Abstract

Rapid Advancement in the field of advance Biocomposite has attracted large number of researchers to diagnose and expand the use of light weighted and environment friendly materials for various applications. In this work, depolymerized natural rubber (DNR) was prepared and used as toughening agents for epoxy resin and almond shell particles are filled in modified epoxy resin as reinforcing material. Further, different tests including Tensile Test, Compression Test, Hardness Test, Impact Test etc. were performed to diagnose the effect of various weight percentage (wt%) of composition of blended DNR for achieving maximum toughness and then its effect on treatment with different weight percentage of Almond Shell Particle. Results were analyzed and finally the conclusion is made based on the experiments.

Keywords: Composite; Epoxy; DNR; Almond shell particle; Tensile property

Introduction

Epoxy resins are very important class of thermosetting polymers that exhibit high tensile strength and modulus, excellent chemical and corrosion resistance, good dimensional stability, low creep and reasonable performance at elevated temperature. Hence, they are widely used as matrix resins for fiber reinforced composite materials and in structural adhesives, surface coatings and electrical laminates. However, such properties in an epoxy require moderate to high levels of crosslinking which can and usually does result in brittle behavior. Toughening of epoxy resin has been the subject of intense investigation, because epoxy resins have low fracture energy [1,2].

Natural rubber has attracted great interest because it is a renewable resource, whereas its synthetic counterparts are mostly manufactured from non-renewable oil based resources. Several studies have already been done on toughening epoxy resin using natural rubber (Figure 1) [3-5].

Epoxy resins are reactive chemicals which are combined with other chemicals known as hardener or curing agent such as triethylenetetramine (TETA) and 4,4´-diaminodiphenylsulfone (DDS) to give systems capable of conversion to predetermined thermoset products.

Natural rubber

One of the most important polymeric materials is natural rubber (NR) which contains 93-94% cis-1, 4-polyisoprene (Figure 2). Natural Rubber latex is the form in which rubber is exuded from the Hevea brasiliensis tree as an aqueous emulsion. The rubber particles range in size from about 50 Å to about 30,000 Å (3μm). Exceptionally particles up to 5-6 μm in diameter are found. The molecular weight (MW) is normally in the range of 10^4-10^6 g/mol, depending on the age of the rubber tree, weather, method of rubber isolation and other factors [6].

The advantages of NR are outstanding flexibility, excellent heat built up properties and high mechanical strength. Moreover, it is a renewable resource, whereas its synthetic counterparts are mostly manufactured from non-renewable oil based resources [7].

Depolymerization of polymer is based on a reaction in which a reagent with reactive polar groups opens the active linkage in the polymer backbone. It can reduce chain length of polymer. Natural rubber that is subjected to depolymerization is called depolymerized natural rubber (DNR) or liquid natural rubber. Having strong adhesive power and excellent crosslinking reactivity, it has been used widely as a raw material for adhesives, pressure-sensitive adhesives, sealing materials etc.

Almond shell particles

Almond shell is an organic residue which is lingo-cellulosic material forming a thick endocarp or husk of the almond tree fruit, which is separated in the process of extracting edible seeds. Almond shells have no importance in industry and generally burnt or dumped. Almond shell and almond shell particles are shown in the Figures 3a and 3b [8].
Preparation of DNR, modified epoxy and then hybrid biocomposite

Natural rubber latex was diluted in deionized water to a concentration of 5 wt% based on rubber content in a 1 liter reaction flask. After that CH$_2$CH$_2$COCH$_3$ and K$_2$S$_2$O$_8$ was added in an amount of 4 v% of total volume and 2 wt% based on the rubber content, respectively. The pH of above solution was adjusted to about 9-10 with 10 wt% aqueous KOH solution. Then, the mixture was mechanically stirred with a speed of 200 revolutions per minute (rpm) at 70°C for 24 hours under flowing air on the magnetic stirrer with hot plate. At the end of reaction, the mixture was coagulated by 1 wt% aqueous CaCl$_2$ solution (Tables 1 and 2).

The coagulated substance was dissolved in hexane and stirred with magnetic bar for 3 hours. Then, resulting solution was stood overnight and filtered with filter paper and dried at 40°C until weight is constant. DNR was blended with epoxy resin in an amount of 0.5, 1, 1.5, 2 and 2.5 wt% of epoxy resin. Blending formulation that showed the highest toughness was applied as matrix for preparation of almond shell particles filled biocomposite. The neat epoxy, modified epoxy and almond shell particles filled modified epoxy resin composites were prepared by vertical casting method. The universal testing machine, digital hardness testing machine and pendulum impact tester were used to study the mechanical properties of different biocomposites [9,10].

Testing and Results

Density

Results indicate that the material having higher wt% of almond shell particles have lower density than unfilled epoxy resin because almond shell particles have very less density and when they are mixed in epoxy resin then the density of biocomposite tends to decrease with the increase in wt% of almond shell particles (Figure 4 and Table 3).

Tensile test

In the present investigation all the tensile tests are conducted as per ISO test procedure with Specimen size based on ISO-1608: 1972 Standard. The tests are conducted on 100 kN servo hydraulic UTM machine (model 2008, ADMET make).

Figure 3a: Almond shells.

Figure 3b: Almond shell particles.

Table 1: Design of experiments.

<table>
<thead>
<tr>
<th>Designation</th>
<th>Epoxy resin (grams)</th>
<th>Hardener (grams)</th>
<th>DNR (grams)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C0</td>
<td>100</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>C1</td>
<td>100</td>
<td>10</td>
<td>0.5</td>
</tr>
<tr>
<td>C2</td>
<td>100</td>
<td>10</td>
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</tr>
<tr>
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<td>100</td>
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<td>10</td>
<td>2.5</td>
</tr>
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</table>

Table 2: Design of experiment for almond shell particles filled composites.

<table>
<thead>
<tr>
<th>Designation</th>
<th>Epoxy resin (grams)</th>
<th>Hardener (grams)</th>
<th>DNR (grams)</th>
<th>Almond shell particle (grams)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA1</td>
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<tr>
<td>CA2</td>
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<td>CA3</td>
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<tr>
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</table>

Table 3: Density of almond shell particles filled composites.

<table>
<thead>
<tr>
<th>DNR (wt%)</th>
<th>Almond shell particles, (wt%)</th>
<th>Weight, (g)</th>
<th>Volume, (cm$^3$)</th>
<th>Density, (g/cm$^3$)</th>
<th>Density, (kg/m$^3$)</th>
<th>Mean density, (kg/m$^3$)</th>
<th>Standard Deviation</th>
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</thead>
<tbody>
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<td>7.06</td>
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<td>1.17667</td>
<td>1176.7</td>
<td>1177.73</td>
<td>3.95</td>
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<td>7</td>
<td>1.18286</td>
<td>1182.9</td>
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<td>2.40</td>
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<tr>
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<td>7</td>
<td>1.10286</td>
<td>1102.9</td>
<td></td>
<td>4.00</td>
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<tr>
<td>1</td>
<td>40</td>
<td>7.72</td>
<td>7</td>
<td>1.10286</td>
<td>1102.9</td>
<td></td>
<td>2.92</td>
</tr>
</tbody>
</table>

Figure 4: Effect of wt% of almond shell particles on density.
From the results, in Figure 5a at initial loading there is an increase in stress followed by a plateau region that may be due to slippage of the Specimen. Remarkable differences can be seen on the ultimate tensile strength of DNR filled cured epoxy having different wt% of DNR given in Table 4. It can be seen from the results that for all specimens containing 1.0 wt% DNR, the ultimate tensile strength is highest among the other composition reported (Figure 5b). About 40% increase in ultimate tensile strength due to addition of 1.0 wt% of DNR has been noticed as compared to pure epoxy. This increase in strength is observed due to inter molecular dispersion of DNR in epoxy resin. Further addition of DNR on the epoxy resin decreases the ultimate tensile strength of the DNR filled cure epoxy due to accumulation of DNR at some places, which is present free without bonding. Similar observations have been noticed for % elongation as shown in Figure 5c. Modulus of elasticity was decreasing with increasing wt% of DNR but about 2.47 times increase in modulus of elasticity has been observed due to addition of 1.0 wt% of DNR in Almond Shell Particle based composite (as compared between Tables 4 and 5). Further addition of the DNR decreases the % elongation but is higher than the neat epoxy material [11].

Figure 5d shows the toughness or Energy/Volume on different DNR wt%. The toughness is calculated by integrating the polynomial which best fit the stress-strain curve for different wt% of DNR and almond shell particles. From Figure 5e it can be concluded that small wt% of DNR has a great effect on toughness of material.

**Compression test**

All the compression tests are conducted on 100 kN servo hydraulic UTM machine (model 2008, ADMET make). Here the ISO Standard ISO-1708: 1960 is used in Specimen preparation and testing. It is found that ultimate compressive strength of 20 wt% of almond shell particles is 145 MPa. This compressive strength is about 1.5 times ultimate compressive strength of the modified epoxy with 1 wt% DNR. From the present results, it can be said that the ultimate compressive strength has increased considerably due to addition of small weight percentage of almond shell particles (Figures 6a and 6b).

**Impact test**

An ISO 180:1993 plastic Standards is considered in Impact testing.

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**Table 4:** Tensile properties of cured epoxy filled with DNR.

<table>
<thead>
<tr>
<th>Designation of Composition</th>
<th>Depolymerized rubber, wt%</th>
<th>Ultimate strength (MPa)</th>
<th>% elongation</th>
<th>Energy/Volume (mJ/mm³)</th>
<th>Modulus of Elasticity (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C0</td>
<td>0.0</td>
<td>47.40</td>
<td>5.10</td>
<td>1.737</td>
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<td>C1</td>
<td>0.5</td>
<td>52.28</td>
<td>9.50</td>
<td>3.001</td>
<td>1.067</td>
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<tr>
<td>C2</td>
<td>1.0</td>
<td>67.33</td>
<td>12.58</td>
<td>5.229</td>
<td>0.912</td>
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<tr>
<td>C3</td>
<td>1.5</td>
<td>41.30</td>
<td>11.00</td>
<td>2.956</td>
<td>0.671</td>
</tr>
<tr>
<td>C4</td>
<td>2.0</td>
<td>39.89</td>
<td>7.17</td>
<td>1.416</td>
<td>0.526</td>
</tr>
<tr>
<td>C5</td>
<td>2.5</td>
<td>35.26</td>
<td>6.80</td>
<td>1.226</td>
<td>0.513</td>
</tr>
</tbody>
</table>

**Table 5:** Tensile Properties with varying wt% of almond shell particles in epoxy and 1wt% DNR blended composite.

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**Figure 5a:** Stress-strain diagram for different wt% of depolymerised natural rubber (DNR).

**Figure 5b:** Stress-strain diagram for different wt% of almond particle with 1.0 wt% of depolymerised natural rubber.

**Figure 5c:** Effect of wt% DNR on ultimate tensile strength and % elongation.

**Figure 5d:** Ultimate tensile strength and % elongation.

ISO-1708: 1960 is used in Specimen preparation and testing. It is found that ultimate compressive strength of 20 wt% of almond shell particles is 145 MPa. This compressive strength is about 1.5 times ultimate compressive strength of the modified epoxy with 1 wt% DNR. From the present results, it can be said that the ultimate compressive strength has increased considerably due to addition of small weight percentage of almond shell particles (Figures 6a and 6b).

---

**Impact test**

An ISO 180:1993 plastic Standards is considered in Impact testing.
The results show that by adding DNR in epoxy resin the impact strength of epoxy resin is increased by 80% on 1 wt% of DNR which is a very remarkable improvement. Also increase in impact strength here might be because DNR which is presented in matrix acted as stress concentrator creating shear yielding and/or crazing in the matrix. This can also be seen that at higher wt% of DNR the impact strength has been lowered it may be due to the rubber aggregation or accumulation because of which there are internal cavities and internal voids in the material [12]. Similarly, in the case of almond shell particles impact resistance is decreasing with the increase in wt% of almond shell particles (Figures 7a and 7b). This decrease in the impact properties might be due to the decrease in the bond strength in almond shell particles and matrix material at higher wt% (Tables 6 and 7).

**Hardness test**

In this study the hardness test have been conducted on L scale on Digital Rockwell hardness testing machine. Above results indicates that the hardness of the material increased with the increase in the wt% of DNR shown in Figure 8a. The increase in hardness might be due to the high hardness of DNR. From Figure 8b this can be seen that hardness of almond shell particles reinforced composite decreases with the increase in wt% of almond shell particles. This may be due to the softness or low hardness of almond shell particles.

The results show that by adding DNR in epoxy resin the impact strength of epoxy resin is increased by 80% on 1 wt% of DNR which is a very remarkable improvement. As Chuayjuljit [3] concluded that ENR product was applied as impact modifier for epoxy resin and Kumar and Kothandaraman [5] modified epoxy resin with maleate depolymerized natural rubber, MDPR so the DNR was used here for testing. Also increase in impact strength here might be because DNR which is presented in matrix acted as stress concentrator creating shear yielding and/or crazing in the matrix. This can also be seen that at higher wt% of DNR the impact strength has been lowered it may be due to the rubber aggregation or accumulation because of which there are internal cavities and internal voids in the material [12]. Similarly, in the case of almond shell particles impact resistance is decreasing with the increase in wt% of almond shell particles (Figures 7a and 7b). This decrease in the impact properties might be due to the decrease in the bond strength in almond shell particles and matrix material at higher wt% (Tables 6 and 7).
Flexural test

The flexural properties have a very important role in structural applications (Figures 9a, 9c and 9e). The flexural stress, flexural modulus and flexural strain are calculated by equations (i), (ii) and (iii) respectively. The flexural stress \( \sigma_f \), flexural modulus \( E_f \) and flexural strain \( \varepsilon_f \) for rectangular cross section are determined by the formula:

\[
\sigma_f = \frac{3PL}{2bd^2}, \quad (i)
\]

\[
E_f = \frac{L^3m}{4bd^4}, \quad (ii)
\]

\[
\varepsilon_f = \frac{6Dd}{L^2}, \quad (iii)
\]

From the Figures 9b, 9d and 9f this can be concluded that 10wt% of almond shell particles is the optimum filling wt% for almond shell particles because it gives the optimum flexural properties. This can also be observed that flexural stress and strain decreases drastically with the addition of more wt% of almond shell particles. This decrease in the flexural properties may be due to the insufficient filling of matrix material in the surrounding of almond shell particles.

Scanning Electron Microscopy (SEM)

Agglomeration of Almond Shell Particle with varying wt% of DNR can be better understood with the help of SEM images. Figure 10a shows the micrograph of 1 wt% of DNR blended in epoxy resin. In this more shearing zone can be seen and the rubber is well dispersed.
in epoxy resin. Good crosslinking of DNR with epoxy resin can be seen here leads to enhanced mechanical properties as this crosslinking overcome the brittle behaviour of epoxy resin.

Figures 10b-10e shows the SEM photograph of composite containing 10, 20, 30 & 40 wt% of almond shell particles respectively. It
is seen from the Figure 9 that almond shell particles are well dispersed in the epoxy resin matrix. Also, the size of almond shell particles was in the range of about 0.39 µm to 1 µm as seen in Figure 10f.

The micrographs of almond shell particles filled composite material shows that materials are failing due to pulling out of particles (Figure 10f).

In Figure 10b shear bands can be seen which leads to shear yielding of the material. And the dispersion of almond shell particles is good and no cavity can be seen. But at some places matrix cracking has taken place. Figure 10c micrograph the cavity which has occurred due to increase in wt% of almond shell particles. This diagram does not show the matrix cracking which has led the material to good strength [13,14].

And at higher wt% the material is failing due to insufficient filling of matrix materials around the particles. Many cavities are also taking place that are decreasing mechanical properties. Also the shearing zone can also be seen in all micrographs and with the wt% of almond shell particles shearing zone and layering of materials can be seen. Also in the micrographs of 30 wt% and 40 wt% of almond shell particles some voids and cracks can also be seen signifying brittle cracking and brittle failure which leads to the poor mechanical properties as seen in Figures 10d and 10e.

**Conclusion**

When 1 wt% of DNR is blended in epoxy resin then there is a substantial growth in the toughness of epoxy resin as well as other tensile properties. Hardness also increases with blended DNR. Flexural strength and compressive strength increases with increasing wt% of DNR till 1% and after that decreases. SEM showed significant dispersion of DNR till 1% and after that DNR started accumulating at one place. Thus, decreasing the Mechanical Properties. Therefore, it can be concluded that 1 wt% of DNR is an optimum concentration for
further mixing of reinforcing particles and fibers and 20 wt% of almond shell particles is the optimum concentration.

Acknowledgement
We are very thankful to Dr. P. C. Gope, Professor and Head, Department of ME (GBPUA&T), Pantnagar for providing guidance and complete infrastructure for performing various tests and experimentation. Also I am thankful to GEU and GBPUA&T.

References