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Ecologic Impact Analysis of Epoxidized Vegetable Oils Used at Polymer Production

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ABSTRACT

As reported in recent reviews and books, vegetable-based oils have been utilized for centuries in the manufacturing of inks, coatings, agrochemicals, plasticizers, and lubricants. Lately, epoxidized vegetable-based oils are having larger interest as they are obtained from renewable, sustainable natural sources and are environment-friendly. Epoxidized vegetable-based oil can act as a feedstock for synthesis of chemicals' diversity including lubricants, carbonyl compound, glycol, polyols, plasticizers for polymerization etc. due to their oxirane ring's high reactivity and significant oxirane oxygen content. At the same time, epoxidized vegetable-based oil has the potential to turn into a principal sustainable raw material in regards to the beneficial environmental effects. The environmental effects of general properties are different as in the case of the accumulated ecological effects from epoxidized vegetable-based oil plantation through refining to manufacture each of vegetable-based oils. In this study, comparison of eight different epoxidized vegetable oils in terms of ten factors is analyzed with multi-criteria decision making model. The primary factors (acid value, iodine value, oxirane value, thermal conductivity coefficient, density, boiling point, ignition point, viscosity, resin, and cross-linker) of general properties of epoxidized oil manufactured from vegetable-based oil are evaluated. The most environment-friendly epoxidized vegetable-based oil is determined. The main contribution of this paper is building a list of properties in evaluating oils, ranking them based on their relative priorities based on expert opinions, and formulating a mathematical model as a basis for comparison among the alternatives.

1. Introduction

Vegetable-based oil is obtained from renewable and sustainable resource of feedstock. By a complex reaction named 'epoxidation', the unsaturation existing in vegetable-based oils can be chemically altered to a worth attached product. Because of the oxirane ring epoxides' superior reactivity can also act as a feedstock for chemicals' variety synthesis such as polyols (alcohols), lubricants, glycols, olefinic compounds, stabilizer and plasticizer for polymerization and their popularity is rising day after day. The polymeric material's life cycle with vegetable-based oils is shown in Figure 1 [1]. The cycle for the products' preparation from vegetable-based oil is given İn Figure 2 [2].

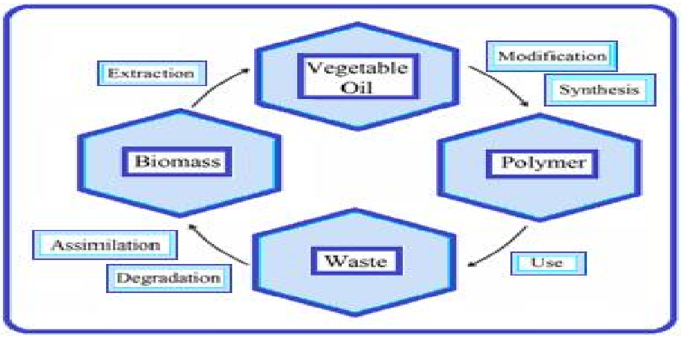


Figure 1. The polymeric material's life cycle from vegetable-based oil

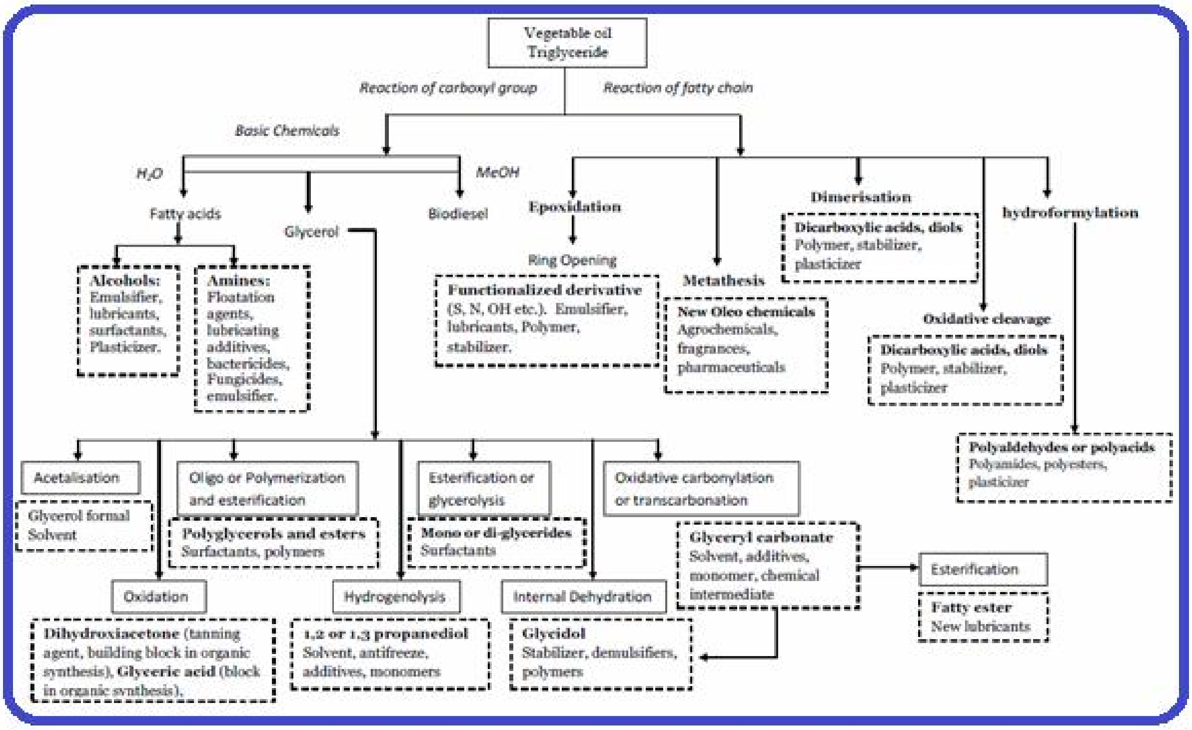


Figure 2. The cycle for the products' preparation from vegetable-based oil

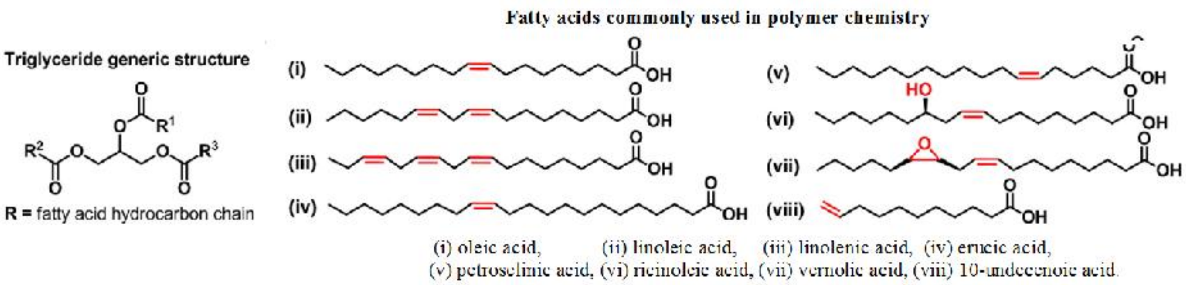


Figure 3. For polymer chemistry, fatty acids % composition generally utilized [3]

Though the renewable polymers' last development has displayed big advancements, the renewable polymers' simple share (<percentage 5) in the market is substantially owing to their inferior performance and high cost compared to petrolium-based polymers made from synthetic chemical materials.

By 3 fatty acids, the vegetable oils' primary constituents are triglycerides which are the glycerol esterification product. The fatty acids constitute a percentage of 95 of triglycerides' total weight and their content is characteristic of each plant oil. Many widely studied fatty acids' chemical structures are summarized in Fig. 3. Such triglycerides include many reactive places, such as ester groups and double bonds, opening up different possibilities for novel structures to be adapted. Most of today's scientific literature focused on epoxidized plant oils to produce well defined linear structures, as well as resins for hybrid materials and biocomposites. Key strategies for producing thermoplastic and thermosetting materials from building blocks derived from triglycerides are given in Fig. 4. Manufacturers combine in a reaction the chemical compounds' two forms to produce plastic. A polyol is one of the chemicals, a compound suitable for reaction with several hydroxyl functional groups. For example; some vegetable oils such as linseed oil have six or five reactive places, making the material harsh. Others have less reactive areas, such as olive oil, making the product more versatile [3].

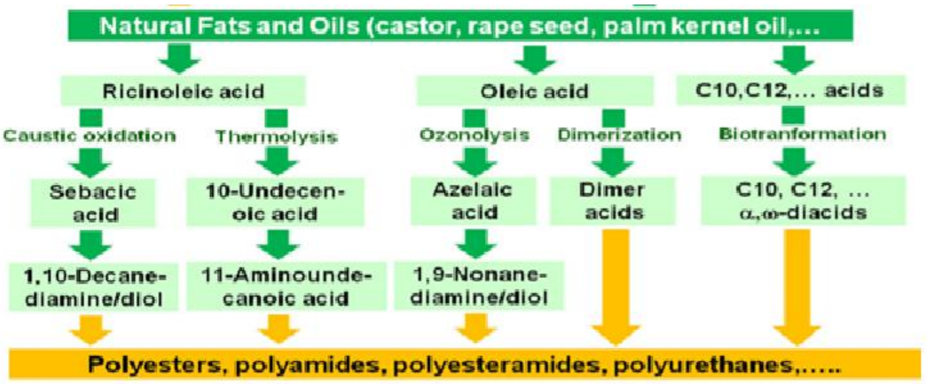


Figure 4. Key strategies for producing thermoplastic and thermosetting materials from building blocks derived from triglycerides [3].

The vegetable-based oil indicates one of most abundant and the cheapest biological raw material available in high amounts and it's utilization as beginning material presents many benefits such as inherent biodegradability and low toxicity [4]. In this way, the vegetable-based oil's financial worth could be raised by transforming the vegetable-based oil into epoxidized vegetable-based oil. By epoxidation process, the double bonds in the vegetable-based oil are utilized as reactive places in the coatings and they can also be functionalized [5]. Thus, the superior molecular weight products can be manufactured by rising the cross-linking. Because of the growing consciousness on environment, use of renewable green materials is on the rise nowadays [6]. The petrochemical-based resin such as vinyl ester, epoxy, and polyester find more engineering implementations due to their benefits to the material characteristics such as high strength and stiffness. But these green resins have important disadvantages on the points of initial processing cost, biodegradability, health hazards and energy consumption [4, 7-8]. As a result, there is a necessity to advance new bio-based products from sustainable raw materials. For this reason, a lot of scholars have been working on vegetable-based oils as an alternative raw material to take the place of petroleum [9]. Diverse polymers have been fabricated from vegetable-based oils and their reproductions such as polyamides, polyurethanes, polyesters, and ox polymerized oils [10-11]. As toughening agents, the vegetable-based oils' implementation within the polymer science is reported. Querishi et al. developed a modified linseed oil-based elastomer and a cross-linked polystyrene's interpenetrating polymer network (IPN) [12]. Barrett and his co-workers studied to fabricate plant oil-based IPN [13]. Mustata investigated the soybean oil composites' efficiency. These composites showed that these sustainable polymeric materials could perform as an option to the conventional fossil-based polymeric materials by means of innovation of constructing because these new bio-derived polymeric materials could be more eco-friendly and cost-effective than the present petroleum-based polymeric materials [14]. The epoxidized vegetable oil-based epoxy materials were examined by Miyagawa et al. [15-17]. The sustainable nanocomposite coatings showing perfect film characteristics and good bio-degradability were improved by Tsujimoto et al. [18]. From Nahar seed oil, Karak et al. synthetized polyester resins [19]. Larock and his co-workers utilized the soybean oil's cationic copolymerization to fabricate polymers varying between hard plastics and soft rubbers, depending on the stoichiometry and the used oil [20]. Petrovic researched the mechanical and thermal characteristics of polyurethanes produced from diverse vegetable-based oils [21].

For manufacturing of polymeric materials, the vegetable-based oils are one of the most significant groups of bio-based resources. The aim of the paper is to analyze the environmental impact of various properties of eight different epoxidized vegetable-based oils. At the same time, the most eco-friendly plasticizer among these epoxidized oils is determined.

2. The Model and the Materials

To obtain a framework for relations with multi-criteria decision-making issues, a hierarchical model is structured. Among decision levels, the model adopts a unidirectional hierarchical connection among the criteria. The selected methodology permits the hierarchical tree building and weighing each indicator through pairwise comparison between indicators and criteria by a matrix to obtain a coherent and consistent administration of both qualitative and quantitative data. To determine weights of criteria, such a method is used in this paper.

Table 1. Hierarchy of Criteria

	Ecologic Impact
Main Criteria	Acid value
	Iodine value
	Oxirane value
	Thermal conductivity coefficient
	Density (25C)
	Boiling point
	Ignition point
	Viscosity
	Resin
	Cross-linker

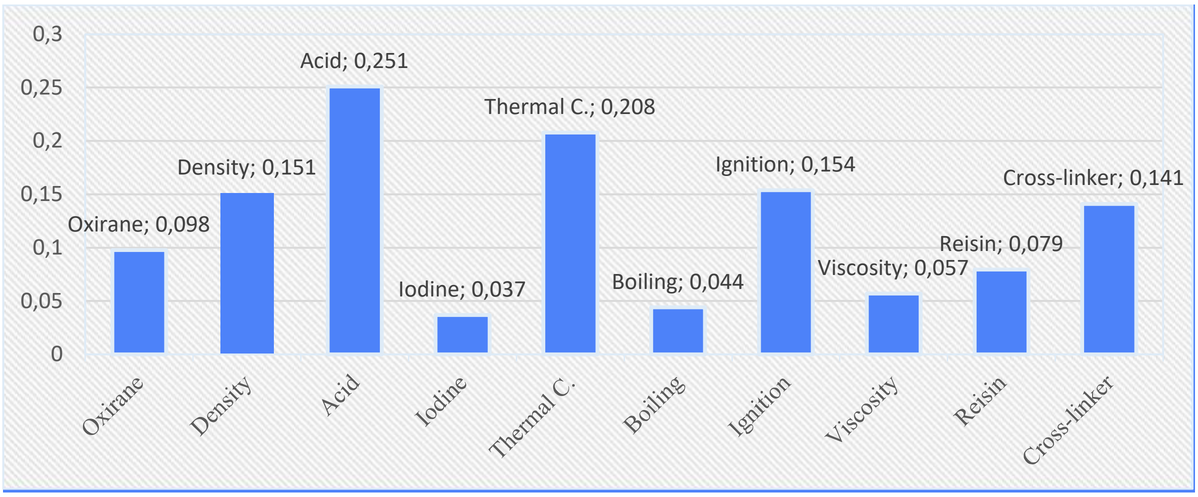


Figure 3. Relative priorities of the factors

In the hierarchy for determining the ecological impact of epoxidized vegetable oils, the ultimate goal would be choosing the most appropriate alternative that satisfies various sets of factors. These characteristics involve acid value, iodine value, oxirane value, thermal conductivity coefficient, density, boiling point, ignition point, viscosity, resin, and cross-linker. Eight different epoxidized vegetable oil alternatives are compared from the perspective of each factor mentioned. The list composed of these factors is constructed as shown in Table 1 above.

While measurements for some factors are readily available, some others can only be estimated with respect to other variables. As it is the case in all multi-factor decision making methods, the relative priorities of such factors need to be determined. This is accomplished by pairwise comparison of the factors. Figure 3 provides the resulting factor priorities. After determining the priorities of the factors with respect to the overall goal, the epoxidized vegetable oils are compared two by two with respect to each factor. All available commercially used vegetable oils are used for the purpose of this investigation to be evaluated. These are: Soybean (ESO), Palm (EPO), Olive (EZO), Linseed (ELO), Sunflower (ESFO), Castor (EHO), Canola (EKO), and Tall (ETO). The properties of the selected oils are presented in Table 2 below.

Table 2. Properties of epoxidized vegetable oils

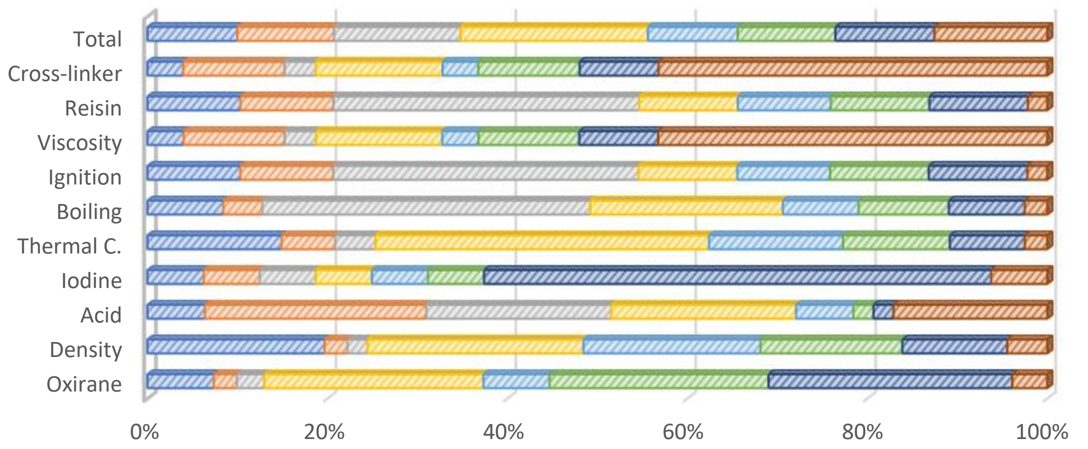
PROPERTIES		ESO	EPO	EZO	ELO	ESFO	EHO	EKO	ETO
Appearance at normal temperature	*colour*	Clear to yellow liquid	Thick to orange liquid	Thick To green liquid	Thick To yellow liquid	Clear to yellow liquid	Thin to Brown liquid	Thin to green liquid	Thick to yellow liquid
Brilliance	*< (Pt-Co)*	*400*	391	*412*	*402*	*400*	*372*	*365*	388
Acid value	*(KOH/g):max. mg*	*2*	1.14	*1.21*	*1.32*	*2*	*3.01*	*2.97*	1. 545
Iodine value	*< max. % [mg I_2 per 100g]*	*3*	0.44	*0.85*	*0.62*	*3*	*1.44*	*131.4*	1.55-1.67
Oxirane value	*%*	*6.4*	3.15	*4.14*	*9.4*	*6.4*	*9.93*	*9.96*	4.43-5.36
Thermal conductivity coefficient	*W/mK*	*0,156*	0,144	*0,14*	*0,163*	*0,156*	*0,151*	*0,147*	0,133
Density (25 ^{o}C)	*g/cm^3*	*0.985-0.995*	0.897-0.941	*0.903-0.926*	*0.991-1.002*	*0.985-0.995*	*0.976-0.997*	*0.966-0.985*	0.919-0.962
Sabonification number	*(KOH/g)*	*183-185*	173-77	*188-196*	*194-88*	*183-185*	*190-195*	*188-191*	162.3-166
Flow point	*^{o}C*	*-1*	4	*12*	*7*	*-1*	*5*	*4*	1
Boiling point	*^{o}C*	*150*	145	*167*	*163*	*150*	*155*	*153*	136
Ignition point	*^{o}C*	*310*	304	*359*	*321*	*310*	*316*	*311*	212
Viscosity	*MPa.s (25^{o}C)*	*325*	390	*276*	*430*	*325*	*400*	*370*	510
Refractive index(at 25^{o}C)	*%*	*1.472*	1.398	*1.865*	*2.153*	*1.472*	*2.07*	*2.01*	1.315
Melting point in water (at 25^{o}C)	*< %*	*0.01*	0.011	*0.035*	*0.032*	*0.01*	*0.0273*	*0.0265*	0.01
Loss on heating	*< %*	*0.5*	0.51	*0.65*	*0.71*	0.5	*0.6*	*0.58*	0.43
Resin	*g*	*145*	42	*56*	*131.5*	136.2	*76*	*131.9*	127.3
Cross-linker	*g*	*15*	6.7	*7.1*	*11.0*	10.8	*9.89*	*9.77*	7.90

ESO: Soybean, EPO: Palm, EZO: Olive, ELO: Linseed, ESFO: Sunflower, EHO: Castor, EKO: Canola, ETO: Tall

The final step in applying the technique is pairwise comparisons of the alternatives with respect to each factor. In order to design an objective scheme for this purpose, the maximum and minimum values of the alternatives for each sub-criteria is determined. This range is divided into nine even ranges on a scale from 1 to 9. Finally each vegetable oil type is placed in one of these ranges based on their values to compare them with each other.

3. Experimental Results

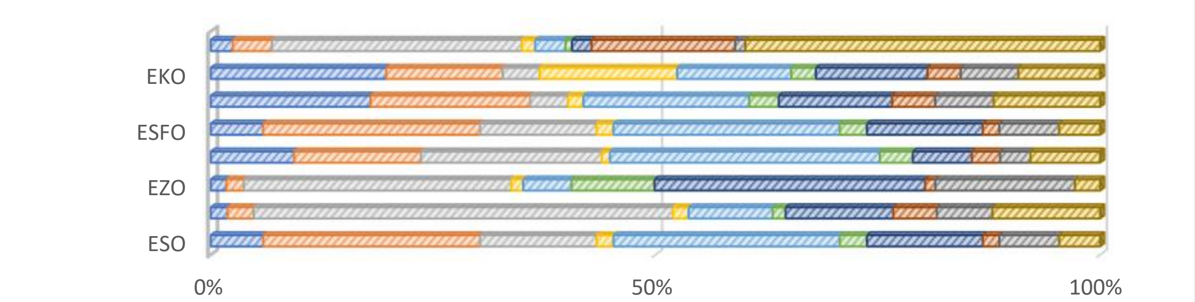
This study aims to investigate the ecological impact of the main epoxidized vegetable oils based on various factors exist in the literature. These factors cover a wide range of potential ecological impact categories. Each factor is appointed a relative priority based on expert evaluations. Then the solution method is applied to the resulting scheme. Based on the calculations above, the relative priorities corresponding to the ecological impact of each oil type about all factors are presented below:



	Oxirane	Density	Acid	Iodine	Thermal C.	Boiling	Ignition	Viscosity	Reisin	Cross-linker	Total
ESO	0,0072	0,0297	0,016	0,0023	0,031	0,0037	0,0159	0,0023	0,0082	0,0056	0,1218
EPO	0,0025	0,0038	0,0618	0,0023	0,0124	0,0019	0,0159	0,0064	0,0082	0,0159	0,1311
EZO	0,003	0,0034	0,0516	0,0023	0,0093	0,016	0,0523	0,002	0,027	0,0049	0,1718
ELO	0,0238	0,0362	0,0516	0,0023	0,0771	0,0094	0,0169	0,008	0,0087	0,0199	0,254
ESFO	0,0072	0,0297	0,016	0,0023	0,031	0,0037	0,0159	0,0023	0,0082	0,0056	0,1218
EHO	0,0238	0,0238	0,0056	0,0023	0,0247	0,0044	0,0169	0,0064	0,0087	0,0159	0,1326
EKO	0,0265	0,0176	0,0056	0,0208	0,0173	0,0037	0,0169	0,005	0,0087	0,0124	0,1344
ETO	0,0038	0,0067	0,0429	0,0023	0,0052	0,0011	0,0034	0,0247	0,0017	0,061	0,1529

Figure 4. Weights of Epoxidized Vegetable Oils

The obtained results indicate that the Epoxidized Linseed Oil (ELO) with a global priority of 0.2540 is the most eco-friendly vegetable oil based on the factors selected. On the other hand, Soybean and Sunflower (ESO and ESFO) obtain the lowest score of 0.1218. The acidic value of 2 KOH/g for these oils has apparently reduced their overall score. Similarly, high acidic value of Castor (EHO) presents itself as an environmental problem although its overall characteristics are slightly higher. Figure 5 summarizes the outcome of the analysis.



	ESO	EPO	EZO	ELO	ESFO	EHO	EKO	ETO
Oxirane	0,0072	0,0025	0,0030	0,0238	0,0072	0,0238	0,0265	0,0038
Density	0,0297	0,0038	0,0034	0,0362	0,0297	0,0238	0,0176	0,0067
Acid	0,0160	0,0618	0,0516	0,0516	0,0160	0,0056	0,0056	0,0429
Iodine	0,0023	0,0023	0,0023	0,0023	0,0023	0,0023	0,0208	0,0023
Thermal C.	0,0310	0,0124	0,0093	0,0771	0,0310	0,0247	0,0173	0,0052
Boiling	0,0037	0,0019	0,0160	0,0094	0,0037	0,0044	0,0037	0,0011
Ignition	0,0159	0,0159	0,0523	0,0169	0,0159	0,0169	0,0169	0,0034
Viscosity	0,0023	0,0064	0,0020	0,0080	0,0023	0,0064	0,0050	0,0247
Reisin	0,0082	0,0082	0,0270	0,0087	0,0082	0,0087	0,0087	0,0017
Cross-linker	0,0056	0,0159	0,0049	0,0199	0,0056	0,0159	0,0124	0,0610

Figure 5. Weights of the Alternatives

Aside from providing a quantitative method to evaluate the alternative materials, the main contribution of this paper is bringing together a list of comprehensive properties, ranking them based on their relative significance determined by expert opinions, and finally constructing a mathematical framework as a basis for comparison among the alternatives. The model developed within the scope of this study can further be enhanced or improved to cover different aspects of materials for the construction and automotive industries as well as others where epoxidized vegetable oils are used and serve both the policy-makers and the industry itself.

4. Conclusions

A petrolium-based challenge for the bio-based renewable sector is to be able to manufacture materials with features that chemicals match those currently in utilization. There's a need to reflect the high mass, high volume, low cost materials as raw materials (polymers) and how to produce these polymer kinds from sustainable sources.

Manufacturers must combine the two forms of the compounds to manufacture plastic in a chemical reaction. A polyol is one of such chemicals which is a compound appropriate for a reaction with numerous functional hydroxyl groups. Some vegetable oils such as linseed oil have six or five reactive places, making the material harsh. Others have less reactive areas, such as olive oil, making the product more versatile.

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