The bio components in the vitrimers reprocessability: A meta-analysis study

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Abstract: Vitrimers consist of polymeric networks capable of reorganizing their topology without harming the integrity of the material. These types of polymers have highly desirable properties, combining malleability, recyclability, cure, and repair at high temperatures with insolubility and low shape changes, which implies that vitrimers can be designed to obtain re-processable materials that can replace traditional thermosets, which is a crucial step to face the problem of the disposal of plastic materials after use. Thanks to these advantages, and intending to make sustainable the production of this kind of materials, various authors have explored the use of raw materials from renewable resources for partial or total replacement of synthetic vitrimers components, thus increasing the environmentally friendly profile of the vitrimers, thanks to the reduction in both, the oil consumption and carbon dioxide emissions. To analyze the possibilities in this field, in this work, we perform a systematic collection of data present in the literature and investigate interactions between reprocessability, the stability of the mechanical properties, and the use of materials of biological origin for the synthesis of vitrimeric polymers. The results obtained show that some of the biomaterials that have been studied to date can improve the reprocessability properties of vitrimers, which indicates that the bio-based vitrimeric polymers can become an attractive option for the development of environmentally friendly materials with good mechanical and reprocessability properties.

Keywords: Vitrimer, reprocessability, bio, Statistical analysis, Data mining, data analysis.

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Adherence to the BJEDIS scope: This work is closely related to the scope of BJEDIS as it presents bibliometric research and meta-analysis regarding bio compounds that have an effect on the reprocessability of vitrimers

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1. INTRODUCTION

Vitrimers represent a third class of materials, in addition to thermoplastics and thermosets, which consist of polymeric networks capable of reorganizing their network topology without harming the integrity of the material with self-healing properties, thus introducing dynamic covalent chemistry into thermoset malleable networks, also known as adaptive covalent networks (CANs). These properties can be achieved through synthesis strategies, where reversible covalent bonds are incorporated in the structure of materials formed by covalently cross-linked networks. These reversible links can form cross-links or be in the main chain structure and aim to facilitate the adaptability of these materials that are difficult to reprocess, leading to cross-linking dynamics (1–10).

Since the first epoxy vitrimer was introduced by Leibler in 2011 (11), who proposed a recyclable thermoset using an inherently constructed catalytic transesterification reaction based on the epoxy acid system, several epoxy vitrimers have been designed based on several dynamic covalent bonds, such as transesterification (12–14), disulfide metathesis (15), Schiff base (imine) exchange (16), siloxane equilibrium (17), and vinyl urethane chemistry (18).

These materials are characterized by highly desirable properties, combining malleability, recyclability, cure, and repair at high temperatures with insolubility and low shape changes, differentiating vitrimers from thermoplastics and thermosets. Its differences are possible thanks to the fact that these materials, at high temperatures, can flow and behave like viscoelastic liquids; so the material relaxes stresses and fluxes, even more, at low temperatures, the exchange reactions decrease, and the lattice topology freezes and the material behaves like classical thermoplastics; even though the total number of links remains constant over time and does not fluctuate. After cooling, the relaxation time and viscosity controlled by the exchange reaction rate slowly decrease (19–26).

So, vitrimers can be designed to obtain self-cure or malleability properties, generating new possibilities in practical applications, such as the production of reprocessable thermostet materials that can replace traditional thermostets used in various fields, opening the opportunity to contribute to society through the decrease of environmental contamination (12, 19). Despite these advantages, most of the vitrimer systems reported in the literature are based on petrochemical and non-degradable polymers, which implies that these materials still face the problem of disposal after being reused or reprocessed several times, and their production, therefore, is also unsustainable in the long term (1, 27, 28). One of the solutions that have been proposed to overcome this problem of the long-term environmental unsustainability of this type of materials is the use of raw materials from renewable resources, which directly reduces oil consumption and carbon dioxide emissions (29–33).

In recent years, intensive research work has been carried out on the partial or total replacement of synthetic epoxy vitrimers components, for example, by renewable sources (29–31). A variety of renewable raw materials such as vegetable oils, fatty acids, isosorbide derived from sugar, eugenol, catechin, and colophony, among others, were used to replace oil-based thermostet polymers (2, 34–44).

Despite these efforts, to date, it is not known with certainty how the use of these compounds of biological origin can impact the properties of vitrimers. Therefore, to analyze if bio-based vitrimers present improvements in their reprocessing properties, we carried out a meta-analysis of the available bibliography, analyzing by statistical methods the interactions between reprocessability, the stability of the mechanical properties, and the use of organic materials. This analysis revealed that some of the biomaterials studied could improve the reprocessability properties of vitrimeric polymers. Therefore, the search for safer substitute vitrimeric polymers becomes an attractive option, intending to develop a fully renewable and environmentally friendly material with good mechanical properties in the reprocessed stages.

2. METHOD

2.1 Study search and identification

The data acquisition was carried out using the Scopus database, the main target of the search in the title, keywords, and abstract was the vitrimer term, and all the results were filtered, selecting for the analysis the data present in scientific articles. Before the filtering process, the number of publications with the word vitrimer from 2004 to 2021 was analyzed using the QtiPlot program. The search was conducted between July and August 2021. The initial search was refined using the terms reprocessability and bio, with the following keyword TITLEABS-KEY (vitrimer AND bio AND repro* AND) AND (LIMIT-TO (DOCTYPE, "ar")). The RIS file containing these data is available at [source of the RIS file].

2.2 Bibliometric network analysis

To perform the bibliometric analysis, the abstract, Author keywords, and index keywords were used. This data was analyzed using VOSviewer software (version 1.6.10) (45). From the first analysis, trend themes were identified, and the terms reprocessability and bio were selected for the refinement of the initial search using the search key: TITLE-ABS-KEY (((vitrimer AND bio * AND repro *) AND (LIMIT-TO (DOCTYPE, "ar")) The bibliometric analyzes of the data obtained from the second search were performed as previously described.

2.3 Data extraction and quality assessment

The articles to be analyzed were selected according to the following criteria: number of reprocesses, tensile properties of reprocessed vitrimers, experimental error, or standard deviation. Information was extracted from the publications according to the inclusion criteria. The data extracted from the trials were the following: study name, year of publication, sample size, number of reprocesses, material composition, tensile properties of reprocessed vitrimers (Young's Modulus (MPa), Stress at break (MPa), Strain at break (%)). When the document did not present the data tables, the data was extracted from the curves of the graphs. Engauge Digitizer software (46) was used to extract data from these figures. From the data obtained, the 95% confidence intervals (CI95%) were calculated.

2.4 Statistical analysis

As there are different compositions of vitrimeric materials, the effect of bio on tensile properties was evaluated after reprocessing the vitrimers employing the correlation between the tensile property data and the number of reprocesses of the polymeric materials. The Jamovi (version 1.8.4) module MAJOR (47) was used to obtain the meta-analysis and the forest diagram. The analysis was carried out using the Fisher r-to-z transformed correlation coefficient as the outcome measure. A random-effects model was fitted to the data. The amount of heterogeneity (i.e., tau²) was estimated using the restricted maximum-likelihood estimator (48). In addition to the estimate of tau², the Q-test for heterogeneity (49) and the I² statistic are reported. In case any amount of heterogeneity is detected (i.e., tau² > 0, regardless of the results of the Q-test), a prediction interval for the true outcomes is also provided. Studentized residuals and Cook's distances are used to examine whether studies may be outliers and/or influential in the context of the model. Studies with a studentized residual larger than the 100 x (1 - 0.05/(2 X k)) percentile of a standard normal distribution are considered potential outliers (i.e., using a Bonferroni correction with two-sided alpha = 0.05 for k studies included in the meta-analysis). Studies with a Cook's distance more significant than the median plus six times the interquartile range of the Cook's distances are considered influential. The rank correlation test and the regression test, using the standard error of the observed outcomes as the predictor, are used to check for funnel plot asymmetry.

3. RESULTS

The search strategy using the Scopus database produced a total of 343 references between 2003 and 2021, and all the results were filtered reviews (20), congresses (6), erratum (3), book chapters (1), limiting the search to scientific articles (313). The number of documents published per year is shown in Figure 1.
The data in Figure 1 follow a polynomial of order 2. The coefficient of determination ($R^2$) found was equal to 0.861. The model and associated R2 show that interest in the issue of vitrimers has increased since 2015, according to Leibelier and his collaborators (11) mentioned the concept for the first time. This result shows that this topic is growing, suggesting a potential field, presenting research and development opportunities for new materials with various applications (10, 50, 51).

In order to identify trends in the showcases, the titles and abstracts of these documents were saved in RIS format and analyzed with the VOSviewer software. The results obtained are shown in Figure 2. In addition, the *MAP.txt and *NET.txt files generated by VOSviewer are available at https://github.com/angelybeclov/Bio-efect-in-vitrimers-reprocessabilily/blob/d52bfd4f38fb560e583b15d3132eb27b3d448288/vitri%202.txt.

Figure 2. Bibliometric analysis VOSviewer a) Network b) Overlay from the key using the key TITLE-ABS-KEY (vitrimer).
Figure 2(a) represents the cluster terms of the public vitrimers and identifies three main clusters. The first, in green, highlights several links related to the mechanical properties and composition of vitrimeric materials. The second group, in red, is dominated by the network topology and structure connections, an aspect of great importance in glass cabinets since this is what allows the cross-link reactions, which give rise to desirable properties such as self-healing and reprocessability. Finally, the third cluster in blue is dominated by the composite node and recyclability.

In Figure 2(b), the size of the circles represents the average publication of a term, and the gradient color from blue to yellow shows the freshness of the articles. The superimposed visualization in Figure 2(b) shows the most relevant terms in the publications in descending order: elongation, Young module, carbon nanotube, and excellent reprocessability. The analysis carried out and highlighted for this article includes terms such as reprocessability, tensile strength, and bio.

The research was refined using the key from the bibliometric analysis, and 28 articles were found (2, 25, 27, 33, 36, 41, 52–73), corresponding to 8.94% of the publications found with the first search key. After assessing eligibility to 28 publications using our inclusion and exclusion criteria described in the methods section, eight studies were included that met our criteria in the current review and statistically relevant information for the construction of the analysis. Table 1 shows the 1st author of the study and the year of publication, the number of reprocessed times, the total number of replicates, and the Adjusted Correlation (adjR).

### Table 1. Statistically relevant data from selected documents.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>Bio compound</th>
<th>Times reprocessed</th>
<th>Total replicates</th>
<th>adjR*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zhu Y. et al (33)</td>
<td>2020</td>
<td>Renewable castor oil and DL-limonene</td>
<td>4</td>
<td>12</td>
<td>0,956350723</td>
</tr>
<tr>
<td>Hajili F. et al (54)</td>
<td>2021</td>
<td>Isobornyl methacrylate (iboma, from pine sap)</td>
<td>4</td>
<td>12</td>
<td>0,939440737</td>
</tr>
<tr>
<td>Hajili F. et al (54)</td>
<td>2021</td>
<td>Isobornyl methacrylate (iboma, from pine sap)</td>
<td>4</td>
<td>12</td>
<td>0,961763301</td>
</tr>
<tr>
<td>Hajili F. et al (54)</td>
<td>2021</td>
<td>Isobornyl methacrylate (iboma, from pine sap)</td>
<td>4</td>
<td>12</td>
<td>0,356501745</td>
</tr>
<tr>
<td>Xu Y. et al (25)</td>
<td>2020</td>
<td>Vanillin</td>
<td>3</td>
<td>9</td>
<td>0,763541667</td>
</tr>
<tr>
<td>Xu Y. et al (25)</td>
<td>2020</td>
<td>Vanillin</td>
<td>3</td>
<td>9</td>
<td>0,669127082</td>
</tr>
<tr>
<td>Chen F. et al (60)</td>
<td>2020</td>
<td>Acetoacetate-modified cardanol</td>
<td>3</td>
<td>9</td>
<td>0,87693783</td>
</tr>
<tr>
<td>Chen F. et al (60)</td>
<td>2020</td>
<td>Acetoacetate-modified cardanol</td>
<td>4</td>
<td>12</td>
<td>0,785717184</td>
</tr>
<tr>
<td>Ma Z. et al (27)</td>
<td>2017</td>
<td>Isosorbide-derived epoxy</td>
<td>4</td>
<td>12</td>
<td>0,488558433</td>
</tr>
<tr>
<td>Geng H. et al (41)</td>
<td>2018</td>
<td>Vanillin</td>
<td>4</td>
<td>12</td>
<td>0,299147163</td>
</tr>
<tr>
<td>Geng H. et al (41)</td>
<td>2018</td>
<td>Vanillin</td>
<td>4</td>
<td>12</td>
<td>0,456045508</td>
</tr>
<tr>
<td>Geng H. et al (41)</td>
<td>2018</td>
<td>Vanillin</td>
<td>4</td>
<td>12</td>
<td>0,292952129</td>
</tr>
<tr>
<td>Memom H. et al (66)</td>
<td>2020</td>
<td>Vanillin</td>
<td>4</td>
<td>20</td>
<td>0,991599386</td>
</tr>
<tr>
<td>Memom H. et al (66)</td>
<td>2020</td>
<td>Vanillin</td>
<td>4</td>
<td>20</td>
<td>0,846873407</td>
</tr>
<tr>
<td>Hajj R. et al (64)</td>
<td>2020</td>
<td>Biobased polyimine vitrimers</td>
<td>6</td>
<td>24</td>
<td>0,995821508</td>
</tr>
<tr>
<td>Hajj R. et al (64)</td>
<td>2020</td>
<td>Biobased polyimine vitrimers</td>
<td>6</td>
<td>24</td>
<td>0,957329202</td>
</tr>
<tr>
<td>Hajj R. et al (64)</td>
<td>2020</td>
<td>Biobased polyimine vitrimers</td>
<td>6</td>
<td>24</td>
<td>0,58162383</td>
</tr>
</tbody>
</table>

* Adjusted Correlation (adjR).
Figure 3. Funnel plot for the selected studies of reprocessability of vitrimers.

It was found that eight articles presented useful data for the proposed meta-analysis. Some articles had more than one useful case and used Fisher's transformation to remove a possible bias in the untransformed correlation coefficient. A total of k=17 studies were included in the analysis. The observed Fisher r-to-z transformed correlation coefficients ranged from 0.3018 to 3.0844, with most estimates being positive (100%). The estimated average Fisher r-to-z transformed correlation coefficient based on the random-effects model was \( \hat{\mu} = 1.2052 \) (95% CI: 0.7824 to 1.6279). Therefore, the average outcome differed significantly from zero (z = 5.5876, p < 0.0001). According to the Q-test, the true outcomes appear to be significative heterogeneous (Q(16) = 170.2953, p < 0.0001, \( \tau^2 = 0.6892, I^2 = 88.6893\% \)), which we can interpret as a moderate case of heterogeneity (74). A 95% prediction interval for the true outcomes is given by -0.4760 to 2.8863. Hence, although the average outcome is estimated to be positive, in some studies, the true outcome may be negative. Examining the studentized residuals revealed that none of the studies had a value larger than ± 2.9738. There was no indication of outliers in the context of this model. According to Cook's distances, one study (64) could be considered to be overly influential. The regression test indicated funnel plot asymmetry (p = 0.0384) but not the rank correlation test (p = 0.4420).

Figure 3 shows the Funnel plot (75) which is a valuable tool to detect biases in a meta-analysis, where the treatment effect is plotted on the horizontal axis and the standard error on the vertical axis. The diagonal lines represent 95% confidence pseudo-limits around the summary effect for each standard error on the vertical axis. These show the expected distribution of the studies in the absence of heterogeneity or selection bias. In the absence of heterogeneity, 95% of the studies must be within the funnel defined by these diagonal lines. In our case, heterogeneity is evident since 11 studies are clearly out of bounds (76).

In Fisher's transformation of the correlation coefficient, the actual effect is 1.21. Most of the studies find the region of standard error between 0.40 and 0.20. 65% of the studies are between the region of the standard error of 0.40 and 0.30, that is, at the base of the funnel chart. 35% of the remaining studies are in the region between 0.20 and 0.30. As described in the source code of the Jamovi MAJOR module, the data is distributed among the regions comprising 90% (white), 95% (gray), 99% (dark gray), and the rest is more beyond 99% probability. Furthermore, visual inspection of the contour enhanced funnel plots did not confirm an evident presence of publication bias in most studies.
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One approach to determining the evidential value of the studies included in a meta-analysis is to determine the statistical power of the reported tests, using forest plots as the critical graphical method used in the meta-analysis. This diagram is the graphical representation resulting from systematic quantitative reviews and is designed to compare the effects of treatments in quantitative studies (77, 78). The Forest Plot, shown in Figure 4, lists all the selected studies. The relevance of the studies is presented as a percentage. All the studies had a similar relevance percentage, where the three studies were carried out by (64). The effects and their 95% probability confidence limits are shown on the right-hand side of the relevance percentage.

<table>
<thead>
<tr>
<th>Study</th>
<th>Relevance</th>
<th>Effect</th>
<th>CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zhu Y. et al (2020)</td>
<td>5.8%</td>
<td>1.90</td>
<td>[1.25, 2.55]</td>
</tr>
<tr>
<td>Hajili F. et al (2021).1</td>
<td>5.8%</td>
<td>0.42</td>
<td>[-0.24, 1.07]</td>
</tr>
<tr>
<td>Hajili F. et al (2021).2</td>
<td>5.8%</td>
<td>1.97</td>
<td>[1.32, 2.62]</td>
</tr>
<tr>
<td>Hajili F. et al (2021).3</td>
<td>5.8%</td>
<td>0.37</td>
<td>[-0.28, 1.03]</td>
</tr>
<tr>
<td>Xu Y. et al (2020).1</td>
<td>5.4%</td>
<td>1.00</td>
<td>[0.20, 1.80]</td>
</tr>
<tr>
<td>Xu Y. et al (2020).2</td>
<td>5.4%</td>
<td>0.81</td>
<td>[0.01, 1.61]</td>
</tr>
<tr>
<td>Chen F. et al (2020).1</td>
<td>5.4%</td>
<td>1.36</td>
<td>[0.56, 2.16]</td>
</tr>
<tr>
<td>Chen F. et al (2020).2</td>
<td>5.8%</td>
<td>1.06</td>
<td>[0.41, 1.71]</td>
</tr>
<tr>
<td>Ma Z. et al (2017)</td>
<td>5.8%</td>
<td>0.53</td>
<td>[-0.12, 1.19]</td>
</tr>
<tr>
<td>Geng H. et al (2018).1</td>
<td>5.8%</td>
<td>0.31</td>
<td>[-0.34, 0.96]</td>
</tr>
<tr>
<td>Geng H. et al (2018).2</td>
<td>5.8%</td>
<td>0.49</td>
<td>[-0.16, 1.15]</td>
</tr>
<tr>
<td>Geng H. et al (2018).3</td>
<td>5.8%</td>
<td>0.30</td>
<td>[-0.35, 0.96]</td>
</tr>
<tr>
<td>Memom H. et al (2020).2</td>
<td>6.2%</td>
<td>1.24</td>
<td>[0.77, 1.72]</td>
</tr>
<tr>
<td>Haj R. et al (2020).2</td>
<td>6.3%</td>
<td>1.91</td>
<td>[1.49, 2.34]</td>
</tr>
<tr>
<td>Haj R. et al (2020).3</td>
<td>6.3%</td>
<td>0.66</td>
<td>[0.24, 1.09]</td>
</tr>
</tbody>
</table>

**Figure 4.** Forest plot of meta-analysis for vitrimers articles selected.

The Forest plot shows the results of the different studies, with a CI of 95%, and the overall effect helped us visualize the heterogeneity between studies, which is expressed by the different confidence intervals with little or no overlap. Each study is represented by a square whose area is usually proportional to the contribution of each one to the overall result. Also, the square is within a segment that represents the extremes of its confidence interval. If these intervals do not cross the null value of the outcome variable, it will be statistically significant; which in our case, ten studies are statistically significant (78–80).

Young's modulus after reprocessing was the typified mean difference, which in this case was calculated so that positive values indicated a favorable result for incorporating bio compounds to improve vitrimer reprocessing (43)(59)(81)(82)(83). Thus, the average effect of the model is 1.21, with an upper limit equal to 1.63 and a lower limit equal to 0.78. Likewise, it is worth highlighting the notable heterogeneity of the results, so the model effect is positive and different from zero. According to this, the meta-analysis shows that bio compounds improve Young's modulus of vitrimers after reprocessing.

**CONCLUSIONS**

Vitrimers consist of polymeric networks capable of reorganizing their topology without harming the integrity of the material. These types of polymers have highly desirable properties, combining malleability, recyclability, cure, and repair at high temperatures with insolubility and low shape changes, which implies that vitrimers can be designed to obtain reprocessable materials that can replace traditional thermosets, which is a crucial step to face the problem of the disposal of plastic materials after use. Thanks to these advantages, and intending to make sustainable the production of this kind of materials, various authors have explored the use of raw materials from renewable resources for partial or total replacement of synthetic vitrimers components, thus increasing the environmentally friendly profile of the vitrimers, thanks to the reduction in both, the oil consumption and carbon dioxide emissions.
To analyze the possibilities in this field, in this work, we perform a systematic collection of data present in the literature and investigate interactions between re-processability, the stability of the mechanical properties, and the use of materials of biological origin for the synthesis of vitrimic polymers. Hundreds of papers were analyzed using VOSviewer, where it was found that only eight articles presented useful data for the proposed meta-analysis, with a total of 17 studies were included in the analysis. Through statistical analysis it was possible to visualize the heterogeneity between the studies.

The results obtained show that some of the biomaterials that have been studied to date can improve the reprocessability properties of vitrimers, which indicates that the bio-based vitrimic polymers can become an attractive option for the development of environmentally friendly materials with good mechanical and reprocessability properties.

CONFLICT OF INTEREST
None.

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Sample CRediT author statement

Angela Yeissel Becerra Lovera: Conceptualization, Methodology, Data analysis, and Writing-Original draft preparation Methodology, Data analysis and Revision
Fernando G. de Souza Junior: Conceptualization, Methodology, Data analysis, Revision and Supervision.

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