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ENR/PCL Polymer biocomposites from renewable resources



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ABSTRACT

Polymers made of renewable raw materials are attracting increasing interest because of diminishing oil deposits and the pro-ecological character of such polymers. The aim of our study was to create composites of polycaprolactone (PLC) and epoxidised natural rubber (ENR) using innovative natural additives. The cross-linking of composites was performed with the use of amino acids, flavonoids and fatty acids to eliminate sulphur and peroxides that are not environmentally friendly. Some of the cross-linkers used fulfilled the role of antioxidants. Based on WAXD, SEM and DSC examinations, we found good miscibility and compatibility of the polymers. All the innovative compounds used appeared to be good cross-linkers. The best ENR/PCL composite cross-linking effect was obtained with the use of quercetin, a flavonoid that also appeared to be a good anti-ageing substance. The mechanical properties of the composites were satisfactory. Their tensile strength ranged from 10 to 22 MPa at elongation in the range of 292–436%. The ENR/PCL composites were more thermally stable than ENR vulcanisates due to their improved resistance to oxidation. Undoubtedly, these composites exhibit the features of innovative pro-ecological products. They meet current ecological requirements and can be widely used in medicine as well as in materials for common use, such as food packaging.

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1. Introduction

Polymeric materials have been used in almost every branch of industry worldwide. Most of them constitute the so-called “petropolymers”, which are obtained from crude oil. However, information in the literature sounds a warning that the global sources of crude oil are being depleted. Thus, it seems advisable to search for polymeric materials made from renewable raw materials belonging to the group of green polymers [1–8].

Concerns for environmental protection and the development of sustainable technologies have spurred achievements in the field of green technology using the engineering sciences to develop composite materials. This trend mainly concerns biocomposites, i.e., materials obtained from the combination of green polymers and other bio- or synthetic polymers. The global development

of new materials made from renewable sources and by modification of existing polymers is growing and is predicted to continue to do so. The advantage of biopolymers is the possibility of chemical, physical or even biological modifications that may lead to improvements in their properties, including their reactivity and functionality in composite mixtures. Many companies are confronted with increasing problems associated with polymeric waste management. This situation has reached a point where the only solution and the best alternative are both to use polymeric materials with controlled degradability, including biodegradable compostable polymers, especially those designed for the packaging industry or other mass products [9–12].

Biodegradable polymers are divided into several groups. The first group consists of agropolymers such as polysaccharides obtained from biomass. Polymers based on carbohydrates have emerged as an exciting topic of polymer research due to worldwide focus on sustainable materials. Almost all walks of life need paradigmatic shift from petroleum and non-renewable source towards

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sustainable materials. Cellulose, chitin and starch, three heavyweights among natural polymers by their sheer abundance and importance, display very different properties, including crystallinity, solubility, and aptitude to chemical modification, and hence quite different applications as macromolecular materials, despite the fact that their basic building blocks are not that different. The polymers containing carbohydrates are useful in various fields like pharmacological and biomedical applications. The class of sugar-based polymers has also been investigated in some detail for a variety of applications, particularly in the biomedical field [13–16]. The second group consists of polyesters obtained from the fermentation of biomass and genetically modified plants in biotechnological processes (PHA, PHB) or from the synthesis of monomers obtained from biomass (PLA). The third group of biodegradable polymers consists of aliphatic or aromatic copolyesters synthesised in petrochemical processes. There are also numerous plant polymers, such as flax, kenaf, and jute, and zoogenic polymers, such as keratin, chitin, silk and wool. Natural rubber obtained from the hevea gumtree, used in many industries, is of great importance due to its elasticity and biodegradability [17–21].

Developing polymer technologies should be directed towards polymers based on renewable raw materials. To this group of polymers undoubtedly belong poly(glycolic acid), poly(lactide) and poly(hydroxyl butyrate), which are both environmentally friendly materials. These are completely biodegradable and have a wide range of functional properties that make them suitable for specific applications. These polymers are obtained by the fermentation of plant materials or are directly synthesised in plant tissues. Among the polymers mentioned, only polycaprolactone is a synthetic thermoplastic polymer obtained by free radical, ring-opening polymerisation of ϵ -caprolactone. Recently, this polymer has been in the background of new green polymers discovered at the turn of the 21st century. However, polycaprolactone (PCL) is receiving renewed interest because of its low price, which is almost competitive with those of PLA and PHB, and its wide range of use, from medicine to commercial materials such as packaging. PCL is biodegradable and biocompatible with human tissues, and therefore it can be used in implants in the human body as well as for nerve regeneration and as a drug carrier. The use of a material in elastic tissues requires that its properties, such as its elasticity, be appropriate [22–34].

The use of PLA or PGA in such applications has been unsuccessful because during prolonged exposure to heat, tissues are deformed by mechanical stresses. To improve the fatigue resistance of PCL, experiments were carried out to synthesise copolymers such as poly(glycolide-co-caprolactone) (PGCL), as reported by Lee, and poly(lactide-co-caprolactone) PLCL, as reported by Jeong. These polymers exhibited elastic properties comparable to those of rubber. Thus, to use PCL as a biomedical material, its resistance to factors affecting its use in human organisms should be improved, increasing its elasticity and maintaining its desirable biological properties. The analysis of the structure of polycaprolactone and information

available in the literature indicate that it can be easily, chemically, physically or biologically modified to obtain products with specific biological properties required in medical engineering.

The main issue in the modification of polycaprolactone properties is doping with other synthetic or natural polymers. In our studies, we have made composites of polycaprolactone and epoxidised natural rubber. What makes these composites innovative is their unique composition, including additives of exclusively natural origin or renewable sources. We have used natural cross-linkers, dispersing agents and biofillers, such as nanocellulose and pyrogenic silica, which have allowed us to obtain environmentally friendly materials with improved functional properties. The degradation of biomaterials used in human tissues is of great importance because they should synchronously degrade during the growth of new parent cells in the organism. The decomposition products of PCL are organism-friendly and undergo natural metabolic processes. PCL is difficult to degrade, compared to other polyesters, because of its high degree of crystallinity. In our studies, we designed the composites of polycaprolactone and epoxidised natural rubber, whose innovation is based on a unique composition consisting of additives of purely natural origin from renewable sources. We used natural cross-linkers, dispersing agents or biofillers, such as nanocellulose and pyrogenic silica, which allowed us to obtain environmentally friendly materials with improved functional properties [35–44].

2. Materials and methods

2.1. Reagents

The subject of the study was polycaprolactone: M_n 70,000–90,000, < 1.0% water, 1.145 g/mL at 25 °C (Aldrich). Epoxidised natural rubber (epoxyprene 50; 50 mol % epoxidation) was obtained from Kumpulan Guthrie Berhad, Malaysia. A mixture of amino acids (98% creatine, 98% cysteine, 98% phenylalanine), 97% dodecanoic acid, and 97% quercetin from flavonoids, obtained from Sigma-Aldrich, was used as a cross-linking agent; 1,2-dimethylimidazole (98%) was used as a cross-linking catalyst. Aerosil 380 silica was obtained from Degussa (Table 1).

2.2. Measurement methods

Rubber blends were prepared using a laboratory mixer of Brabender with a front-roll rotation speed of $V_p = 60$ rpm and friction of 1.1. The average temperature in the

Table 1
Polymer blend composition (PCL, polycaprolactone; ENR(50), epoxidized natural rubber; A380, Aerosil 380 silica; imidazole, 1,2-dimethylimidazole).

Composition	(phr)
PCL	40
ENR (50)	60
Cross-linking agent	1.0
Imidazole	0.5
A380	20

Brabender mixer was approximately 180 °C, and the mixing time was 60 min.

The vulcanisation of rubber blends was carried out with the use of steel vulcanisation moulds placed between the shelves of an electrically heated hydraulic press. Teflon films were used as spacers to prevent the adherence of the blends to the press plates. Samples were vulcanised at a temperature of 160 °C under a pressure of 15 MPa for 30 min.

The density of cross-links in the vulcanisates network was determined by the method of equilibrium swelling according to standard PN-74/C-04236. The vulcanisates were subjected to equilibrium swelling in hexane for 48 h at room temperature. The swollen samples were then weighed on a torsion balance and dried in a dryer at a temperature of 60 °C to a constant weight, and after 48 h they were reweighed. The cross-linking density was determined based on Flory–Rehner's equation:

$$\nu_e = \frac{1}{V_0} \cdot \frac{\ln(1 - V_r) + V_r + \mu V_r^2}{(V_r^{\frac{1}{3}} - \frac{V_r}{3})} \quad (1)$$

The Huggins parameter of the polymer-solvent interaction (χ) was calculated from the equation:

$$\chi = 0.24 + 0.78 V_r \quad (2)$$

where V_r is the volume fraction of the elastomer in the swollen gel.

The tensile strength of vulcanisates was tested according to standard PN-ISO 37:1998 by means of a ZWICK tester, model 1435, for dumbbell w-3.

Ageing characteristics were determined according to standard PN-82/C-04216. Samples were exposed to air at elevated temperature (383 K) for 10 days in a dryer with thermo-circulation. UV ageing was performed using a UV 2000 apparatus from Atlas. The measurement lasted 288 h and consisted of two alternately repeating segments with the following parameters: daily segment (radiation intensity 0.7 W m⁻², temperature 60 °C, duration 8 h), night segment (no UV radiation, temperature 50 °C, duration 4 h). Climatic ageing was carried out using a Weather-Ometer (Atlas; Ci 4000). The test was based on two variable segments simulating day and night conditions, and the samples were subjected to two different cycles: daily cycle (radiation intensity 0.4 W m⁻², temperature 60 °C, duration 240 min, humidity 80%, rain water on), night cycle (no radiation, temperature 50 °C, humidity 60%, duration 120 min).

The ageing coefficient was calculated according to the relationship:

$$K = \frac{[TS' \cdot E_b']}{[TS \cdot E_b]} \quad (3)$$

where TS indicates tensile strength, E_b indicates elongation at break and TS' and E_b' are the corresponding values after ageing.

The dispersion degree of the fillers in the elastomeric matrix was assessed from images obtained using a LEO 1530 scanning electron microscope (SEM). The samples tested consisted of vulcanisate fractures in liquid nitrogen dusted with carbon.

The oxygen induction time (OIT) test was performed on a Mettler Toledo DSC instrument. Samples with a mass of 4 mg were heated from room temperature to the test temperature, 220 °C, at a rate of 20 °C min⁻¹ under a nitrogen atmosphere. After 5 min at 220 °C, the gas was switched from nitrogen to air at a flow rate of 60 ml·min⁻¹. When all the antioxidants are consumed, the sample starts to oxidise, producing a deviation in the baseline. The OIT was measured as the time between the switch to airflow and the intersection with a tangent from the maximum derivative after oxidation has started. Two analyses of each sample were performed to ensure the accuracy of the results. The OIT was measured according to national and international standards such as ASTM D 3895.

The crystallized specimens were characterized by using differential scanning calorimeter (DSC) and wide-angle X-ray diffraction (WAXD).

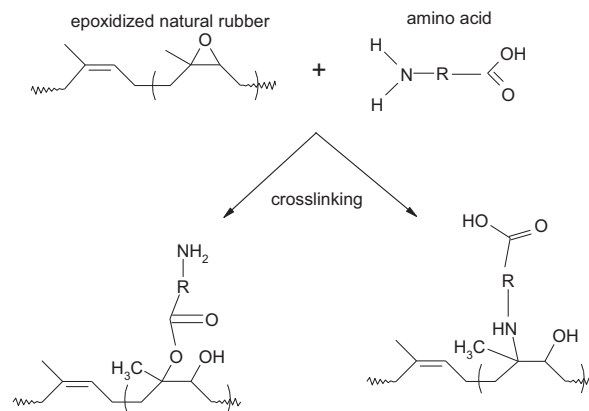
WAXD analyses were performed for WX1 and PLAWX1 on an Mxlabo diffractometer (MAC Science Co.; 3 kW, graphite monochromator, Cu K α radiation ($\lambda_x = 0.154$ nm), operated at 40 kV and 20 mA). Samples were scanned in fixed time mode with counting time of 2 s under a diffraction angle 2θ in the range of 5–60°.

The crystallized specimens were characterized by using temperature-modulated DSC (TA 2920; TA Instruments) at the heating rate of 5 °C min⁻¹ with a heating/cooling cycle of the modulation period of 60 s and an amplitude of ± 0.769 °C, to determine the glass transition (T_g) crystallization temperature (T_c) and the melting temperature (T_m). The DSC was calibrated with indium before use. For the measurement of T_c , we used amorphous samples after quenching from melt state (~ 200 °C).

3. Results and discussion

3.1. The properties of ENR/PCL composites

The presence of an oxyrane ring in the structure of natural rubber creates opportunities for various reactions to proceed for modification purposes. In polymers containing epoxide groups, cross-linking is carried out using compounds containing amine groups. The cross-linking of



Scheme 1. Cross-linking of an epoxidized natural rubber (ENR) by an amino acid.

composites of epoxidised natural rubber and polycaprolactone was performed using amino acid derivatives (Scheme 1). The choice of the cross-linkers was also dictated by the pro-ecological character of amino acids that are widely used in medicine. The amino acids used had carboxyl and amine groups. We also used fatty acids (dodecane acid). The primary aim was to obtain the best possible elastic properties in ENR/PCL composites. The best cross-linking effects were obtained using quercetin, a natural derivative of flavonoids. The composite tensile strength was 22.50 MPa, the elongation was 436%, and the cross-link density was $21.15 \cdot 10^{-5} \text{ mol cm}^{-3}$. Amino acids such as phenylalanine and asparagine or cysteine, used as natural cross-linking agents, yielded decreased cross-linking effectiveness. The best cross-linker was phenylalanine. The composite cross-linked with phenylalanine had a tensile strength of 13.9 MPa, an elongation of 443%, and a cross-link density of $8.89 \cdot 10^{-5} \text{ mol cm}^{-3}$. However, the use of asparagine, cysteine and dodecane acid in the ENR/PCL composite allowed us to obtain a lower elongation at break ($\leq 350\%$) and a tensile strength ranging from 13.8 to 14.92 MPa. Undoubtedly, the use of a flavonoid as a cross-linker constitutes an undeniable element of scientific novelty. Quercetin and phenylalanine were the best cross-linkers for the biocomposites we developed. The pro-ecological matrix of these composites makes them environmentally friendly and human-friendly and, therefore, widely applicable in many fields. Based on the positive results concerning the action of quercetin as a cross-linker, the mechanical properties of composites

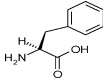
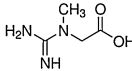
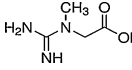
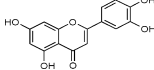
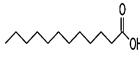
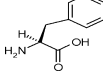
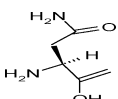
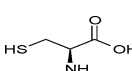
cross-linked with various quantities of quercetin were determined (Table 2). From the results listed in Table 2, it follows that the optimal content of quercetin in the composite ranges from 0.75 to 1 phr per 50 phr of ENR/PCL. When the content of quercetin used for cross-linking amounted to 0.75–1.5 phr, the composite elongation at break ranged from 18.4 to 19.20 MPa, and with increasing quercetin content, the elongation at break decreased to the minimum value of 250% at a quercetin content of 1.5 phr. The cross-link density of the composite slightly changed with increasing quercetin content, ranging from 19.3 to $24.70 \cdot 10^{-5} \text{ mol cm}^{-3}$ (Table 3).

3.2. Effect of cross-linking agents on the stabilisation of biocomposites

Natural cross-linkers such as amino acids, fatty acids and quercetin, from the group of flavonoids, can also be used as anti-ageing compounds. Therefore, the aim of the tests concerning the influence of simulated ageing by various climatic conditions on the properties of biocomposites was to assess their resistance to those conditions.

Biocomposites cross-linked with quercetin and asparagine exhibited greater resistance to UV ageing than the other biocomposites tested, as confirmed by the high ageing coefficients measured: 0.72 for the composite containing quercetin and 0.82 for the composite containing asparagine. The other ENR/PCL composites exhibited UV ageing resistance similar to that of ENR vulcanisate. As in the case of UV ageing ($K = 0.52$), the sample of ENR/PCL

Table 2
Mechanical properties of the ENR/PCL (60phr/40phr) composites cross-link by natural substances.

Composite	Cross-linking agents	SE ₁₀₀ [MPa]	SE ₂₀₀ [MPa]	SE ₃₀₀ [MPa]	TS [MPa]	E _b [%]	$\nu \cdot 10^{-5}$ [mol cm ⁻³]
ENR		1.52	2.50	3.03	3.12	276	2.50
ENR		1.28	2.57	4.06	4.78	348	1.47
ENR/PCL		7.24	9.48	11.1	10.90	292	12.25
ENR/PCL		7.50	11.30	15.80	22.50	436	21.15
ENR/PCL		7.23	9.83	12.60	13.80	353	14.30
ENR/PCL		6.13	8.46	10.80	13.90	443	8.89
ENR/PCL		8.29	11.0	13.9	14.90	333	6.04
ENR/PCL		8.29	11.1	14.6	14.92	311	7.77

TS: tensile strength [MPa]; E_b, elongation at break [%]; 100, 200, 300%, stress at 100–300% of elongation, ν crosslinking density calculated on the basis of swelling in hexane.

Table 3
Mechanical properties of the ENR/PCL (60phr/40phr) composites cross-link by quercetin.

Composite	Quercetin [phr]	SE ₁₀₀ [MPa]	SE ₂₀₀ [MPa]	SE ₃₀₀ [MPa]	TS [MPa]	E _b [%]	$\nu \cdot 10^{-5}$ [mol cm ⁻³]
ENR/PCL	0.75	7.81	10.80	13.60	18.40	437	19.30
ENR/PCL	1	9.90	14.20	18.00	19.20	289	21.15
ENR/PCL	1.25	12.60	17.40	–	20.40	223	24.70
ENR/PCL	1.5	10.30	15.30	17.80	18.20	251	19.30

TS: tensile strength [MPa]; E_b: elongation at break [%]; 100, 200, 300%, stress at 100–300% of elongation; ν , cross-linking density calculated on the basis of swelling in hexane.

containing phenylalanine was degraded to the greatest extent by thermo-oxidising ($K=0.31$) and climatic ageing ($K=0.52$). The ENR/PCL biocomposites exhibited lower resistance to thermal ageing than ENR vulcanisate ($K=0.87$), with ageing coefficients that ranged from 0.31 to 0.87. The samples tested showed good resistance to climatic ageing, as confirmed by their ageing coefficients, which approached 1. Among all of the biocomposites, the samples cross-linked with asparagine and quercetin were the most resistant to climatic ageing; their ageing coefficients were $K=0.82$ and $K=0.72$, respectively (Table 4).

Additionally, DSC examinations were conducted to determine the oxygen induction time (OIT), expressed by the OIT index. It appears that the OIT of the ENR/PCL biocomposite cross-linked with dodecane acid began at a temperature of 410 °C and amounted to 0.32 min. The energy of this process amounted to 935 J·g⁻¹, which is similar to the energy value obtained by the oxygen induction process of the ENR/PCL composite cross-linked with quercetin. The OIT index of this composite was 3.35 min. However, the vulcanisate of ENR rubber had an OIT index equal to 1.36 min, and the energy of his process amounted to 2721 J·g⁻¹. It should be emphasised that the oxidation of this sample began at 210 °C. ENR/PCL biocomposites are characterised by low oxidation energy, although their oxidation energy was comparable in the case of cross-linking with quercetin and lower in the case

Table 4
Ageing parameters (K) of the composites ENR/PCL (60phr/40phr) subjected to UV, thermal and weathering ageing.

Composite	$\frac{(TS)_{\text{after ageing}}}{(TS)_{\text{before ageing}}}$	$\frac{(E_b)_{\text{after ageing}}}{(E_b)_{\text{before ageing}}}$	K [a.u.]
<i>UV ageing</i>			
ENR	0.80	0.51	0.58
ENR/PCL quercetin	0.43	0.60	0.72
ENR/PCL asparagine	0.59	0.71	0.82
ENR/PCL cysteine	0.32	0.58	0.56
ENR/PCL phenylalanine	0.27	0.52	0.52
<i>Thermo-oxidation</i>			
ENR	1.11	0.78	0.87
ENR/PCL quercetin	0.53	0.84	0.64
ENR/PCL asparagine	0.59	0.83	0.72
ENR/PCL cysteine	0.58	0.91	0.63
ENR/PCL phenylalanine	0.15	0.50	0.31
<i>Weathering</i>			
ENR	1.22	1.08	1.32
ENR/PCL quercetin	0.43	0.60	0.72
ENR/PCL asparagine	0.59	0.71	0.82
ENR/PCL cysteine	0.32	0.58	0.56
ENR/PCL phenylalanine	0.27	0.52	0.52

TS: tensile strength [MPa]; E_b: elongation at break [%]; $K = (TS \cdot E_b)_{\text{after ageing}} / (TS \cdot E_b)_{\text{before ageing}}$ [arbitrary unit].

of the remaining samples. However, increasing the quercetin content did not significantly influence the oxygen induction time: at a content of 0.75 phr, the oxidation was more energetic than that of samples with higher quercetin contents.

3.3. The crystallized specimens of biocomposites ENR/PCL

To assess the crystallinity of the biocomposites designed, we used wide-angle X-ray diffraction (WAX) and DSC methods. The results of the WAX measurements indicate a lower crystalline content in the ENR/PCL composite than in polycaprolactone (Fig. 1). The diffractometric diagram of polycaprolactone shows two peaks located at angles $2\theta \approx 21.45$ and $2\theta \approx 23.7$, indicating a high degree of crystallinity in this polymer. However, the diffractometric diagram of ENR/PCL composite only shows one broad reflection at $2\theta \approx 10$ to $2\theta \approx 22$, with a much lower intensity than that of PCL. The addition of amorphous epoxidised natural rubber to the crystalline polycaprolactone can cause a considerable decrease in the crystalline phase of such a composite. The crystalline phase decay in the ENR/PCL composite was confirmed by the DSC diagram, showing an intensive peak of PLC at approximately 71.11 °C, which was considerably decreased in the ENR/PCL composite at 63.13 °C (Fig. 2). The crystallization enthalpy is for PCL $\Delta H_c = 71.11$ J·g⁻¹ and for ENR/PCL composite $\Delta H_c = 24.30$ J·g⁻¹ (Table 5). This crystalline phase decay indicates good miscibility and compatibility of these polymers, thus yielding a composite with very good properties.

The compatibility and good miscibility of epoxidised natural rubber with polycaprolactone were confirmed by the images obtained using the SEM technique. These images show that the composite has a compact uniform

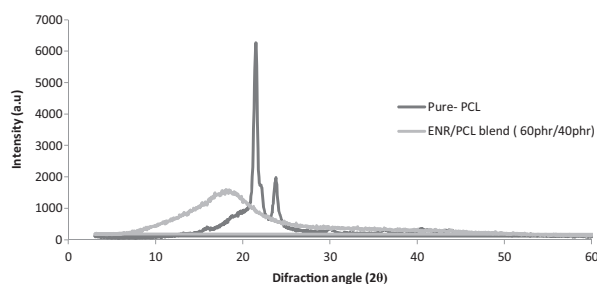


Fig. 1. Characterization of crystallized specimens of pure PCL ($M_n = 70,000$ – $90,000$) and ENR/PCL (60phr/40phr) composites by using WAXD methods.

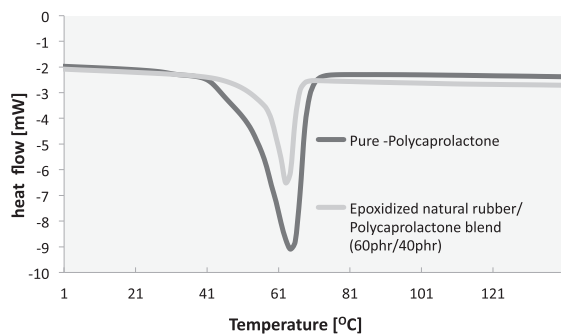
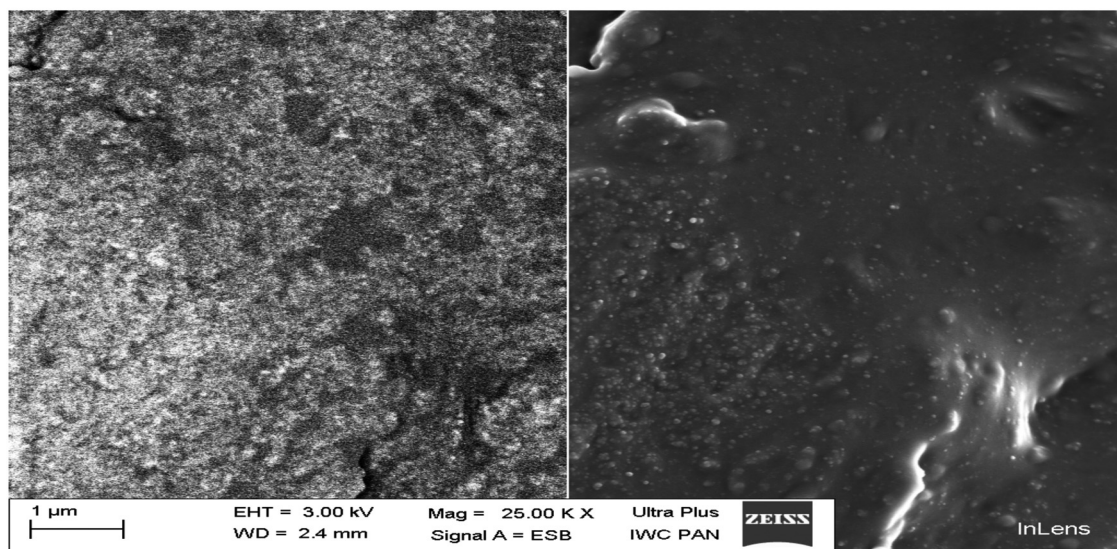


Fig. 2. DSC tracings (with the heating rate of $5^{\circ}\text{C min}^{-1}$) of pure PCL ($M_n = 70,000\text{--}90,000$) and ENR/PCL (60phr/40phr) blend based composites.

structure containing evenly dispersed fillers (Figs. 3 and 4). Because of the different entropy and enthalpy among polymers, phase separation generally occurs in most polymer blends and leads to a multiphase morphology. The properties are dependent not only on the physical properties of each component but also on the dispersed phase microstructure and the interfacial chemistry. Figs. 3 and 4 show SEM micrographs of fracture surfaces of ENR/PCL blends. In our work, the ENR/PCL blends revealed a spherical-particle-dispersed morphology, because the non-polar ENR was immiscible with the polar PCL and led to phase separation. That ENR with higher degree of epoxidation can induce more molecular interactions and entanglements with PCL because polarity of the ENR increases with epoxidation content. During processing, the

a



b

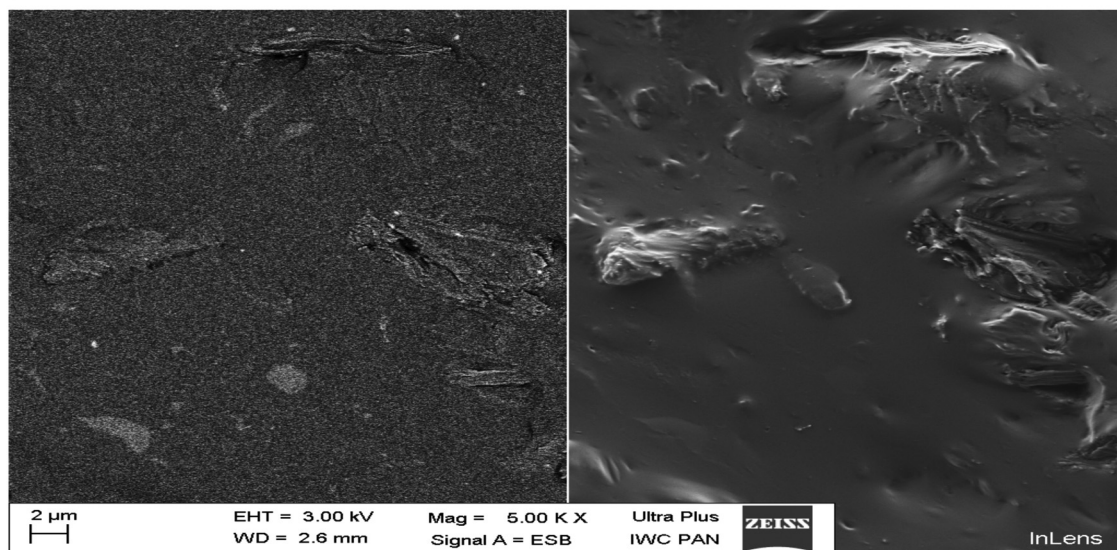


Fig. 3. Scanning electron micrographs of fracture surfaces ENR/PCL (60phr/40phr) composite materials (a, b).

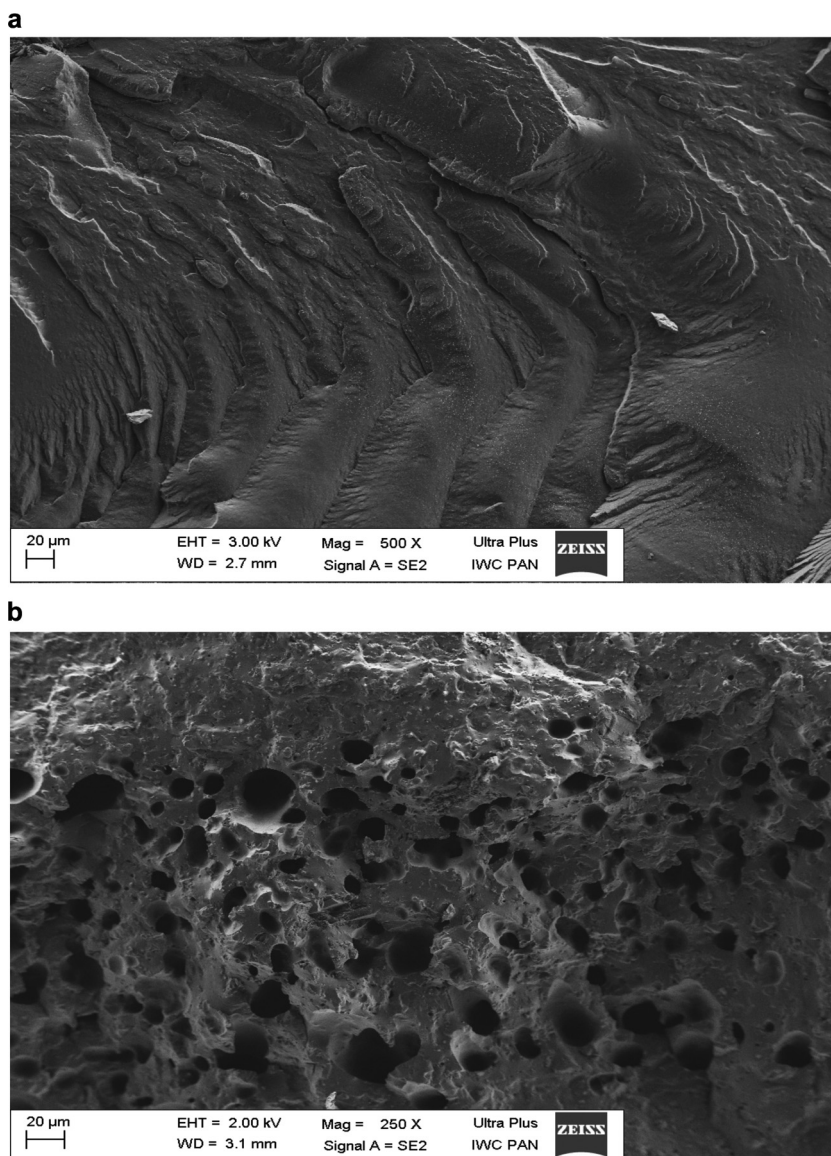


Fig. 4. Scanning electron micrographs of freeze-fractured surfaces of the ENR/PCL (60phr/40phr) composite materials (a, b).

components are melt-blended, and the minor phase is broken up to form the dispersed phase. Fig. 4 shows the SEM micrographs of freeze-fractured surfaces of the ENR/PCL blend. This SEM image presents scaffolds with interconnected porous structures of ENR/PCL blend. ENR/PCL blend (Fig. 3) presents quite coarse phase morphology with small amount of elongated rubber

domains. Fig. 3 shows a compatibility increase in ENR/PLA blends, which is indicated by an obscure interphase. No visible agglomerates or irregularities can be observed, and there is a clear isolation of one polymer phase.

4. Conclusions

All of the innovative cross-linkers examined in this study, namely those from the group of amino acids and quercetin from the group of flavonoids, as well as dodecanoic acid were successfully used to create cross-linking biocomposites of epoxidised natural rubber and polycaprolactone. The most effective cross-linkers were quercetin and phenylalanine, which provided optimal cross-linking, as reflected by the composites' elongation at break of over 400% and a tensile strength close to 20 MPa

Table 5
Thermal properties and crystallinity of PCL and ENR/PCL blends.

Material	T_c [$^{\circ}\text{C}$]	ΔH_c [$\text{J}\cdot\text{g}^{-1}$]
PCL	64.22	71.11
ENR/PCL	63.13	24.30

ΔH_c , Crystallization enthalpies [$\text{J}\cdot\text{g}^{-1}$], T_c , crystallization temperature [$^{\circ}\text{C}$].

(for quercetin). The optimal content of the natural cross-linking substance was 0.75 to 1 phr. It was also confirmed that these substances could be used successfully as anti-ageing agents in the composites under investigation. This finding was confirmed by the ageing coefficients, which were calculated on the basis of a change in the composite deformation energy before and after ageing under UV, climatic and thermal conditions. The best ageing resistance was exhibited by the ENR/PCL composite containing quercetin, while the addition of phenylalanine accelerated the degradation of the composite. DSC measurements allowed us to determine the oxidation induction time and thereby showed that the biocomposite has high resistance to oxidation, as its oxidation induction was observed at temperatures as high as 410 °C, while the oxidation of the ENR vulcanisate began at 210 °C.

The biocomposites described in this paper are suitable for many applications because of their very good functional properties and their resistance to ageing. The pro-ecological character of biocomposites derived from renewable materials enables their widespread application in various products while meeting current ecological requirements.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.crci.2013.10.008>.

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