, 128 scans, and 4 cm^{-1} of resolution, by using a KBr round crystal window. The spectra acquisition was carried out before and after the UV/ozone or UV exposure, in order to study the epoxidation process.

In order to evaluate the number of epoxy groups formed after the exposure to UV/ozone radiations, titration analysis was carried out, according to Method A of ASTM D 1652-97 (ASTM D (1652) – 97, 1997), as follows:

(a) 5.5 mg of sample was dissolved in a mixture 1: 1 Chloroform-Chlorobenzene;

(b) two drops of Crystal Violet (used as indicator) were added to the previous mixture;

(c) a solution of HBr in 0.1 N acetic acid was added drop by drop.

Since the amount of the consumed acid is an index of the epoxy content of the sample, the epoxy content (E) and the equivalent epoxy weight (WPE) were calculated by using the following equations:

$$E = N(V - B)/(10xW) \qquad (2)$$

$$WPE = \frac{1000W}{N(V - B)} \qquad (3)$$

where

– N = normality of HBr in acetic acid [eq/L]
– V = volume of HBr solution used for titration of the sample [ml]
– B = volume of HBr solution used for white titration [ml]
– W = sample used, in g

The amine hydrogen equivalent weight (AHEW) was calculated by using the following equation:

$$HEW = \frac{\text{molecular weight of the amine}}{\text{number of active amine hydrogens}} \qquad (4)$$

The isophorone diamine with a molar mass of 170.3 g/mol contains four active hydrogen atoms and acts theoretically as a tetramine. Thus AHEW of isophorone diamine is equal to 170.3/4 = 42.57 g/eq. Since it is assumed that one amine hydrogen reacts with one epoxy group the stoichiometric ratio of hardener to use with the epoxy resin is given by the ratio (Karayannidou et al., 2006):

$$phr = \frac{HEW * 100}{WPE} \qquad (5)$$

2.2.3. Waste bio-resins precursors mixtures characterizations

The complex viscosity of the bio-resin mixtures, obtained both from starch and waste materials, was measured by a controlled rheometer (Ares TA Instrument), by heating the samples from 20 °C to 160 °C, at 3 °C/min. According to the results obtained from the titration and rheological analyses, a range of 30–40 wt% of amine was added to the epoxy component. A selected amount of a natural solvent, i.e. water, was also added to the mixture composed of the bio-epoxy resin and IPDA, in order to improve their mixing and fluidization.

The rheological steady measurements were performed by adding to the eCMS_a60 formulation 12, 16, and 20 wt% of water. Because of a better reproducibility of the results, only the control system eCMS was used to optimize the water amount. On the other hand, the water amount can significantly affect the quality of the produced samples, particularly in terms of porosity and ease of flow during the production by pouring. Therefore, after optimization of the water amount for eCMS, the same water amount was added to the waste materials, too.

2.3. Waste bio-resin precursors samples production

The production of samples from waste bio-resin precursors was performed by mixing the epoxidized component with the selected range of IPDA. Furthermore, the right amount of a natural solvent, i.e. water, was also added to the mixture composed of the bio-epoxy resin and IPDA, in order to improve their mixing and fluidization. All the components were mixed for 10 min at 100 rpm by using a mechanical stirrer, then the blend was poured in a silicon mold and put in oven. The optimization of the curing process will be described below. As described in previous works (Ferrari et al., 2019a, 2019b, 2020), an adequately low viscosity is required for an easy pouring.

2.3.1. Waste bio-resin cure process and characterization

The curing process of the mixtures composed of bio-epoxy resin, IPDA, and water (see Table 1) was optimized in order to avoid the fast evaporation of the solvent, responsible for high porosity and, then, low mechanical properties. The optimization of the curing process was carried out by an indirect analysis method. In detail, after casting in silicone molds, the selected mixtures were held in an oven at different temperatures (in a range of 110–150 °C according to rheological results) upon to reach the complete curing. The standard curing time of the epoxy resins mixed with IPDA (about 1–2 h) (Stasi et al., 2019) was not enough to complete the cure for the epoxied waste-based mixtures; for such reason, the curing time was extended up to 4 h. DSC dynamic scans from 25 °C to 230 °C at 10 °C/min in nitrogen atmosphere were performed on the cured samples by means of differential scanning calorimeter (DSC; Mettler Toledo 622). The glass transition temperature, Tg, was, thus, measured for each formulation analyzed; at least three tests on each sample were performed. The optimal curing process, obtained from the DSC results, and adopted for the production of the cured samples for the following physic-mechanical characterizations, consisted of two steps: the first one at 60 °C for 24 h and the second one at 150 °C for 4 h, except for eOFMSW$_{55}$ that was cured at a lower temperature (i.e. 120 °C) for 4 h.

The FTIR measurements were carried out on cured samples in order to verify the absence of the typical peaks of the epoxy ring.

2.3.2. Waste bio-resins cured samples characterizations

The flexural properties of each cured sample were measured using a dynamometer, Lloyd LR5K, according to ASTM D790 (ASTM D790 – 17, 2017) (three points bending with specimen dimension: 80 mm × 10 mm × 4 mm). Five tests were performed on each sample. The density expressed as mass/volume ratio was calculated. An average of at least 3 measurements was carried out for each cured sample. Optical microscope Zeiss AXIO-LINKAM was used for the morphological characterization of the bio-resins cured samples. The imagines at 50× of magnification were acquired and the size of the pores as an average of 50 measurements was calculated.

For each of the presented experimental method, at least three replicates were performed on each sample.

3. Results and discussion

3.1. Waste based bio-resins precursors: Characterization and epoxidation

XRD analyses were carried out on CMS and WF samples, in order to evaluate eventual changes in the starch crystalline structure, compared to that reported in the literature (Van Soest et al., 1996), due to the flour processing. Results in Fig. 1B confirm the semi-crystalline nature of all samples (see literature data reported in the inset of Fig. 1B) for both commercial starch and waste flour, without any significant change in the crystalline fraction and the crystal planes, for the waste flours.

A comparison between the FTIR spectra of neat starch and starch exposed to UV /ozone radiation for 5 h is reported in Fig. 2A. In order to highlight the effect of UV exposure on the epoxidation of neat starch (CMS), FTIR curves are shown in the wavelength range of 1300–650 cm^{-1}. As it can be observed, UV/ozone exposition involved several modifications of the CMS bonds.
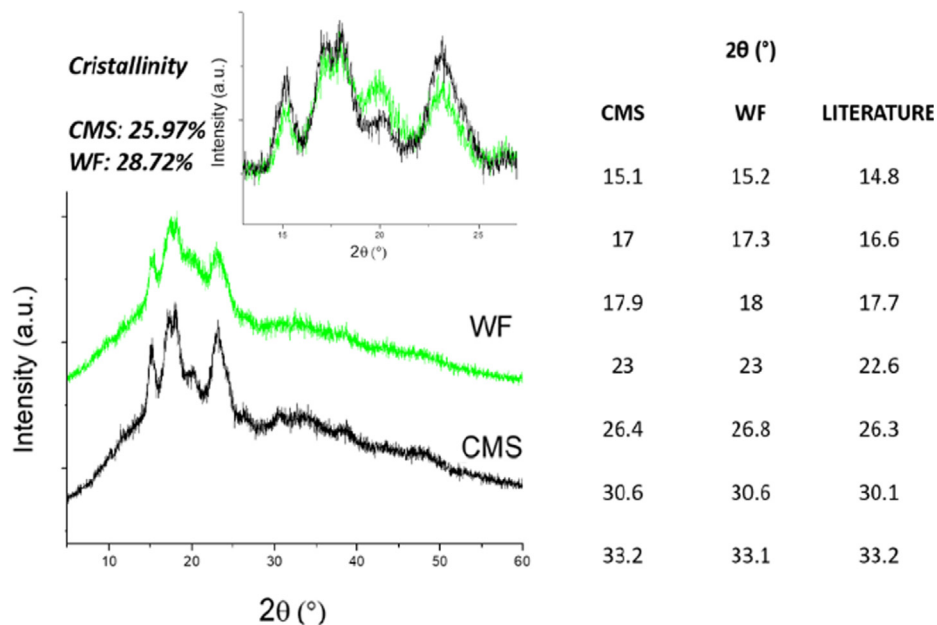
Fig. 1. XRD data of CMS and WF powders.

Among these, the presence of the peaks at 1260, 890, and 827 cm^{-1} after UV treatment indicates the formation of an epoxy ring (Nyquist, 2001).

Besides the modification of the chemical structure, which involves the appearance of new signals in the FTIR spectrum, the UV exposure caused an increase in the intensity of some peaks. In particular, a significant increase in peak intensity can be noticed for the C—O—C stretch at 1050–1080 cm^{-1} (Fig. 2A). A possible mechanism for the epoxidation of the starch bonds could involve two main steps, as following described.

(a) UV exposure

The photo-degradation of the carbohydrates has long been well known and widely studied in the literature (Phillips and Rickards, 1969; Phillips, 1963). The UV irradiation on the starch induces the photolysis of hydroxyl and C—O—C groups (Bajer et al., 2013) and a subsequent formation of double bonds could occur. As demonstrated by Bertolini et al. (2001) on cassava and corn starch, the UV irradiation induced the starch photo-oxidation. Quispe et al. (2019) found that the exposure to ultraviolet (UV) radiation causes significant degradation of starch-based materials, inducing photo-oxidative reactions which result in breaking of polymer chains, production of free radical, and reduction of molar mass. In particular, by comparing IR spectra before and after the UV exposure, the presence of an additional band located at 1726 cm^{-1} in samples exposed to UV radiation was detected, thus indicating the formation of a new functional group (C=O).

The comparison between the FTIR curves before and after UV exposure in Fig. 1S shows the appearance of a peak at 3000 cm^{-1}, due to C—H stretching of alkene, and at 1650 cm^{-1}, due to the stretching of the carbon double bond. Finally, IR spectra before and after UV exposure differ for the presence of a strong peak at 950 cm^{-1}, attributable to the C=C bending of the alkene.

(b) UV/Ozone exposure

As shown in Fig. 2B, the exposition to the ozone could have involved the cleavage of the double bond with the consequent generation of the epoxy ring (Bailey et al., 1985).

The effect of the UV radiation on the starch bonds is shown in Fig. 1S and it is also supported in the literature (Bajer et al., 2013). As explained before, the FTIR curve of CMS exposed to only UV radiation, without ozone contribution, shows the presence of different peaks typically attributable to the carbon double bond. The formation of the epoxy ring is instead clearly visible in the FTIR curves of dry CMS after 5 h of UV/ozone exposure (Fig. 2A); in particular, the curve shows the disappearance of the double bond peak at 1650 cm^{-1} and the presence of the typical signals of the epoxy ring at 1260, 890 and 827 cm^{-1} (González et al., 2012).

Once established the mechanism responsible for the epoxidation of the starch, the same procedure was applied to selected carbohydrate waste (WF) and mixed waste (OFMSW). Therefore, WF and OFMSW samples were exposed to 5 h of UV/ozone irradiation, then the modification in the chemical structure was assessed by FTIR analysis.

As shown in Fig. 2C, the presence of the epoxy ring is visible on the waste flour sample at the same wavenumber found for CMS; moreover, a structural modification occurs for the mixed waste. As reported in Fig. 2D, a strong reduction of C=C stretching band (1652 cm^{-1}) occurs, and in the inset of Fig. 2D the peaks related to epoxy ring stretching appear after the exposure at 1250, 937 and 870 cm^{-1}.

The confirmed formation of the epoxy ring in the mixed waste posed the question about the capability of other biomolecules, besides complex carbohydrates, to undergo epoxidation. To this purpose, UV/ozone exposure was carried out on selected wastes with higher content of lipids, proteins and simple carbohydrates (Abdulla et al., 2010). Further FTIR analysis performed on the treated samples confirmed the epoxidation only for simple carbohydrates (Fig. 4S), where epoxy peaks are clearly visible at 1250, 937, and 870 cm^{-1}. On the other hand, FTIR analysis after UV exposition of samples with high lipid and protein content (Figs. 2S and 3S, respectively) did not show any peaks which can be correlated to the epoxy ring. Although the FTIR spectra were carried out in order to highlight the epoxidation after UV exposure, the analysis of the most relevant IR peaks of lipids, proteins and simple carbohydrates was performed and reported in Table S1.
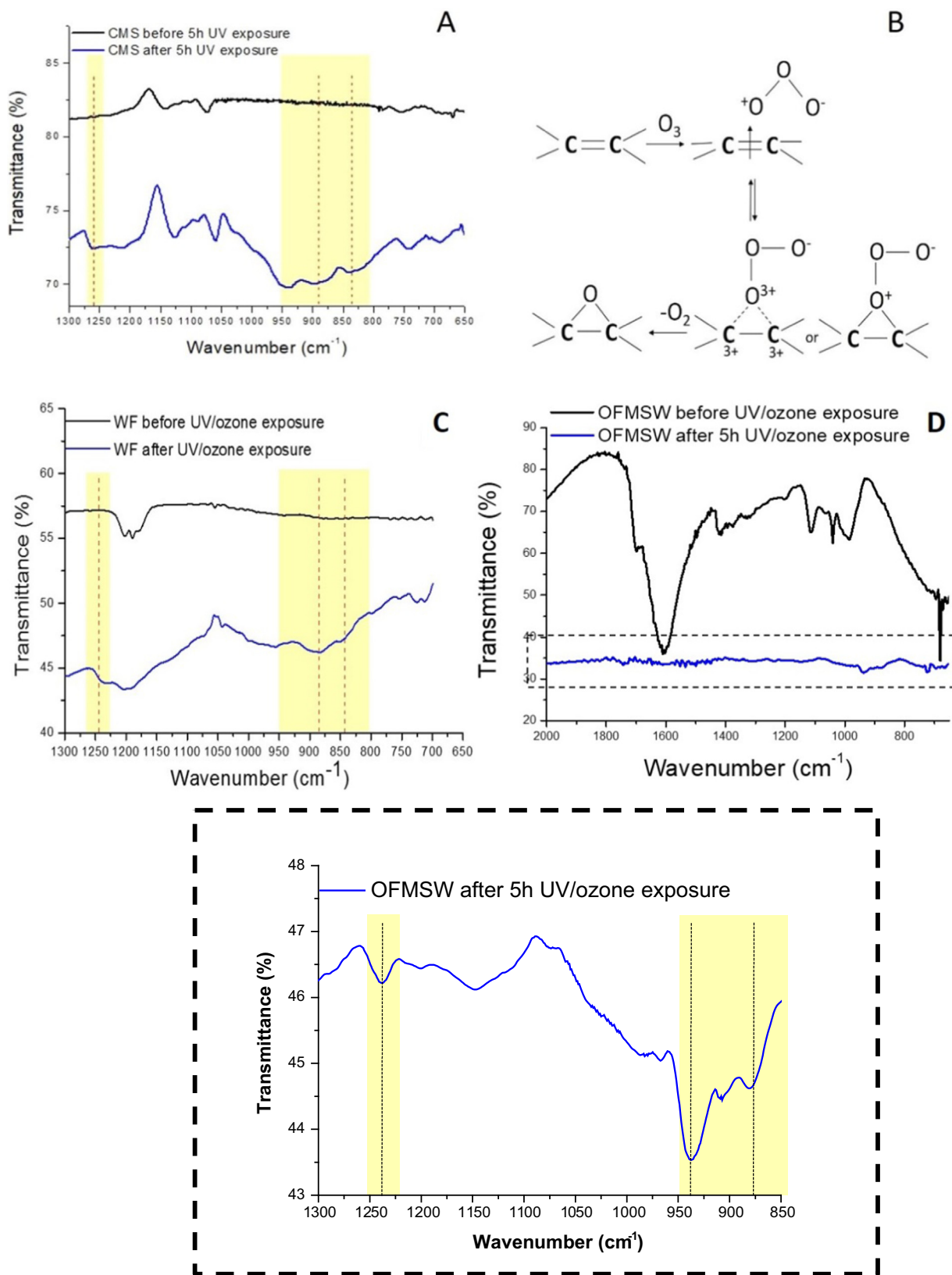
Fig. 2. FTIR curves of CMS (A), WF (C), and OFMSW (D) before and after UV exposure (the latter highlighted in the inset) and epoxidation reaction (B).

3.2. Waste based bio-resins: Characterization

Once assessed the epoxidation of neat carbohydrates and mixed wastes, the epoxy content, present in the epoxied systems, was estimated by the titration method. According to Eq. (2), titration allowed calculating the epoxy content E (i.e gram equivalents of epoxy groups per 100 g of resin), which was equal to 1.47 eq/g for eCMS, 1.36 eq/g for eDWF, and 1.15 eq/g for eOFMSW.

According to equation (3), the weight per epoxy equivalent, WPE (i.e. grams of resin containing 1 g equivalent of epoxy groups) resulted equal to 68.1 g/eq for eCMS, 73.7 g/eq for eDWF, and 87 g/eq for eOFMSW.

Afterwards, by using Eq. (4), the wt% of IPDA was calculated: 38.5 wt% for eCMS; 36.7 wt% for eDWF and 32.3 wt% for eOFMSW.

In order to evaluate the effect of other functional groups in the organic molecules, the titration analysis was also performed for the samples before epoxidation. Results showed that the same volume of HBr solution used for white titration was needed for the titration of the sample, thus confirming that the amount of the consumed acid was not influenced by other functional groups.

Starting from titration results, rheological analyses were carried out on eCMS and eOFMSW mixtures obtained with different amounts of IPDA. As shown in Fig. 3, independently from the composition of the mixture, the complex viscosity (η^*) of epoxy-amine blends decreases up to a minimum value (η_{min}), then an increase in viscosity occurs until the reaction is completed. The reaction rate was then monitored by calculating the slope of each curve in the range of 100–140 °C, in order to evaluate the optimal amine content to be added to the mixture. In particular, a higher slope value corresponds to a faster reaction between the precursor and the amine.

Results, reported in Table 2, revealed a reaction starting at about 113 °C for all eCMS samples, almost independently of the amine content. Also in the case of eOFMSW samples, the onset temperature of the reaction is about 109 °C, independently from the precursor amount. Based on these results, it can be assessed that the reaction between the epoxidized precursors and IPDA occurs earlier in the case of mixed waste. On the other hand, the lower slopes of eOFMSW samples indicate a lower reaction rate if compared to eCMS. The highest reaction rate is reached with the correct ratio between epoxy rings and amine groups; therefore, the optimization of the composition was attained by comparing the slope of each sample and by choosing 40 wt% for eCMS and 35 wt% for eOFMSW as IPDA optimal amount. In accordance with titration results, the higher IPDA amount found for eCMS is due to a higher epoxy content compared to eOFMSW.

As shown in Table 2, the initial viscosity η_0 resulted too high to allow an easy pouring of the compounds inside the mold. As a consequence, different amounts of water, were added to eCMS samples and its effect on the viscosity of the samples was monitored by steady rheological analyses.

The rheological analyses on eCMS samples (Fig. 5S) show that the addition of 12 wt%, 16 wt% and 20 wt% of water caused a decrease in initial viscosity from 1.88×10^4 to 3.46×10^3 and 6.21×10^2, respectively, thus allowing choosing 20 wt% of water as the optimal amount.

The optimization of the curing process involved a step of evaporation before the cure, to avoid any possible inhibition due to the presence of water. In order to obtain a slow evaporation, without strongly compromising the properties of the cured samples, the curing process for all the systems was carried out by drying the mixtures at 60 °C for 24 h and, then, by heating at higher temperatures. According to the rheological analysis results of Fig. 5S, a range of temperature of 110–150 °C was chosen for each kind of mixture, in order to reach the complete cure after 4 h. The curing process was monitored by FTIR and DSC analyses, which allowed providing the conversion degree of epoxy group (Fig. 4A–C) and the glass transition temperature (Fig. 4D), respectively.

The FTIR curves reported in Fig. 4A show the total disappearance of the epoxy peak (1250 cm^{-1} and 950 cm^{-1}), evidencing the complete reaction of the epoxy ring with IPDA.

DSC results, reported in Fig. 4B and in Table 3, show, for all systems, the presence of a glass transition temperature in the range of 160–180 °C. Although the highest Tg value was found for eCMS samples, all the bio-resins produced revealed a higher Tg compared to the typical Tg value of the commercial DGEBA epoxy resins, named EC01/WH91 (Esposito Corcione et al., 2013), thus confirming a successful curing process for all the epoxidized bio-precursors. Moreover, Tg values of all produced samples are higher, or comparable, to most of the bio-based epoxy resins. As reported by Baroncini et al. (2016), only epoxidized catechin (Tg of 178 °C) and glycidyl ether of limonene alkylated naphtholformaldehyde based-epoxy resins (171 °C < Tg < 182 °C) showed comparable Tg to those found in this work.

Flexural tests were then carried out in order to assess the mechanical behaviour of the waste-based bio-epoxy resins. The obtained results, reported in Table 3, evidence that a sufficiently high stiffness was reached for eCMS and eWF samples. In particular, a comparable flexural modulus to that of EC01/WH91 resin was found for eCMS samples, while a decrease of about 20% was found for eWF sample; eOFMSW bio-resins showed the worse mechanical response, with a flexural modulus approximately 50% lower than that of EC01/WH91.
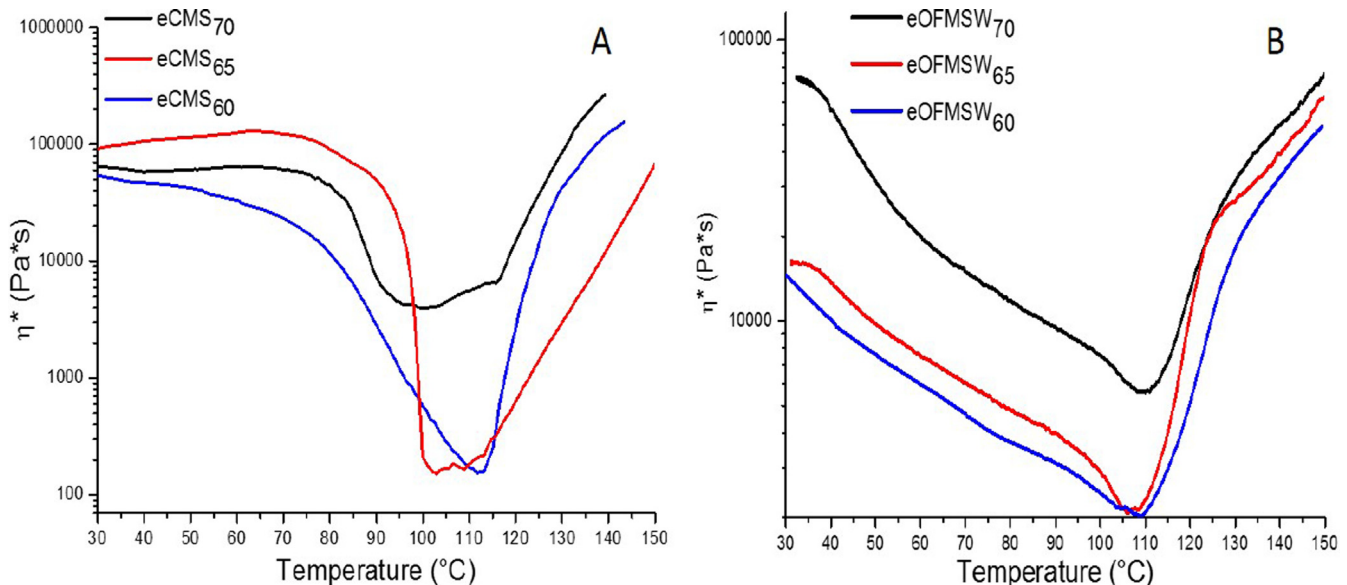

Fig. 3. Dynamic rheological analyses on eCMS (A) and eOFMSW (B) samples.
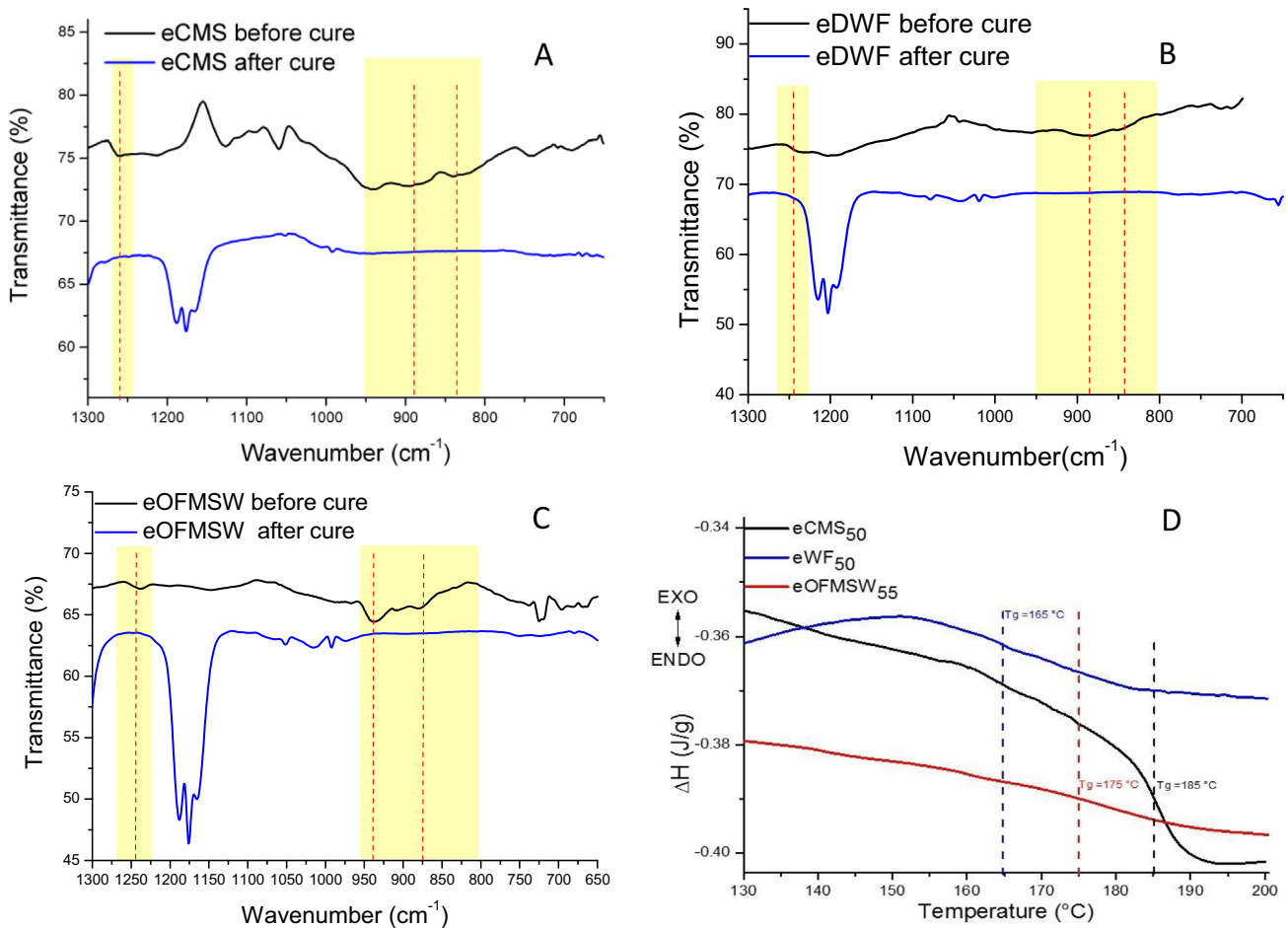
Fig. 4. FTIR curves of CMS (A), DWF (B) and OFMSW (C) before and after cure and DSC thermograms (D) of bio-epoxy cured samples.

The tensile strength of eCMS was found comparable to other bio-epoxy resins. As reported by Baroncini et al (2016), epoxidized soybean oil-based epoxy resins show a tensile strength of about 12–15 MPa. On the other hand, lower values were detected for eWF, with a decrease of about 40% in tensile strength, and, again, the worse mechanical response was detected for eOFMSF, which showed a tensile strength four times lower than eCMS one.

In order to assess the effect of water on the mechanical response of the produced samples, also $eOFMSW_{65}$ samples were subjected to flexural tests. Results, shown in Table 3, indicate a decrease of about 55% in flexural strength and 70% in elastic modulus, compared to $eOFMSW_{55}$. Thus, the addition of water has the double effect of improving the processability of the slurry and increase the consistency of the final component. This result is supported by the comparison of the density between $eOFMSW_{65}$ and $eOFMSW_{55}$ samples: as reported in Fig. 5, the latter has a density of 0.64 ± 0.15 g/cm^3, whereas a lower value (0.41 ± 0.11 g/cm^3) was found for samples produced without water.

Furthermore, very low flexural strength was found for all the produced samples. This can be ascribed to a high number of voids and defects occurring both during the water evaporation and the curing process. The presence of imperfections was confirmed by the optical analyses, as shown in Fig. 5. An increase in pores size, which in turn involved a decay in mechanical response, was found for bio-resin samples obtained from selected and mixed wastes. According to the results shown in previous works (Esposito

Table 3
Thermal and mechanical properties of the bio-epoxy cured samples compared to commercial epoxy DGEBA resin (EC01/WH91) (Esposito Corcione et al., 2013).

Bio-epoxy resin	σ (MPa)	E (GPa)	Inflection point, Tg (°C)
$eCMS_{50}$	12.82 ± 1.15	2.84 ± 0.59	185 ± 0.5
eWF_{50}	7.32 ± 0.65	2.37 ± 0.27	165 ± 0.4
$eOFMSW_{55}$	3.70 ± 0.73	1.65 ± 0.19	175 ± 0.4
$eOFMSW_{65}$	1.59 ± 0.16	0.49 ± 0.15	155 ± 0.3
EC01/WH91	120–135	2.9–3.3	120–130

Table 2
Rheological results: T_{start} is the reaction starting temperature; η_0 is the initial viscosity.

Sample	T_{start} (°C)	η_0 (Pa*s)	η_{min} (Pa*s)	Slope (Pa*s/°C)[i]
$eCMS_{70}$	114.13 ± 1.65	6.88E4 ± 3.32E3	3.97E3 ± 1.08E2	7.12E-2
$eCMS_{65}$	108.88 ± 1.76	9.07E4 ± 2.56E3	1.62E2 ± 5.28E0	6.67E-2
$eCMS_{60}$	113.72 ± 2.24	5.08E4 ± 7.92E2	1.55E2 ± 3.67E0	1.75E-1
$eOFMSW_{70}$	109.72 ± 1.85	7.38E4 ± 1.22E3	6.03E3 ± 1.78E2	4.96E-2
$eOFMSW_{65}$	108.57 ± 3.25	1.64E4 ± 3.23E2	2.02E3 ± 3.15E1	8.43E-2
$eOFMSW_{60}$	109.68 ± 1.82	1.35E4 ± 2.31E2	2.02E3 ± 9.37E1	5.29E-2

[i] The slopes values were calculated in the temperature range of 115–125 °C for all the samples.
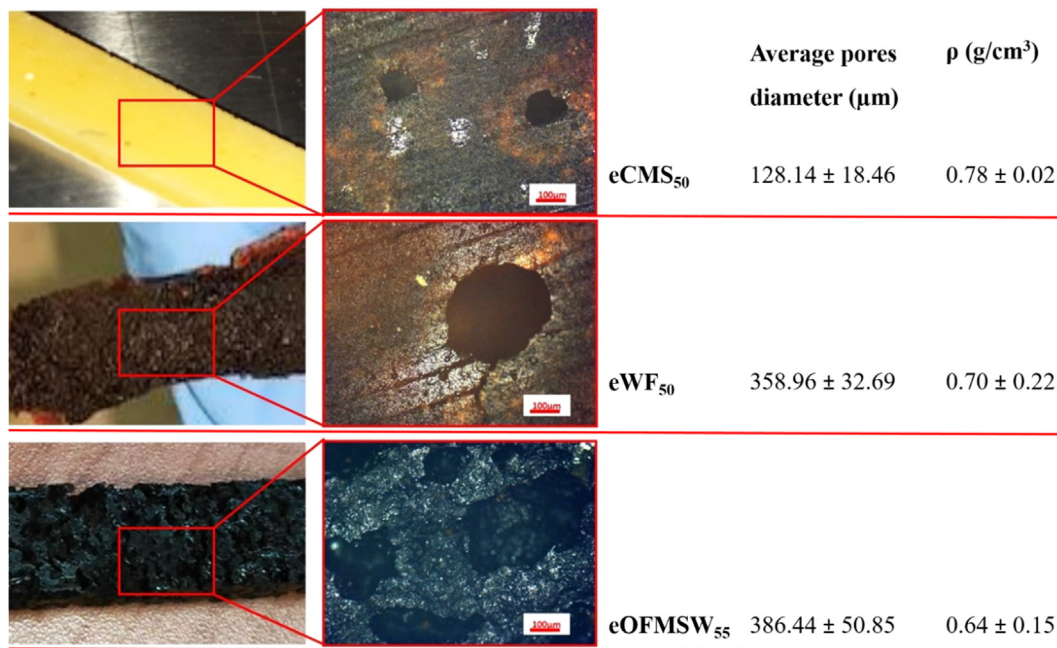
	Average pores diameter (μm)	ρ (g/cm³)
eCMS₅₀	128.14 ± 18.46	0.78 ± 0.02
eWF₅₀	358.96 ± 32.69	0.70 ± 0.22
eOFMSW₅₅	386.44 ± 50.85	0.64 ± 0.15

Fig. 5. Optical microscope analysis of eCMS$_{50}$, eWF$_{50}$ and eOFMSW$_{55}$ samples (magnification of 50×) and their physical properties.

Corcione et al., 2019a, 2019b, 2020; Greco et al., 2019), the addition of waste strongly increases the pores' average size, negatively affecting the mechanical properties.

4. Conclusion

The experimental activity carried out in this work investigated the possibility of chemically activating waste flours or the organic fraction of the municipal solid waste (OFMSW, which contains biomolecules such as carbohydrates, proteins, lipids) to produce bioresins. The potential activation of biomolecules of the wastes was achieved through their contemporary exposure to ultraviolet radiation (UV) and ozone (O_3) for different time durations.

FTIR analyses, evidenced the formation of an epoxy ring after 5 h of UV/O_3 exposure only for neat starch, sugar, waste flour and the carbohydrate fraction of OFMSW.

From the titration tests, the epoxy content, was found to be 1.47 eq/g for eCMS, 1.36 eq/g for eDWF, and 1.15 eq/g for eOFMSW.

Dynamic rheological analysis allowed defining the optimal content of the cross-linking agent (isophoronediamine-IPDA) in a range of 35–40%. Steady-state rheological analyses allowed choosing 20 wt% as the optimal content of water in order to allow efficient processing of the blends. The curing process was indirectly monitored by DSC; it consisted of a first drying step at 60 °C for 24 h for all the blends and a second step at 150 °C for 4 h for eCMS50 and eWF50 and at 120 °C for 4 h for eOFMSW55. A high glass transition temperature (Tg) of the cured epoxy bio-resins in the range of 155–185 °C was reached, evidencing a high potentiality of the produced bio-resins to be able to substitute the commercial DGEBA epoxy resins.

The elastic modulus for eCMS and eWF bio-resins was found to be compartable to that of commercial epoxy resins, (around 2.4–2.8 GPa). OFMSW-based bio-resin showed a lower bending modulus compared to the commercial epoxy resins. Nevertheless, very low flexural strength values were found for all the resins produced. This result is attributable to the presence of voids and defects within the samples, which can be decreased by optimizing the

mixing times, by reducing the evaporation rate of the water, or by selecting an alternative green solvent with lower evaporation rate or choosing different curing procedures, which involve the use of vacuum bag or pressure.

Future works will investigate the replacement of the commercial synthetic amine, with a natural one extracted from protein-based waste bio-molecules, such as eggs, legumes, or cereals.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wasman.2020.05.004.

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