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Research article

Assessing novel thermoset materials from Brazil nut oil: Curing, thermal and mechanical properties

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Abstract. The present work describes, for the first time, the chemical modification and characterization of epoxy resins derived from Brazil nut oil (BNO). The development of a bio-based resin has been carried out by chemically modifying BNO, resulting in epoxidized Brazil nut oil (EBNO). Moreover, through a maleinization process, a crosslinker based on maleinized Brazil nut oil (MBNO) has been employed. Analysis using techniques like iodine value (IV) and oxirane oxygen content (Oo) indicate successful chemical modification. FTIR analysis confirms the presence of reactive functional groups in both EBNO and MBNO, which are responsible for resin crosslinking. Mechanical testing of the different bio-resins developed shows that, in the cured resins, flexural strength and modulus decrease with increasing MBNO content, indicating improved flexibility due to the introduction of MBNO as a crosslinker. Thermal analysis using differential scanning calorimetry (DSC) reveals exothermic peaks corresponding to resin curing appearing at progressively lower temperatures. Therefore, this study successfully modifies BNO and demonstrates its effectiveness as a precursor to develop bio-based epoxy resins. The resulting resins exhibit improved ductile and thermal properties, making them suitable for various applications requiring low mechanical stresses.

Keywords: *bio-based thermoset, epoxidized Brazil nut oil, maleinized Brazil nut oil, mechanical properties, ductility, thermal properties*

1. Introduction

Thermosetting polymers or thermosets are widely used in different engineering sectors, such as automobiles, navigation, communication, or construction, as coatings, adhesives, and polymeric matrices for composite materials [1, 2]. They account for approximately 18–20% of the total polymeric material manufactured worldwide, with an annual production of about 65 million tons [3, 4]. Thermosets are characterized by a permanently crosslinked network, which gives the material excellent chemical resistance, thermal and mechanical properties, and dimensional stability. However, this is also a major drawback for recycling due to the difficult degradation, reprocessing, and dissolution of the polymer [5]. In addition to this disadvantage, the vast majority of thermosets are derived from petroleum-based chemicals such as bisphenol A, which results in this material having a significant carbon footprint, besides possible negative health impacts [6].

In particular, epoxy resins are one of the most important commercial thermosetting polymers due to their outstanding properties for their use in the production of composite materials [7, 8]. These properties,

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which include mechanical strength, chemical resistance, adhesion, low shrinkage, electrical insulation, dimensional stability, and processability, lead to a high demand for this material, with an estimated production volume of more than 3 million tons [5, 9]. This value makes it very significant to develop eco-efficient epoxy resins. Even though compared to thermoplastics, much less research has been done on sustainable thermosets, there is a growing interest in more environmentally friendly solutions, especially focusing on their chemical perspective. Numerous studies have been conducted using precursors from renewable resources to develop bio-based thermosetting resins [10]. Examples include vegetable oils (VOs), cardanol, lignin, itaconic acid, or tannins, among others [11–17].

VOs, especially polyunsaturated oils, are among the most widely used natural raw materials in polymer synthesis, not only because of their physicochemical properties but also due to their abundance in nature, low cost, and easy extraction [18, 19]. In addition, the wide variety of VOs with different monomers, functionalities, and reactivities provide different results in the properties of the polymer obtained [1]. In this context, VOs have proven to be attractive as substitutes for petrochemical epoxy resins for specific low-load-bearing applications. They also ameliorate the brittleness issues that these materials present due to their highly crosslinked structure and sensitivity to moisture [20].

VOs mainly comprise triglycerides formed by the esterification of three fatty acids and glycerol. These fatty acids are classified according to the number of unsaturation (C=C, double bonds) they contain, and they can be saturated fatty acids (SFAs), monounsaturated fatty acids (MUFAs), and polyunsaturated fatty acids (PUFAs). These double bonds are reactive sites that can be easily modified for functionalisation with active molecules such as oxirane oxygen, maleic anhydride, hydroxyl, or acrylate [21, 22]. This functionalisation of triglycerides allows these VOs to be employed in polymer engineering in different ways: plasticisers, compatibilisers, stabilisers, and also to develop bio-based thermosetting resins [23, 24]. A standardized way of expressing the average unsaturation value is theiodine value (IV), expressed in I g I_2·(100 g)$^{-1}$ oil, meaning that the higher the amount of double bonds, the higher the IV value. Those oils that possess a high IV have more potential to be modified and, therefore, used in industrial applications. For this reason, some of the most commonly used VOs are those shown in Table 1, where their iodine content is indicated.

Table 1. IV content of different VOs.

VOs	IV [I g I_2·(100 g)$^{-1}$ oil)	References
Linseed	155–205	[25]
Soybean	124–139	[26]
Cottonseed	99–113	[25]
Rapeseed	91–108	[27]
Sunflower	110–143	[27]
Brazil nut	94–106	Current study

Brazil nut (*Bertholletia Excelsa*) oil (BNO) has an IV of 94–106 I g I_2·(100 g)$^{-1}$ oil [28], indicating a great potential for developing thermosets. This nut has an oil content of between 60–70% [29], with around 75.6% unsaturated fatty acids (UFAs) [30], including MUFAs such as palmitic, stearic, and oleic, and PUFAs such as linoleic, this one accounting for 36% [30] of the total. Despite the interesting lipid profile of BNO, there is hardly any literature related to its functionalisation for use in industrial applications.

As aforementioned, unsaturation (C=C) are reactive sites to functionalise the triglycerides for using these modified VOs (MVOs) to synthesise polymers. Especially the epoxidation process has received special attention. In this process, epoxy groups (oxirane rings) are introduced into the carbon-carbon double bonds of unsaturated fatty acids with peracids, resulting in epoxidized vegetable oils (EVOs) [31]. The reactive points, *i.e.* the oxirane rings as an end group of the triglycerides, will act as crosslinking points of the three-dimensional chain to form these thermosets. Some of the commercially available EVOs are epoxidized soybean oil (ESBO) and epoxidized linseed oil (ELO) and have been demonstrated for use in developing bio-based thermosetting epoxy resins as coating and polymer matrices [32, 33].

On the other hand, to convert the uncured epoxy resin into a hard, infusible thermosetting network with the desired properties, it is necessary to have the presence of a hardener acting as a curing agent [34]. Some of the most commonly used hardeners for epoxy-type resins are petrochemical-based, such as amines or anhydrides [35]. They are not only environmentally unfriendly but also toxic to humans. Aliphatic amines, cycloaliphatic amines, and anhydride-curing agents can be responsible for skin, eyes,

and lung problems [36]. In literature, many works have been carried out to develop bio-based thermosets from EVOs such as ESBO, ELO, or epoxidized canola oil (ECO) using these types of hardeners [37–39]. Nevertheless, fewer studies have combined both EVOs and bio-based hardeners, obtaining promising results. For instance, Stemmelen *et al*. [40] have demonstrated the feasibility of synthesising a fully biobased epoxy resin by amination of VO's, in this case using an aminated grapeseed oil (AGSO) as a hardener of ELO. Chen *et al*. [41] synthesized a high bio-content epoxy resin by developing a maleopimaric acid by grafting anhydride maleic groups onto the molecular structure of rosin to act as a curing agent for ESO. Samper *et al*. [42] also developed an epoxy resin using ELO and a mixture of a petroleum-derived crosslinking agent, methyl nadic anhydride (MNA), and a VO-based maleinized linseed oil (MLO). Following this line, Fombuena *et al*. [43] developed a composite with over 98% bio-based content, using solely derivates from linen.

Therefore, the novelty of the present work lies in the study of a novel source of VO, which is highly abundant and can aspire to replace part of the petrochemical resins used to manufacture composite materials or coatings, among many other applications. This study aims to develop and optimise a novel epoxy resin obtained from the use of BNO. On the one hand, EBNO is used as a thermosetting matrix and, on the other hand, a petroleum-derived hardener methylhexanhydrophtalic anhydride (MHHPA) is combined with maleinized Brazil nut oil (MBNO) to achieve a high bio-based content comprised between 56.3 and 75.2 as will be seen in Table 2. The ratio of MBNO and MHHPA is systematically varied to analyse the variability of the mechanical and thermal properties that can be obtained. Finally, it should be noted that the results of this work allow the study of future works of composite materials with a high content of bio-based material and low impact on the environment if compared to those obtained from petrochemical resins.

2. Materials and methods

2.1. Materials

Brazil nuts were provided by FrutoSeco S. L. for this project (Alicante, Spain). The mechanical extraction method at room temperature was used to obtain BNO with a pressing machine model DL-ZYJ05 purchased from Nanchang Dulong Industrial Corporation (Zucheng, China).

Afterwards, the BNO is chemically modified by the epoxidation process to obtain EBNO, used as an epoxy matrix. It was performed in situ using hydrogen peroxide (30% v/v) (CAS: 7722-84-1), acetic acid (99.7%) (CAS: 64-19-7), and sulfuric acid (97%) (CAS: 7664-93-9) supplied by Sigma Aldrich (Madrid, Spain).

Two different hardeners were used to crosslink EBNO. On the one hand, MBNO was used as a hardener of biological origin to increase the bio-based content of thermosets. The maleinization of BNO was performed by adding maleic anhydride (MA) of >98% purity (CAS: 33225-51-3), supplied by Sigma Aldrich (Madrid, Spain). On the other hand, MHHPA (CAS: 25550-51-0), which has an anhydride equivalent weight (AEW) of 168.19 $g \cdot eq^{-1}$ and was provided by Sigma Aldrich (Madrid, Spain), was used as a petrochemical crosslinker.

Besides, glycerol (CAS: 56-81-5) was used as an initiator and 1-methylimidazole (CAS: 616-47-7) as an accelerator, both supplied by Sigma Aldrich (Madrid, Spain).

All chemical structures of all the components used (epoxy resin (EBNO), crosslinkers (MBNO and MHHPA), initiator (glycerol), and accelerator (1-methylimidazole)) are shown in Figure 1.

2.2. Chemical modifications of BNO

To conduct the epoxidation reaction of BNO to obtain the bio-based epoxy matrix, the method described by Dominguez-Candela *et al*. [44] was followed. The BNO was introduced into a three-neck round-bottomed flask immersed in a thermostatic water bath at a constant internal flask temperature of 60 °C. After the oil reached this temperature, glacial acetic acid was introduced at a stirring speed of 220 rpm. After 10 min, sulfuric acid and hydrogen peroxide were mixed and added dropwise for approximately 30 min. Then, the reaction was carried out for 8 h, cooled at room temperature, and cleaned by decantation and centrifugation.

On the other hand, to carry out the maleinization of BNO to obtain a bio-hardener, the process described in previous works [45] was used. The maleinization was conducted with a molar ratio of 2.4:1 of maleic anhydride to virgin oil, also in a three-neck round-bottomed flask stirred at a constant speed of 300 rpm.

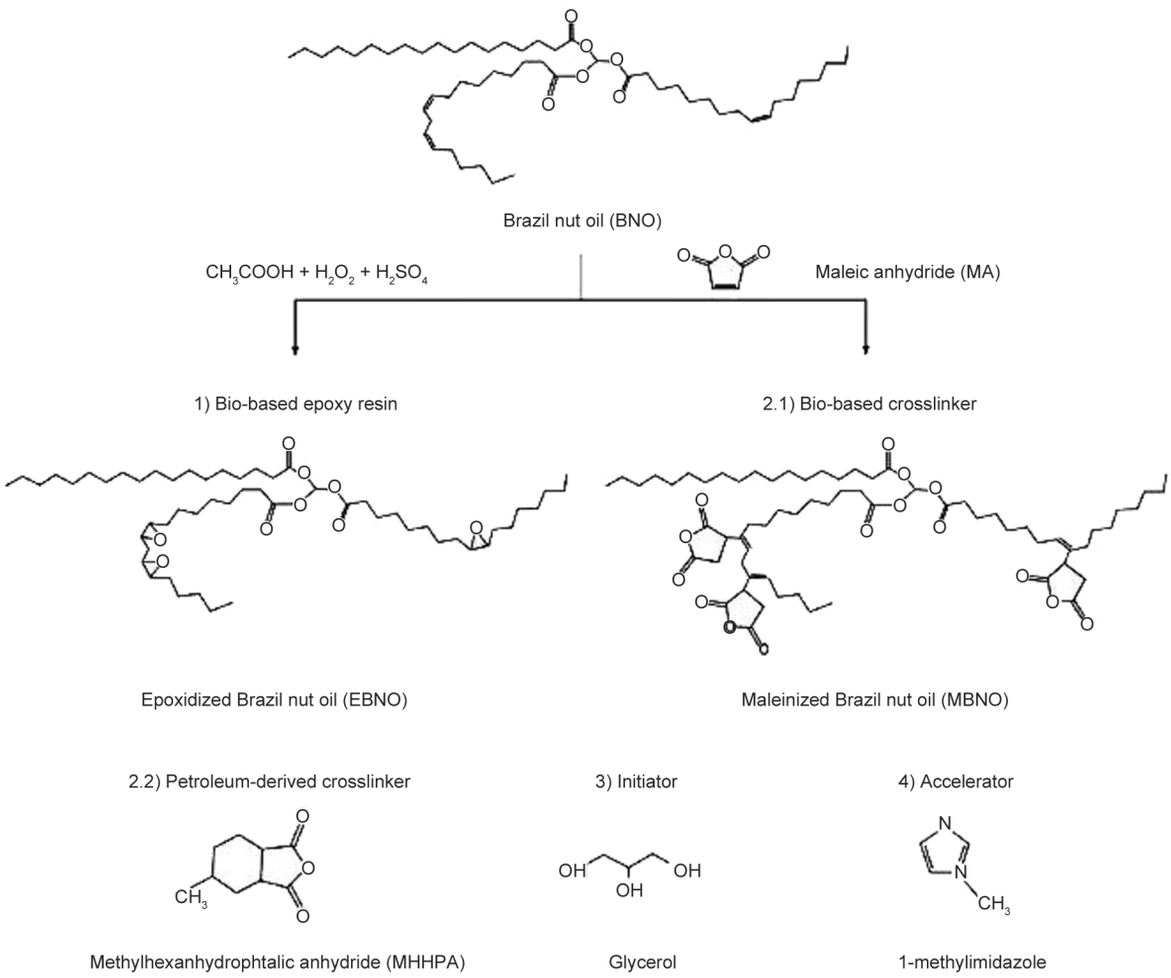

Figure 1. Chemical structures of the components used to obtain the bio-based epoxy resin.

Three temperature steps, 180, 200, and 220 °C, were used, split over the 3 h of reaction.

2.3. Characterization of chemically modified EBNO and MBNO

The Oo of EBNO was determined. This value allows for assessing the number of oxirane oxygen groups in the fatty acids due to their substitution by the double bonds through the epoxidation of the oil. For this purpose, the process described in ASTM D1652 was followed. According to this standard, a sample must be dissolved in chlorobenzene, followed by the addition of crystal violet drops and titration with a solution of hydrobromic acid (HBr) in glacial acetic acid. By using the Equation (1), the Oo content is calculated:

$$\mathrm{Oo}\,[\mathrm{wt}\%] = 1.6 \cdot N \cdot \frac{V-B}{W} \tag{1}$$

where V is the volume of HBr solution used for titration sample [ml], B is the volume of HBr solution used for blank titration [ml], and W refers to the sample mass of oil used [g].

The epoxy equivalent weight (EEW) expressed in grams of epoxy resin containing one equivalent of the epoxy group [g·eq^{-1}] is one of the most relevant parameters to characterize epoxy resins. It is related to the crosslinking density and allows the calculation of the required amount of crosslinking agent for the curing process. It was also determined following ASTM D 1652 by titration using the Equation (2):

$$\mathrm{EEW}\left[\mathrm{g}\cdot\mathrm{eq}^{-1}\right] = \frac{1000 \cdot W}{(V-B)\cdot N} \tag{2}$$

where N is the equivalent concentration of HBr to glacial acetic acid. At least five measurements are made for each sample, and the average value is given.

On the other hand, IV refers to the mass of iodine absorbed by 100 g of oil. It is an index used to assess the amount of double bonds available in fatty acid chains. Therefore, when epoxidation occurs, this value decreases. The IV was determined with a Wijs

solution that reacted with the double bonds and by titration process using sodium thiosulfate solution following the guidelines of ISO 3961. The value was calculated using the Equation (3):

$$IV = \frac{12.69 \cdot c \cdot (V_1 - V_2)}{m} \quad (3)$$

where IV refers to the iodine value in g $I_2 \cdot (100\ g)^{-1}$ oil, c is the normality of sodium thiosulfate solution, V_1 is the volume of thiosulphate sodium needed for titration of the blank [ml], V_2 is the volume of sodium thiosulphate used for titration [ml], and m is the mass of the oil sample [g].

The acid value (AV) is a parameter that allows to assess the degree of maleinization of the MBNO. As the maleinization takes place, the value of AV increases since the molecules of anhydride maleic are added to the double bonds. It was obtained according to ISO 660 by titration of a sample of the oil dissolved in ethanol using a potassium hydroxide solution. Then, the AV is calculated with Equation (4):

$$AV = \frac{56.1 \cdot V \cdot C}{m} \quad (4)$$

where C refers to the concentration of the potassium hydroxide solution [$mol \cdot l^{-1}$], V to the potassium hydroxide volume used for the sample titration [ml], and m to the mass of oil used for the titration [g].

2.4. Samples preparation

Several epoxy resin formulations were developed to evaluate the highest percentage of bio-based resins that can be obtained with good performance. For this purpose, the amounts of EBNO, glycerol, and 1-methyl imidazole have been kept constant in the way that glycerol was incorporated at 0.8 wt% and 1-methylimidazole at 2.0 wt% concerning the mass of the epoxy component, as recommended in the literature [46]. The molar ratio of the hardeners, MBNO and MHHPA, has been modified to replace MHHPA with the bio-based hardener as much as possible. All the formulations are prepared using a ratio EEW:AEW of 1:1.5 since this relationship seems appropriate to achieve a good curing degree of EBNO. This ratio depends on the epoxy groups contained in the EVO that will allow its crosslinking with the hardener [47]. The different formulations are gathered in Table 2.

The formulations were carried out manually, stirring all the components vigorously at room temperature in aluminum containers, ensuring a homogeneous mix. After, the mixtures are poured into a silicone mold with dimensions of 80×10×4 mm to obtain samples for standard tests, according to ISO 178 and ISO 179. The mold is placed into an air oven model Conterm 80L from J. P Selecta (Barcelona, Spain) to perform the curing. The curing cycle was carried out at 90 °C for 3 h and post-curing at 120 °C for 2 extra hours. The appearance of the cured samples is shown in Figure 2.

Figure 3 shows a schematic approach to the process of proposed polymerisation through the interaction of EBNO and MHHPA (Figure 3a) and EBNO, MBNO and MHHPA (Figure 3b). In it, the black dots refer to the reactive oxirane groups in EBNO, red dots represent the maleic groups anchorage in the structure of MBNO, and green dots represent the chemical structure of the MHHPA. Figure 3a shows the reaction using only MHHPA as the crosslinker for the EBNO epoxy resin. It shows how the structure

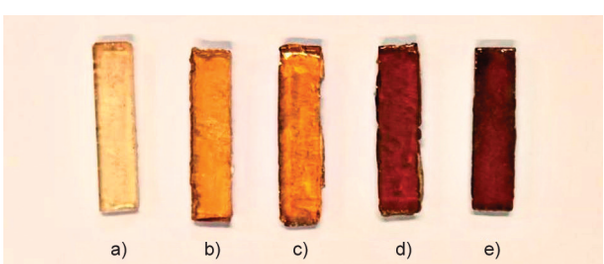

Figure 2. Cured samples a) MHHPA100, b) MHHPA90:MBNO10, c) MHHPA80:MBNO20, d) MHHPA70:MBNO30, e) MHHPA60:MBNO40.

Table 2. Composition of different samples of epoxy resin based on EBNO.

Sample	MHHPA [%]	MBNO [%]	Glycerol [wt%]	1-methylimidazol [wt%]	Bio-based content [%]
MHHPA100	100	0	0.8	2	56.3
MHHPA90:MBNO10	90	10	0.8	2	61.4
MHHPA80:MBNO20	80	20	0.8	2	66.2
MHHPA70:MBNO30	70	30	0.8	2	70.8
MHHPA60:MBNO40	60	40	0.8	2	75.2

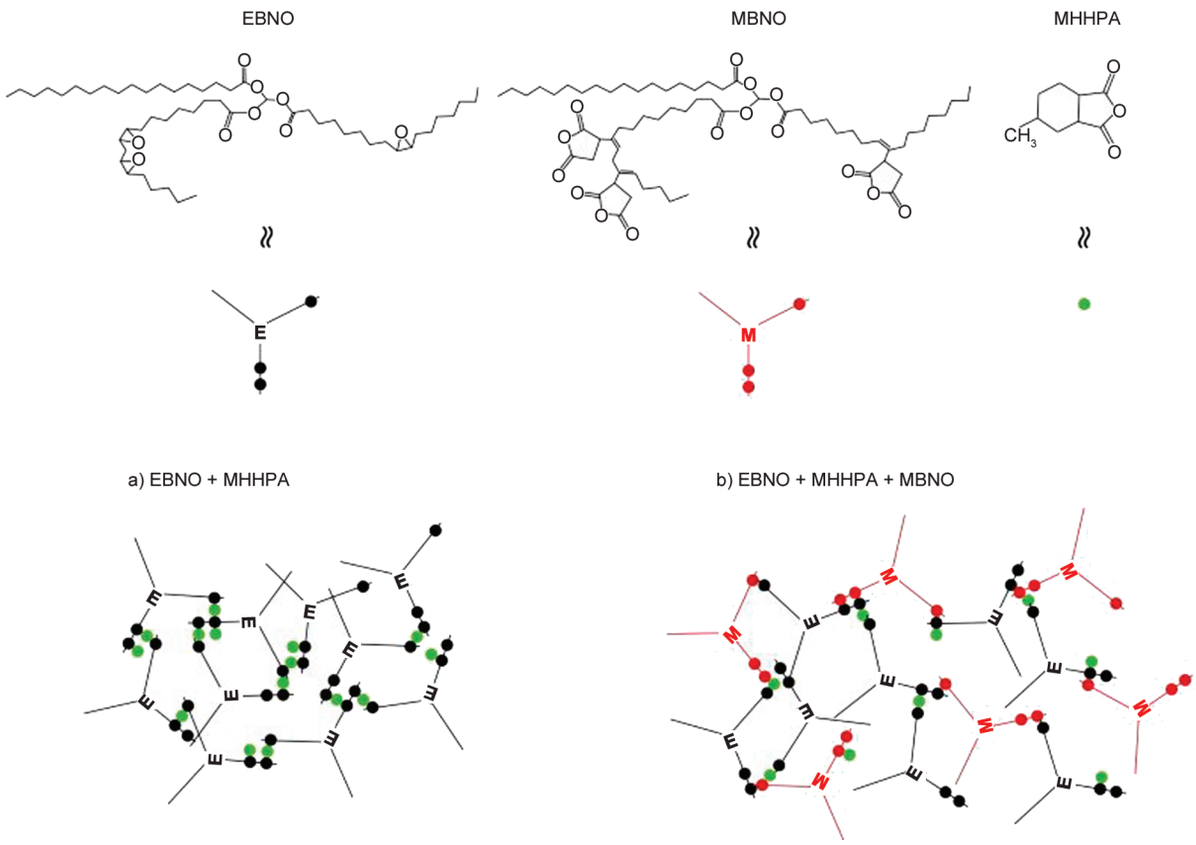

Figure 3. Schematic representation of polymerization effect of EBNO with MHHPA (a) and MHHPA:MBNO mixture (b).

resulting from this reaction is more compact and clustered due to the lower length, viscosity, and molecular weight of the petrochemical hardener, MHHPA. However, as shown in Figure 3b, when MBNO is added, the free volume between molecular chains increases, contributing to better mobility and, thus, flexibility of the final thermoset resin [48].

2.5. Fourier transform infrared spectroscopy (FTIR)

FTIR was performed using a Bruker Vector 22 spectrometer from Bruker Española, S. A. (Madrid, Spain) to analyse the chemical structure of BNO, EBNO, and MBNO, as well as that of the cured samples. The wavelength range employed was 4000–400 cm^{-1}, with a spectral resolution of 4 cm^{-1} and performing an average of 20 scans. All the FTIR spectra obtained were normalized with a limit ordinate of 1 absorbance unit by using the Perkin-Elmer Software Spectrum.

2.6. Mechanical characterization

Flexure, impact, and hardness tests of the different solid samples were conducted to analyse their mechanical properties. The flexural test was carried out using an Ibertest ELIB 30 universal testing machine from S.A.E. Ibertest (Madrid, Spain) at room temperature and a crosshead speed of 5 $mm \cdot min^{-1}$ using a load cell of 5 kN, according to ISO 178. The impact test was conducted using a 6 J Charpy pendulum from Metrotec S.A (San Sebastian, Spain), following the guidelines of ISO 179. For both tests, flexural and impact, the samples tested had the mentioned dimensions, 80×10×4 mm, according to their respective standards. Lastly, the hardness test was performed (15 tests per sample) using a Shore D durometer 673-D from J. Bot S.A. (Barcelona, Spain), according to ISO 868. The reported results are obtained by averaging the test over a minimum of 5 samples. The Dixon Q test was applied to the mechanical characterization values in order to provide more reliable values.

2.7. Thermal characterization

Differential scanning calorimetry (DSC) was carried out to analyse the curing process and the post-cured samples of the different combinations of novel epoxy bio-resins. The DSC test was performed on a Mettler Toledo DSC 821 (Schwerzenbach, Switzerland). The test conditions were under a nitrogen atmosphere with a flow rate of 66 $ml \cdot mm^{-1}$, with a thermal program consisting of a temperature ramp of 30–340 °C at a

heating rate of 10 °C·min^{-1}. From the calorimetric curves resulting from the test, the values of the initial temperature, the maximum crosslinking temperature (peak), and the final temperature of the process are obtained. Likewise, from the integration of the area of the exothermic peak of each sample, the normalized enthalpy values are determined in J·g^{-1}. The normalized enthalpy of the exothermic peak was obtained using Mettler Toledo's STARe Evaluation software, explicitly using the 'integration' function and selecting an equal temperature range for all samples. In addition, to determine the T_g of the cured samples, three analyses (temperature ramp of 30–340 °C at a heating rate of 10 °C·min^{-1}) per sample were performed, and the mean value was chosen.

Thermogravimetric analysis (TGA) was carried out to analyse the thermal stability with model TGA PT1000 from Linseis Inc. (Selb, Germany). The analysed samples have a weight between 20–25 mg, with the temperature program from 30 to 700 °C with a speed of 10 °C·min^{-1} and with a constant nitrogen flow of 30 ml·min^{-1}. Three analyses were performed for each sample to try to provide average values.

2.8. Morphological characterization

The morphologies of the cross-sectional areas of the fractured samples collected from the impact test were evaluated. For this, a field emission scanning electron microscopy (FESEM) model Zeiss Ultra 55 from Oxford Instruments (Oxfordshire, UK), was used. The samples were previously coated with a thin layer of gold-palladium alloy under vacuum conditions employing an EM MED020 sputter coater from Leica Microsystems (Wetzlar, Germany). The surfaces were observed applying an acceleration voltage to an electron beam of 2 kV.

3. Results

3.1. Chemical characteristics of the oils

Concerning the values obtained with the characterization of BNO, EBNO, and MBNO by the different titration methods, all of them have demonstrated that the chemical modifications of the oil have occurred. Starting with IV, BNO was found to have a value of 102.4 g I_2·(100 g)$^{-1}$. This high unsaturation value is related to the fatty acid composition of BNO, which is rich in MUFA and PUFA. The most representative fatty acids determined by gas chromatography were briefly: MUFA, consisting mainly of oleic acid (34.56%) and PUFA, highlighting linoleic acid (37%), which has the highest number of double bonds with two double bonds for each fatty acid [30]. These results show the high availability of double bonds that can react during the epoxidation or maleinization of the oil and be replaced by oxirane oxygen or maleic anhydride molecules. This value of IV decreases in the case of EBNO to 11.6 g I_2·(100 g)$^{-1}$, which indicates that the epoxidation process took place. This success in the modification of the oil is also corroborated by the values of EEW and Oo, which indicates that this decrease in the amount of the double bonds is due to their substitution with the epoxy groups. The value of EEW is 365 g·eq^{-1}, and the Oo value was 4.22%, representing a conversion of 69%, determined from the theoretical Oo value of 6.11%, calculated from the average of its fatty acids. These values are similar to the ones reported by Kim and Sharma [49], who obtained the IV and the Oo of several EVOs such as linseed (IV 31.02 g I_2·(100 g)$^{-1}$ and Oo 8.91%), soybean (IV 17.11 g I_2·(100 g)$^{-1}$ and Oo 6.65%) or radish (IV 20.30 g I_2·(100 g)$^{-1}$ and Oo 4.89%). Regarding the maleinization, MBNO also shows a decrease in the availability of the double bonds. The IV was found to be 49.3 g I_2·(100 g)$^{-1}$. Moreover, the AV increased from 0.20 mg KOH g^{-1} of BNO to 130 mg KOH g^{-1} with the MBNO, indicating that the maleinization process occurred. This value is in line with the one reported by Ferri *et al*. [50] who indicates a value from 105 to 130 mg KOH g^{-1} for a commercial MLO.

3.2. Functional group analysis of raw materials and cured samples

To verify the chemical modification performed on the BNO, Figure 4 presents FTIR spectra of the BNO, the EBNO, and the MBNO. On the one hand, the spectrum of BNO was characterized by the appearance of the band at 3006 cm^{-1} assigned to the C–H stretching vibration of the cis-double bond (=CH). Also, in the fingerprint region, two peaks appear at 1170 and 1236 cm^{-1} related to the stretching vibration of the C–O ester groups. At 1748 cm^{-1}, in the double bond's stretching region, appears an ester carbonyl functional group of the triglycerides [51]. On the other hand, the spectrum of EBNO was characterized by the epoxy group's appearance at the band 824 cm^{-1} and the disappearance of the carbon-carbon double bond absorption band at 3006 cm^{-1}, indicating that the epoxidation reaction took place. In addition, a broad band was observed at 3300–3600 cm^{-1} that

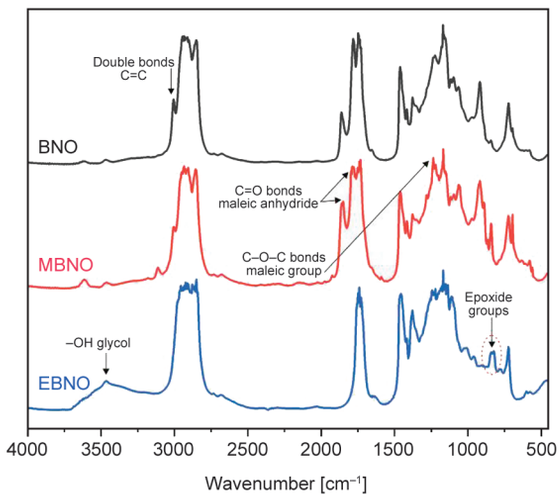

Figure 4. FTIR spectra of BNO, EBNO, and MBNO.

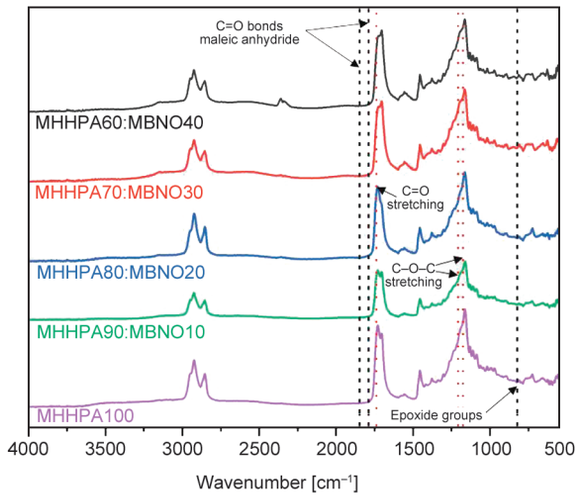

Figure 5. FTIR of cured samples based on EBNO crosslinked with different MHHPA:MBNO mixtures.

could be associated with the glycol's production in the epoxidation process, as shown in other studies [52]. This is because other reactions, such as hydrolysis, can occur, leading to the opening of the oxirane ring and, therefore, to the formation of other subproducts. Epoxides can be attacked by water (acid-catalysed), acetic acid, and peracetic acid [53].

About the FTIR spectrum of the bio-based crosslinker MBNO, the characteriztic bands of the maleic group of MBNO can be observed, especially highlighting the increase in the intensity of the peaks at 1850 and 1788 cm^{-1} corresponding to the symmetric and asymmetric stretching of the C=O bond of the maleic anhydride. Additionally, at 1250 and 1170 cm^{-1}, the symmetric and asymmetric stretching of the C–O–C bonds of the maleic groups are observed [54]. Therefore, from the FTIR spectrum of MBNO, it can be confirmed that the maleic anhydride has been anchorage to the triglyceride structure of the BNO and, as a consequence, it was modified, providing a more reactive oil to be used as a crosslinker.

After analysing the starting materials, the crosslinking reaction was monitored by FTIR to verify the formation of chemical bonds between EBNO and the different crosslinker mixtures (MHHPA:MBNO) in the cured samples. Figure 5 shows the FTIR spectra of all resins developed, highlighting the main characteriztic peaks. As previously discussed in the FTIR of raw materials, the characteristic peaks of the functional groups are located mainly at 1850 and 1788 cm^{-1}, corresponding to the anhydride groups in the MHHPA or MBNO structure, and at 824 cm^{-1} for the epoxy group in the EBNO structure. These peaks, highlighted with vertical black dashed lines, disappeared in all samples due to the opening of the epoxy ring and anhydride groups as a consequence of the crosslinking reaction. In the FTIR spectra of the different resins cured, the main groups evidencing the chemical bonds formed. It is important to highlight the group related to the carbonyl C=O stretching at 1730 cm^{-1} and the C–O–C stretching at 1184 and 1162 cm^{-1}, which were highlighted with vertical red dotted lines in the FTIR spectra. Therefore, the disappearance or decrease of the main reactive groups in epoxidized and maleinized oils and the change in the intensity of new groups related to the chemical interaction of the compounds provide evidence of the observed crosslinking at the macroscopic level through the hardening of the new bio-resins.

3.3. Mechanical properties

After characterizing the crosslinking of the resins using FTIR, Table 3 and Figure 6 show a summary of the macroscopic behavior through the flexural properties. As it can be clearly seen, as the MBNO content increases, both the flexural strength and modulus decrease, thus indicating the flexibilisation effect provided by the introduction of the MBNO. The EBNO system cured with a petrochemical anhydride shows a flexural strength of 11.3 MPa and a flexural modulus of about 210 MPa. As can be seen, when 10 wt% MHHPA is replaced by MBNO, MHHPA90:MBNO10, the flexural strength decreases to 6.1 MPa while the flexural modulus goes down to 95.4 MPa. At first, the decrease in both flexural strength and modulus follows a linear tendency, although, from the MHHPA70:MBNO30 mixture

Table 3. Influence of cured samples based on EBNO crosslinked with different MHHPA:MBNO mixtures in terms of flexural strength and flexural modulus.

Samples	Flexural strength [MPa]	Flexural modulus [MPa]
MHHPA100	11.3±0.5	210.1±10.2
MHHPA90:MBNO10	6.1±0.5	95.4±7.9
MHHPA80:MBNO20	2.3±0.1	14.1±0.1
MHHPA70:MBNO30	0.9±0.1	6.7±0.7
MHHPA60:MBNO40	0.9±0.1	5.6±0.6

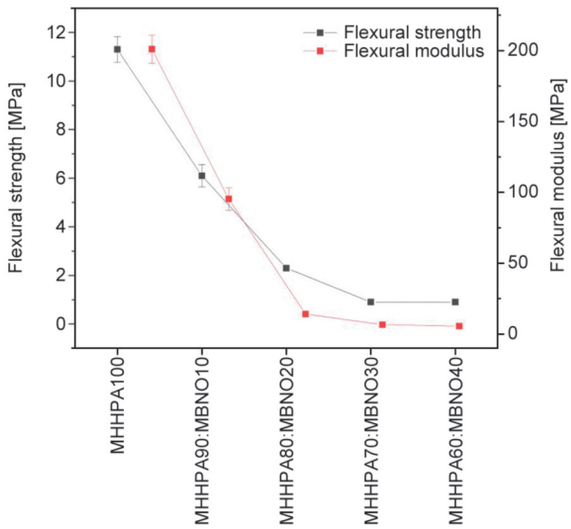

Figure 6. Influence of cured samples based on EBNO crosslinked with different MHHPA:MBNO mixtures in terms of flexural strength and flexural modulus.

onwards, flexibility is high that both flexural strength and modulus strength show values close to zero, as can be seen in Figure 6. Dominguez-Candela *et al*. [55] showed values of 57.0 and 765.0 MPa for flexural strength and modulus, respectively, using an epoxidized chia oil (ECO) cured with methyl nadic norbornene anhydride (MNA). These differences with the present study can be ascribed to different amounts of linkage points of epoxy resins used. While EBNO has an EEW of 365 g·eq^{-1}, ECO has an EEW of 219 g·eq^{-1}, which justifies that some mechanical parameters, such as flexural modulus, are practically three times higher. MBNO, therefore, serves as an efficient crosslinker to replace current petrochemical hardeners. However, due to its high molecular weight formed by the long chains of triglycerides, it imparts excellent ductile properties to the resulting resins, making it suitable for applications subjected to low mechanical stress. It should be noted that the mechanical properties of the samples are strictly related to the chemical structure of the crosslinker, as observed. While MNA or MHHPA provides a very compact and semi-rigid crosslinking unit, functionalized long fatty acid chains lead to an increase in free volume and, thus, to an increase in chain mobility, which contributes to improved flexibility of the thermosetting resins. Other studies showed similar properties to the present work. Lerma-Canto *et al*. [56] showed similar results in their work employing an epoxidized hemp oil (EHO) crosslinked with an MNA and maleinized hemp oil (MHO) mixtures. They recorded a flexural modulus of 300 MPa and a flexural strength lower than 7 MPa for the samples crosslinked using lonely MNA. Furthermore, as the crosslinker MHO content increased in the mixture of MNA/MHO, the modulus decreased constantly up to the samples crosslinked with the MNA50/MHO50 mixture, in this case, the modulus being around 60 MPa and the flexural strength around 6 MPa. At higher contents, the flexural modulus remained constant at around 7 MPa.

As for the mechanical characterization of the bioresins developed, Table 4 shows the results obtained for the Impact-absorbed energy and Shore D hardness of the cured samples. Following the same trend observed previously in the flexural assay, the hardness decreases linearly as the MBNO content in the samples increases. In this case, the maximum hardness is obtained for the sample crosslinked with MHHPA100, with a value of 57 Shore D. This value is very similar to that achieved by Samper *et al*. [57] when crosslinking of ELO with phthalic anhydride (PA) and maleic anhydride (MA), obtaining a value of 66 Shore D. The lowest hardness value obtained, 21.2 in the sample MHHPA60:MBNO40, once again provides an idea of the elevated ductile properties achieved using MBNO as a crosslinker.

The results of impact-absorbed energy determined by the Charpy impact test demonstrate how the resin developed solely with the petrochemical hardener has a toughness of 1.4 kJ·m^{-2}. This reduced value results from the stiffness provided by the petrochemical hardener due to its low viscosity, molecular weight, and high reactivity. In the case of sample MHHPA100, it is observed that the value obtained is 1.4 kJ·m^{-2}. When the content of MBNO increases up to 30%, MHHPA70:MBNO30, its value increases, reaching 6.5 kJ·m^{-2}. As a result of the increased ductility, the sample developed with a 40% content of

Table 4. Influence of cured samples based on EBNO crosslinked with different MHHPA:MBNO mixtures in terms of impact-absorbed energy and Shore D hardness.

Samples	Impact-absorbed energy [kJ·m^{-2}]	Shore D hardness
MHHPA100	1.4±0.2	56.9±5.0
MHHPA90:MBNO10	2.5±0.2	54.1±5.1
MHHPA80:MBNO20	4.7±0.6	35.9±3.2
MHHPA70:MBNO30	6.5±0.3	27.8±2.7
MHHPA60:MBNO40	Did not break	21.2±2.1

maleinized oil-based hardener did not break after being subjected to the impact of the pendulum in the test, demonstrating its ductility and flexibility. Therefore, this increase in flexibility and ductility can be beneficial in preventing impact fractures and rapid crack propagations typically associated with three-dimensional networks of high density, which are characteristic of thermoset resins [58]. Samper *et al.* [57] studied ELO and ESO mixtures cured with a crosslinker mixture based on PA and MA and obtained similar impact energy absorption values. Specifically, for the 100% ELO with PA/MA, the energy absorption was 4.2 kJ·m^{-2}, lower than that of the present work.

3.4. Thermal properties

The exothermicity characteriztic of the curing process of thermoset resins has been evaluated using DSC. As can be observed in Figure 7, the calorimetric curves are characterized by an exothermic peak, which provides information about the reaction between the EBNO-based epoxy resin and the MBNO and MHHPA hardeners. The main parameters obtained from each curve are summarized in Table 5. The onset and the end represent the start and end of the crosslinking reaction, while the peak of the exothermic curve represents the temperature at which the maximum crosslinking rate occurs. Furthermore, the area under each curve is representative of the normalized enthalpy of cure for the samples, measured in

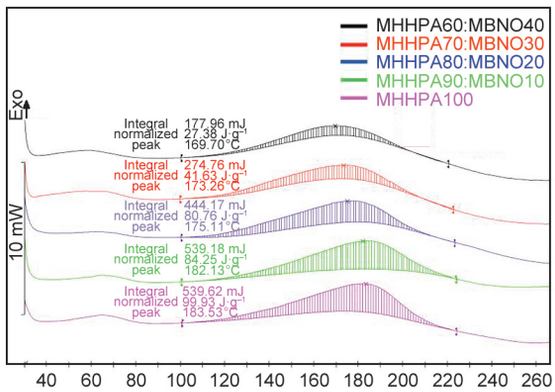

Figure 7. Plot comparison of the dynamic DSC thermograms of the curing process of EBNO crosslinked with a mixture of MHHPA and MBNO.

J·g^{-1}. As can be seen in Table 5, the crosslinking process starts at about 101–109 °C and ends between 203–224 °C, depending on the mixture of hardeners used. It is possible to observe in Figure 7 that as the ratio of MBNO increases, the curves tend to shift towards lower temperatures. This results in a lower peak temperature. It moves from 183.5 °C for the EBNO system crosslinked with MHHPA100 to values of 169.7 °C for the system crosslinked with a MHHPA60:MBNO40 mixture. This decrease in peak temperature can have a positive effect at an industrial level, as it requires lower temperatures and, therefore, lower energy costs for the crosslinking of the resins. The same trend is observed for the normalized enthalpy, which is maximum for the sample crosslinked with MHHPA100 with a value of 99.9 J·g^{-1}. As the MBNO content in the crosslinker mixture increases, the maximum enthalpy decreases, indicating that MBNO leads to lower exothermicity. Hence, the EBNO resin cured with the MHHPA90:MBNO10 mixture shows a slight decrease in the enthalpy value (84.3 J·g^{-1}), while the system crosslinked with the MHHPA60:MBNO40 mixture reaches minimum values of 27.4 J·g^{-1}. The lower exothermicity provided by the presence of MBNO is directly related to the chemical structure

Table 5. Main parameters obtained by DSC of EBNO crosslinked with different MHHPA:MBNO mixtures.

Samples	Onset [°C]	Peak temperature [°C]	Endset [°C]	Enthalpy [J·g^{-1}]
MHHPA100	109.0	183.5	223.4	99.9
MHHPA90:MBNO10	106.8	182.1	223.6	84.3
MHHPA80:MBNO20	103.4	175.1	213.4	80.8
MHHPA70:MBNO30	102.7	173.3	207.2	41.6
MHHPA60:MBNO40	101.8	169.7	203.6	27.4

of MBNO, and can result in resins with higher ductile properties, as demonstrated in the previous section of mechanical characterisation.

Once the materials were cured, the T_g amount of MBNO in the MHHPA:MBNO mixtures increases. The sample with the highest T_g is MHHPA100 with a value of 55.1 °C. On the other hand, a significant decrease in T_g is observed with the addition of MBNO, with the lowest T_g value being obtained for the MHHPA60:MBNO40 sample with a value of 46.2 °C. This decrease in T_g after adding MBNO results in materials with higher ductility. If we compare these values with those obtained by Boonlert-uthai *et al*. [59] when curing a conventional resin from diglycidyl ether of bisphenol A (DGEBA), which is 140.2 °C (Table 6), it can then be observed that the thermoset materials fabricated in this work are significantly more ductile.

Furthermore, the thermal stability of the cured materials was measured. In general, it is observed that the maximum degradation rate (T_{max}) appears at a higher temperature, which corroborates a greater degree of crosslinking. Specifically, the T_{max} values range between 334–360 °C, with the lowest thermal stability for materials cured with the 60MHHPA:40MBNO mixture and the highest stability for those cured with 100MHHPA (Table 6).

3.5. Morphological properties

The analysis using FESEM can complement the mechanical study conducted through flexural, hardness, and Charpy impact tests. The FESEM analysis of the fracture surface details the deformation patterns and helps identify whether the fracture is brittle or ductile. In this case, the FESEM analysis provides valuable insights into the microstructural characteristics and failure mechanisms of the materials, enhancing the understanding of their mechanical behavior and response. In our particular case, as it is possible to observe in Figure 8a the EBNO system crosslinked with a MHHPA shows a smooth and homogeneous surface, typical of brittle polymers. Adding only 10% of MBNO does not influence the fracture surface, as its impact-absorbed energy is only 2.5 kJ·m^{-2}, as shown in Figure 8b. The effects of MBNO incorporation on fractured surfaces are visible from the MHHPA/MBNO (80/20) mixture, as can be seen in Figure 8c where several crack fronts are observed, which are directly related to the increase in flexibility. As MBNO increases in the MHHPA/MBNO crosslinked mixtures, the number of crack fronts increases in both size and number, indicating increased ductility (Figure 8d). The sample made with 40% of MBNO is not analysed using FESEM as it does not break during the impact tests. These results are in agreement with the mechanical results indicating the role of MBNO in increasing ductility. Several studies where the maleinized oil content in the sample is increased show the same morphological aspects and, therefore, the same effect on mechanical properties, namely higher ductility [42, 55, 56].

4. Conclusions

For the first time, an EBNO has been used to develop a bio-based thermosetting epoxy resin. To minimise petrochemical components, MBNO has been developed as a curing agent, achieving over 75% bio-content. The modification of BNO to EBNO has been optimcharacteriz, resulting in a reduction of the IV from 102 to 11.6 g I_2·(100 g)$^{-1}$, resulting in an Oo of 4.22%, similar to some commercially available EVOs. Analysis by FTIR has confirmed these two modifications made to BNO, with characteristic peaks of MBNO (1850 and 1250 cm^{-1} corresponding to the C=O and C–O–C from maleic bonds primarily) and EBNO (824 cm^{-1} corresponding to the epoxy group). FTIR analysis of the cured samples shows how these bonds tend to disappear because of the crosslinking of the resin's three-dimensional network. At the macroscopic level, the bio-based resin

Table 6. Main thermal parameters obtained by DSC and TGA of cured samples.

Samples	DSC results	TGA results		
	T_g [°C]	T_5 [°C]	T_{max} [°C]	T_{90} [°C]
DGEBA	140.2	–	–	–
MHHPA100	55.1	227.3	360.0	440.1
MHHPA90:MBNO10	52.6	224.7	349.8	422.1
MHHPA80:MBNO20	51.3	227.1	345.1	439.6
MHHPA70:MBNO30	48.8	225.3	341.5	429.5
MHHPA60:MBNO40	46.2	220.9	334.0	433.3

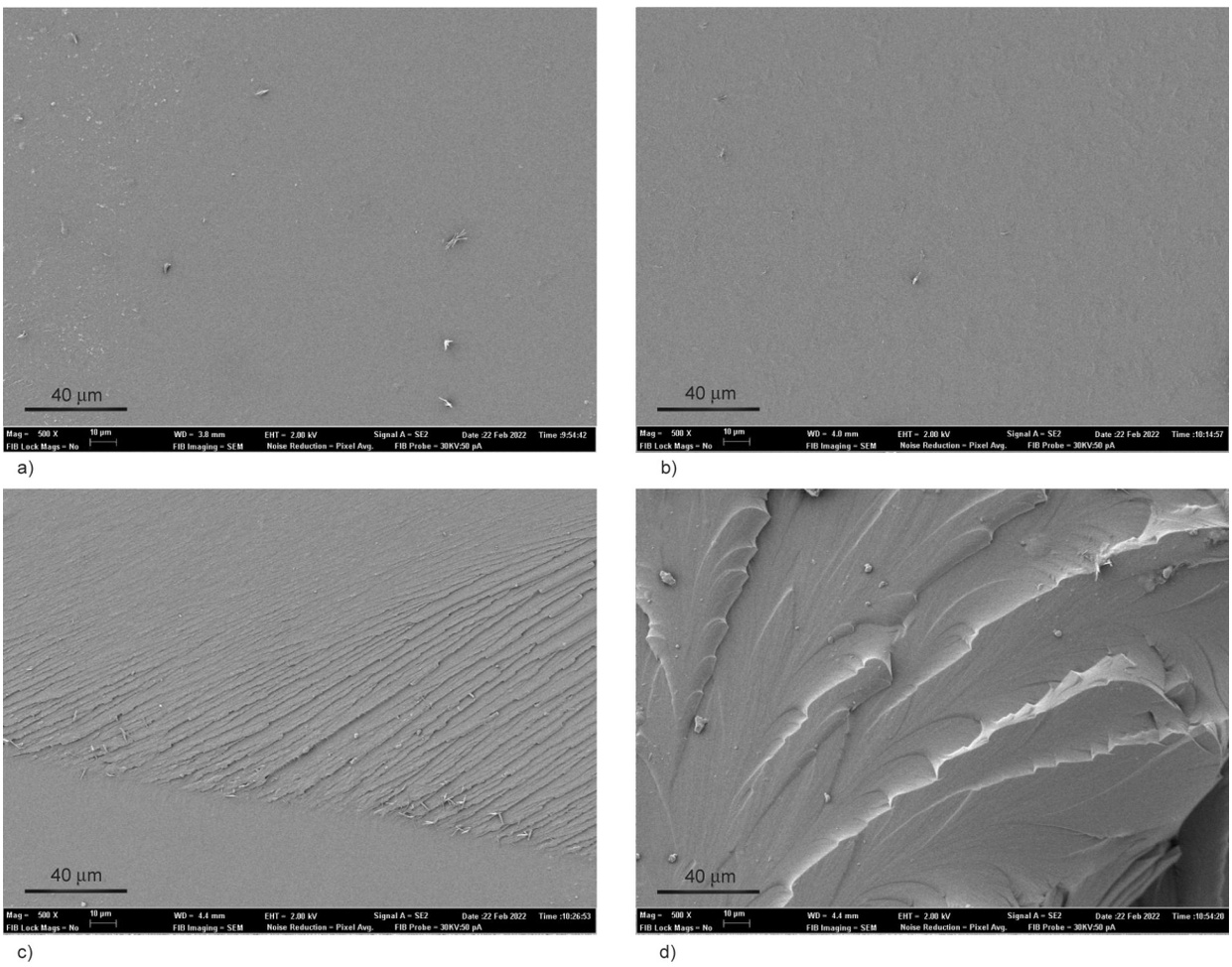

Figure 8. Field emission scanning electron microscopy (FESEM) images corresponding to fractured samples of crosslinked EBNO with a mixture of MHHPA:MBNO, a) MHHPA100, b) MHHPA90:MBNO10, c) MHHPA80:MBNO20 and d) MHHPA70:MBNO30.

developed using MBNO as a crosslinker results in a ductile and flexible resin, as evidenced by a decrease in its flexural strength from 210 to 5.6 MPa and an increase in its toughness from 1.4 to 6.5 kJ·m^2 for a sample with 30% MBNO. Additionally, at the thermal level, the addition of this new bio-based crosslinker leads to lower peak temperatures, with a reduction of 15 °C compared to the use of petrochemical hardeners, which can result in lower energy costs during the crosslinking process. FESEM images corroborate the ductile properties of the developed resins. Finally, based on the obtained results, it can be concluded that a bio-based thermosetting resin has been developed using EBNO as matrix and MBNO as crosslinker, achieving over 75% bio-based resin. This resin, with high ductile properties, minimises the risk of impact breakage and rapid crack propagation, making it a promising thermosetting material for applications where mechanical stress is low or even for coatings. In future works, the intention is to study the incorporation of natural reinforcements (natural fibers) into the optimal resin-crosslinker formulation to achieve composite materials with higher stiffness and sustainability.

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