Life Cycle Assessment and Characterization of Tincal Ore Reinforced Polyester and Vinylester Composites

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Abstract: In this study, the quality performance, compressive strength, surface hardness, electrical conductivity, and life cycle assessment (LCA) of the composites produced by reinforcing tincal \((\text{Na}_2\text{B}_4\text{O}_7\cdot10\text{H}_2\text{O})\) into polyester and vinylester resins at different rates have been determined. Tincal ore, which is ground with a particle size of 74-149 microns, is dried in an oven at 105 °C for 2 hours and then added to the resins at the ratios of 0 wt.%, 1 wt.%, 2 wt.%, and 3 wt.%. According to the results obtained, it has been determined that the compressive strength and Shore D hardness of the composite raises as the tincal mass ratio increases up to certain amounts. According to the mechanical test results, it is found that 3 wt.% tincal reinforcement maximized the compressive strength of the polyester composite, and 2 wt.% tincal reinforcement maximized the compressive strength of the vinylester composite. In the electrical conductivity test results, it is seen that the first relaxation time of the polyester composite is \(2.14\times10^{-4}\) s and the relaxation times of vinylester composite vary between \(10^{-4}\) and \(10^{-6}\) seconds. LCA results showed that vinylester composite had more environmental effects than polyester composite except for ozone layer depletion (ODP) effect. Although there is a partial increase (<0.5%) in the environmental impact of composites with tincal reinforcement, it is thought that the increase in the technical performance of the composites will tolerate this partial increase.

Keywords: Polyester, vinylester, tincal, hardness, compressive strength, dielectric properties, life cycle assessment.

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INTRODUCTION

Resins are widely used in many different sectors as the basic raw material in the production of high-performance composite materials. Some of the resins commonly used in the production of fiber-reinforced composite materials are polyester, vinylester, polyurethane, and epoxy resins (1-8). Many natural and synthetic fillers are preferred to increase the technical properties of materials obtained from resins and to reduce the amount of petrochemicals used. With the help of these additives and fillers, some physical and chemical properties of the synthesized products can be improved (9-15). Besides, there are improvements in the mechanical and thermal properties of composite materials produced from resins reinforced with various additives and fillers (16).

In a study in the literature, it has been determined that the fire safety performance of the composites obtained by adding boron nitride to the epoxy resin increases. It has been observed that the composite materials produced by reinforcing different proportions of boron nitride (filler) into vinylester...
resin have improvements in impact, hardness, and abrasion resistance (17,18).

In another study, composite samples are obtained by reinforcing unsaturated polyester with borax at different mass ratios. It has been observed that the addition of certain amounts of borax increases the mechanical strength, Shore D hardness, and thermal conductivity coefficient of polyester composites (19). There is also a need to make environmental assessments in studies to increase the performance of such resin composites. For example, the life cycle assessment (LCA) method is used in environmental sustainability studies of composite materials (20-22). In the literature, there are studies for the production of composite materials and determining the environmental performance of these materials by LCA method (23-25). With LCA studies, environmental effects of composite materials such as climate change impact, acidification, and eutrophication potentials are shared transparently (26,27).

In this research, composite materials have been produced by reinforcing tincal at different rates into orthophthalic-based unsaturated polyester and bisphenol-A epoxy-based vinylester resins. It was determined that certain amounts of tincal reinforcement increase the compressive strength and surface hardness of polyester and vinylester composites. In addition, the dielectric properties of the produced composites and by LCA method their environmental effects were investigated.

MATERIALS AND METHODS

Unsaturated polyester (UP), methyl ethyl ketone peroxide (MEKP), and cobalt octoate (Co Oc) components were supplied from Turkuaz Polyester. Vinylester resin and its components were purchased from Poliya Company (Turkey). Besides, tincal used in this study was supplied from the Eti Maden (Eskişehir Kirka Boron) factory.

Tincal was added to the UP at different rates (0 wt. %, 1 wt.%, 2 wt.%, and 3 wt.%) and mixed at 1000 rpm for 4 minutes. After adding 0.5 wt.% Co Oc and 1.5 wt.% MEKP, respectively, at room temperature at a mixing speed of 750 rpm for 90 seconds, they were poured into standard molds. After waiting 24 hours for the curing of the obtained samples, necessary tests and analyses were carried out (28-35).

Also, tincal was added to the bisphenol-A epoxy-based vinylester resin. After providing a homogeneous mixture of vinylester resin and tincal, certain amounts of the hardener were added and the mixture was mixed and heated (600 rpm, 2 min, and 45 °C). After the mixture obtained was poured into standard molds and waited for one day for curing, necessary tests and analyses were carried out.

Ultrasonic water bath was used to prevent air bubbles that may occur in the prepared mixtures. Besides, mold release agents are applied to standard steel cylindrical molds, allowing the samples to come out easily. In Figure 1, the mixtures prepared under laboratory conditions and the samples obtained are shown.

![Figure 1: Preparation of tincal-reinforced vinylester and polyester composites.](image)

As seen in Figure 2, the samples are produced in a cylindrical shape with a diameter/length ratio of ½ (40 mm/80 mm). Compressive strength is performed by ASTM C 579-01. In the experimental study, a loading rate of 41MPa/min is applied for all samples. Three samples are produced from each mixture to perform the compressive strength.
Shore D hardness tests were carried out by ISO 868 (ASTM D 2240) standard. As seen in Figure 3, cylindrical samples with a diameter of 4 cm are used to determine the hardness values of polyester and vinylester composites. Hardness measurements have been made from 5 different points on 3 different samples and calculated by averaging.

Samples with a diameter of 4 cm were used to determine the dielectric properties of the composites (Figure 4). The dielectric properties have been measured with the Novacontrol Alpha-A impedance analyzer at a temperature of 300 K in the frequency range of 10 Hz and 10 MHz.

**Life Cycle Assessment**
In this study, ISO 14040 and ISO 14044 standards were used to evaluate the environmental impact of the composite materials produced (36).

**Purpose and Scope**
The aim of the study is to estimate the main environmental effects of polyester and vinylester composites produced with tincal reinforcement at different rates. The system boundaries of the presented composites follow a cradle-to-gate approach and include manufacturing steps of polyester and vinylester composites. The functional basis chosen for this study is the production of 1 kg of tincal reinforced resin composites. In the life cycle analysis shown in Figure 5, raw material procurement (1), transportation of raw materials to the mixing laboratory (2), and composite products in the laboratory (3) stages.
Inventory Analysis
The production process of the examined composites is explained in detail in the sections above. The inventory data presented in Table 1 were obtained from laboratory measurements as part of the experimental work conducted in this study and converted to the functional unit “1 kg of tincal-reinforced resin composite”. It is assumed that all transportation is done by road using diesel fuel. A distance of 100 km is assumed to transport all raw materials to the mixing plant. The mixers and ultrasonic baths used in the preparation process of resin composites are low voltage and 0.022 kWh energy is used to produce 1 kg of resin composite. Life cycle inventory data is taken from the Ecoinvent V3.5 database.

Table 1: Inventory for the production of 1 kg of tincal-reinforced resin composites.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Resins (g) (polyester and vinylester)</th>
<th>Co Oc (g)</th>
<th>MEKP (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 wt.%</td>
<td>980</td>
<td>4.90</td>
<td>14.70</td>
</tr>
<tr>
<td>1 wt.%</td>
<td>971</td>
<td>4.86</td>
<td>14.57</td>
</tr>
<tr>
<td>3 wt.%</td>
<td>952</td>
<td>4.76</td>
<td>14.28</td>
</tr>
</tbody>
</table>

Impact Assessment
LCA modeling was performed in SimaPro 9.1.1.1. As in similar studies (37), CML-IA baseline method created by Center for Environmental Sciences (Leiden University) has been chosen for life cycle impact assessment. Six environmental impact categories are considered in the analysis, including climate change, acidification, eutrophication, fossil fuel, photochemical oxidation, and ozone depletion.

RESULTS AND DISCUSSIONS
In Figure 6, the compressive strength values of tincal reinforced polyester and vinylester composite samples are seen comparatively. When the graph is examined, it is seen that the highest compressive strength value (124.95 MPa) is reached when 2 wt.% tincal is added to the vinylester resin. When 2 wt.% tincal is added to the vinylester resin, the compressive strength increases by 4.2%. It has been determined that the compressive strength increases with the increase in the amount of tincal in the polyester resin. When 3 wt.% tincal is added to the polyester resin, the compressive strength raises by 14.6%.
In Figure 7, Shore D hardness of tincal reinforced resin composites is compared. The addition of tincal up to 2 wt.% to the vinylester resin increased the surface hardness (3.6%) of the composite. However, the addition of tincal up to 3 wt.% decreases both Shore D hardness of the vinylester composite. The addition of tincal up to 2 wt.% to the orthophthalic-based polyester resin increases the surface hardness (4.1%) of the composite. However, up to 3%, tincal reinforcement slightly decreases Shore D hardness of the polyester composite.

The images of tincal reinforced resin composites after compression tests are given in Figure 8. The vinylester composite samples do not disperse after the compression test and the experiments are completed with a shortening in height. It is in the form of deformation that occurs with an overlapping agglomeration in the middle regions of the samples. However, the lengths of the polyester
composites are shortened and the samples are deformed vertically. It has been observed that the shortening in length decreases as the amount of tincal increases. In contrast to the vinylester samples, cracking occur in the polyester composites.

Figure 8: Tincal-reinforced composite specimens after compression strength test.

Dielectric Polarization and Relaxation Mechanisms of Tincal-Reinforced Resin Composites

It provides information about the dielectric properties of materials, and their mechanisms such as conduction, and polarization/relaxation. Many parameters such as thickness, structure, and surface area of the material are effective when examining dielectric properties. With the help of these parameters, real and imaginary dielectric constants are obtained from the capacitance and conductance value of the material. While the real dielectric constant ($\varepsilon'$) is a measure of the resistance of the material against charge transmission in its internal structure, the imaginary dielectric constant ($\varepsilon''$) is a measure of the energy lost during the charge transition in response to the material to the electric field. Since these two parameters do not react to the electric field at the same time, a phase difference occurs between them. However, to obtain comprehensive information about the conduction and polarization/relaxation mechanisms in the material, it is necessary to look at the loss tangent, which is defined as the ratio of energy loss to resistance and is a measure of the phase difference angle.

$$\varepsilon^* = \varepsilon' - j \times \varepsilon'' \quad (\text{Eq. 1})$$

$$\tan(\delta) = \frac{\varepsilon''}{\varepsilon'} \quad (\text{Eq. 2})$$

In Figure 9, the dielectric properties of the tincal-reinforced polyester composite are shown.
When Figure 8 is examined, it is seen that there is no change in the tan(δ) or dielectric properties of the materials with doping, but two spot frequencies (475 Hz and 175 kHz) with full polarization is provided for each material. Alternating current at frequencies ranging from 100 Hz to 1 MHz is applied to these materials and they are exposed to an electric field. From 100 Hz, positive charges and negative charges start to polarize in the direction of the field by forming dipoles, and after this frequency, all polarized dipoles start the relaxation process. The relaxation process can be roughly described by the following spot frequency-period relationship.

\[ \omega \times \tau = 1 \]  

(Eq. 3)

According to this relationship, the first relaxation time for all the materials is obtained as \(2.14 \times 10^{-4}\) s. The polarization type that completes the relaxation in this time interval is dipole or Maxwell-Wagner polarization. In other words, dipole or Maxwell-Wagner type polarization takes place around 475 Hz in all materials. This relaxation process continues up to about 10 kHz according to Figure 8. After 10 kHz, all of the dipoles begin to polarize again in the direction of the applied AC (alternating current) field, and full polarization is achieved a second time around 175 kHz. According to Equation 3, the relaxation process here is obtained as \(9 \times 10^{-7}\) s. The relaxation time at this spot frequency indicates that the polarization mechanism shifts from dipole or Maxwell-Wagner type polarization to ionic polarization.

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**Figure 9:** Dielectric properties of tincal-reinforced polyester composites.
Figure 10: Cole-Cole diagram of tincal reinforced vinylester composites.

It contains at least one semicircle for materials that operate as a mechanism of characteristics, polarization, and relaxation of dielectric properties as a smooth behavior and is known as Cole-Cole Diagram. The completion of a semicircle can be depicted with an RC circuit in the material. If an unfinished semicircle reveals that the polarization is realized, but the relaxation does not occur, such behavior means that there is no resistance to polarization. Thus, the depicted circuit can be expressed as a single capacitor in this case. In Figure 10, it is seen that a semicircle is completed in all of the vinylester composites with tincal reinforced vinylester and the continuation of a quarter circle. In this form, the materials can be expressed by a capacitor depiction in the series with an RC circuit consisting of an electrically connected resistance (R) and a capacitor (C) in parallel with each other in the internal structure. This depicted circuit is called an equivalent circuit and its diagram is as in Figure 11. Equality is used on the top of the semicircle to calculate relaxation times from Cole-Cole diagrams. According to Figure 10 is examined, the relaxation times of vinylester and tincal reinforced vinylester composites vary between $10^{-4}$ and $10^{-6}$ seconds. Also, it is seen that their amplitude increases with reinforcement rates in the first and second semicircles. We can say that the increase in amplitude reduces relaxation times. Finally, polarization and relaxation mechanisms of tincal reinforced vinylester composite composites can be attributed to the dipole type relaxation, which we call Maxwell Wagner or orientation.

Figure 11: Tincal reinforced resin composites equivalent circuit diagram.

Environmental Sustainability Assessment
The environmental impact results for the production of 1 kg of tincal reinforced polyester and vinylester resin composites are presented in table 2. The total CC effect of polyester composite (P (3 wt. %)) and vinylester composite (V (3 wt. %)) with the best compressive strength performance was estimated to be 3.77 kg CO$_2$/kg and 4.29 kg CO$_2$/kg, respectively. In both composite materials, the resin is the main hotspot, contributing 97%.


When Table 2 is examined, it is seen that the environmental impacts of vinylester resin composites, except for ODP, are higher than the environmental impacts of polyester resin composites. It is seen that the contribution of accelerators, electricity, transportation, and tincal used in composite production to environmental effects is quite low. In this case, the environmental effects of bisphenol A epoxy-based vinylester resin (except for ODP) are observed to be higher than those of orthophthalic acid-based unsaturated polyester resin.

It was calculated that there is an increase in environmental effects with the increase of tincal ratio in polyester and vinylester resins, but this increase contributes less than 1% to the total effect. When Figure 5 and Table 2 are evaluated together, the compressive strength increases with the increase of tincal in the polyester resin and when 3 wt.% tincal is added to the resin. It has been determined that there is an increase of 0.12% in the climate change category, 0.07% in fossil resource consumption, 0.11% in ozone depletion, 0.02% in photochemical oxidation, 0.34% in acidification and 0.15% in eutrophication. The highest compressive strength and surface hardness values are obtained when 2 wt.% tincal is added to the vinyl ester resin. When this 2% change is examined in terms of environmental impact, it was found that there is an increase of 0.10% in the climate change category, 0.07% in fossil resource consumption, 0.19% in ozone depletion, 0.02% in photochemical oxidation, 0.29% in acidification, and 0.14% in eutrophication.

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REFERENCES


