THERMO-PHYSICAL PROPERTIES OF LIGHT WEIGHT EPOXY FOAMED BY SILOXANE BLOWING AGENT

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Abstract: The purpose of this study is to investigate the direct effect of using a blowing agent of siloxane (1, 1, 3, 3-tetramethydisiloxane) on the thermo-physical properties of the foamed epoxy. These properties are: density, glass-transition temperature, thermal conductivity and thermal expansion. The work has been conducted experimentally by manufacturing several specimens with different siloxane contents as: 0, 5, 10, 15 and 20 wt%. The properties of the specimens have tested under suitable conditions using different reliable instruments: differential scanning calorimetry, Lee-discs apparatus, and push rod dilatometer. Scanning electron microscope was used as well to analysis the morphological characteristics of the epoxy with respect to the pores generated by the blowing agent. In general, the foamed epoxy has shown different sizes of pores and extra crosslinking which leads to increase the glass-transition temperature of the material. Results show that the addition of 20% siloxane to the neat epoxy (as maximum) leads to: decreasing by 50% in bulk density, increasing by 20% in glass-transition temperature, decreasing by 30% in thermal conductivity, and decreasing by 75% in thermal expansion.

Keywords: Thermal properties, foamed epoxy, blowing agent, siloxane, insulation material.

1. Introduction

A wide range of important industrial applications uses epoxy resins, which have been Commercially accessible for decades and offer a long list of benefits that make up for their higher price tag. The interesting chemistry of these resins has drawn the attention of a number of accomplished scientists. Epoxy resins' technical uses are quite demanding, and new improvements are introduced on a yearly basis. Epoxy is a solid thermoset polymer has a strong structure due to the crosslinking bonds that gives the material many preferable physical properties, such good thermal, mechanical and chemical resistance [1-2]. The thermo-physical characteristics of pure epoxy are listed in Table 1.

Table 1. The thermo-physical characteristics of pure epoxy [1-5]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>1.2-1.4 g/cm³</td>
</tr>
<tr>
<td>Glass-transition temperature</td>
<td>350-380 K</td>
</tr>
<tr>
<td>Thermal conductivity coefficient</td>
<td>0.2-0.3 W/m.K</td>
</tr>
<tr>
<td>Thermal expansion coefficient</td>
<td>10-20 x10⁻⁵ 1/K</td>
</tr>
</tbody>
</table>

Light weight epoxy (LWE) is extensively utilized in a broad range of industries because of its inexpensive cost as well as adequate physical and mechanical qualities, as well as high...
resistance to moisture, heat, and solvents. Consequently, the necessity to explore and anticipate the behavior of light weight epoxy based materials under specified situations and to increase their properties for many applications is on the rise.

Light weight epoxy can be obtained from different methods due to different processability, such as high speed blending to generate air bubbles, pumping air or any gas into the resin, using suitable blowing agents, mixing with micro or nano particles within the resin to generate the vacancies, such as using aerogels and hollow spheres [6-8]. The mode of these materials is influenced either by the morphology of the epoxy matrix, additives and manufacturing used. Interest of developing light weight epoxy extended to generate bubbles or cavities in the resin in what so-called “foamed epoxy” which has increased in recent years since it is an effective way to decrease the weight of the material thus reduce its cost as well as to enhance its properties for example the thermal insulation which plays a key role in the energy saving.

Recently, there has been a significant advancement in syntactic epoxy by considering nano-gel particulate composites, in which hollow spherical bubbles are inserted into the resin before curing to form controlled porosity. Epoxies are appealing for composite structural applications because of their ability to attach efficiently to a wide range of substrates, exhibit strong mechanical qualities, thermal insulation, and are chemically durable. Another advantage of incorporating foam into an epoxy construction is that it reduces the overall density of the structure [9-10].

Many investigations have studied the thermo-physical properties of light weight epoxy for certain cases. Most of these studies are mainly looking for improving physical, mechanical and chemical properties by reinforcement methods. These methods include mixing the neat epoxy with different materials such as: particles, fillers, fibers or solutions, as mentioned by the references [11-14]. Some researchers have studied LWE obtained by involving nano-materials in the composite, as mentioned by the references [15-26], or LWE due to the use of hollow glass spheres, as mentioned by the references [27-30] or by foaming the epoxy using blowing agents, as mentioned by the references [31-39]. The last references have served many blowing agents such as: siloxane, CO₂ and pentane. Usually the percentage added to the epoxy was not exceeding 10%. Most of these studies have studied the mechanism of mixing these materials to reduce the weight of the epoxy as well as the corresponding changes in some mechanical or physical properties. However, the current work investigates the direct effect of adding a blowing agent on the thermo-physical properties of the resultant foamed epoxy. The main characteristics under study are: density, glass-transition temperature, thermal conductivity and thermal expansion. The work tends to relate these properties to the percentage of siloxane added to the epoxy.

2. Materials and Methods

The study proposes preparing several specimens of epoxies incorporated with different contents of blowing agent, and evaluating the thermal characteristics of the produced foamed epoxy as a light weight composite. The epoxy used in this study was SIKADUR-52 which is produced by Swiss company (Sika). The product is a 2-component: resin and hardener, moisture-tolerant, low-viscosity and high strength adhesive. The blowing agent used was 1,1,3,3-tetramethyldisiloxane which is produced by Chinese company (Jinan). The specifications of the materials used are shown in Table 2.
Table 2. Specifications of the materials used in this study*

<table>
<thead>
<tr>
<th>Material</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy resin (SIKADUR-52)</td>
<td>Two-component liquid, viscosity: 500 mPa.s at 20 °C, compressive strength: 53 MPa after 10 days, Modulus: 1000 MPa</td>
</tr>
<tr>
<td>Blowing agent (1,1,3,3-tetramethydisiloxane)</td>
<td>Clear colorless liquid, CAS: 3277-26-7, MW: 134.32, Boiling at 70 °C, Flash at -10 °C.</td>
</tr>
</tbody>
</table>

* Supplied by the product data sheets.

The experimental works have done in the Department of Materials, Mustansiriyah University to prepare specimens of different siloxane contents as: 0, 5, 10, 15 and 20 wt%. Samples of bulk epoxy have been prepared by mixing a suitable amount of the resin and the hardener using a precise weight scale in order to get the desired quantity. The epoxy resin has mixed with the amine hardener by 2/1 ratio (epoxy/hardener) and left for 2 hours. Then blowing agent (1,1,3,3-tetramethydisiloxane) has been added with continuous mixing. The solution was then poured into the mold and allowed for 24 hours at room temperature before being post-cured at 70 °C for 4 hours [34]. Due to the lengthy gel time of the epoxy resin at room temperature, and to prevent the early reactivity of the blowing agent with the epoxy, the siloxane was added to the mixture after 2 hours of pre-curing interval, while the viscosity was still low [34]. It should be noted that skipping the final operation exposes the resin to rapid thermal curing. This causes a sudden fall in viscosity and results in coalescence and escape of the majority of the bubbles created [34].

Differential scanning calorimetry (DSC) brand NETZSCH-214 has been used to determine the glass-transition temperature of the samples during exothermic process. The measurements were carried out at the Laboratory of Materials in the University of Tehran according to ASTM D3418, where the solid polymer should be grinded into small particles, so that the average size of the particle was not exceeded 2.36 mm in diameter or Mesh 8. In order to measure the thermal conductivity, several specimens have circular shapes of 4 cm diameter and 0.5 cm height, as shown in Figure 1, according to ASTM C518.

Figure 1. Specimens manufactured in this study for thermal conductivity tests

The measurements were done at the Test Lab, University of Technology, where the thermal conductivity of the selected specimens have tested under suitable conditions using the Lees discs apparatus shown in Figure 2.

Figure 2. Lee discus apparatus used to measure thermal conductivity

Some other specimens have cylindrical shapes of 1 cm diameter and 2 cm height, as shown in Figure 3, are manufactured for the measurement of thermal expansion according to ASTM E228.
The measurements were done at the Test Lab, University of Technology, where the thermal expansion of the selected specimens have tested under suitable conditions using the push rod dilatometer shown in Figure 4.

Furthermore, images of scanning electron microscope (SEM) for internal partitions of the samples have been captured, by VEGA-II TESCAN device, to analyze the structure morphology of the epoxy before and after the addition of siloxane.

3. Results and Discussion

Many variables impact the foaming response in epoxy such as type and concentration of blowing agent, type and concentration of amine curing agent, temperature and heat transfer of the mixed resin, water absorption, as well as the viscosity of the resin [40-44]. Curing is an important stage for a correct foaming process, and the curing kinetics may shift the gel formation process rapidly, offering a significant processing challenge. Also, due to the low viscosity of the resin, an early foaming gas release will cause coalescence and escape of the bubbles; a delayed release will result in inadequate or inhomogeneous foaming [44, 45]. Figure 5 shows the bulk density of foamed epoxy produced samples as a function of siloxane concentration, which ranges from 5 to 20 wt%. As predicted, the bulk density of the sample synthesized with the addition of blowing agent has decreased significantly, from 1.25 g/cm³ for the neat epoxy to 0.64 g/cm³ (or 50%) for the sample synthesized with the addition of 20% blowing agent (as maximum).

Figure 6 shows SEM images for two selected samples, 0% as a neat epoxy and 15% as a foamed epoxy. In the first image (neat epoxy), there are many packed continuous clusters and amorphous groups. By looking to the second image (foamed epoxy), the structure was less uniform and showed the presence of many pores with different sizes and distributed randomly. The difference in the structure between the two images is most apparent in the side-by-side comparisons. It is clearly recognized how the pores are mainly closed, fairly spherical with an average pore size in the order of the tens of micrometers.
The average diameters and distribution of pores in 1 mm³ volume for the selected samples according to the amount of siloxane added has been calculated from the SEM images as presented in Table 3. The calculation depends on the scale of the image (250x250 μm²) multiplying by the diameter of the largest pore (50 μm) which is approximated. In general, increasing the blowing agent content has increased the number and size of pores. This is due to coalescence events, which are aided by increased blowing agent concentration. As a result, the perceived density is reduced.

**Table 3.** Average diameters and distribution of pores in 1 mm³ volume

<table>
<thead>
<tr>
<th>Sample</th>
<th>Distribution</th>
<th>Diameter of pore (μm)</th>
<th>&lt;10</th>
<th>10-25</th>
<th>25-50</th>
<th>&gt;50</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>Quantity</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Percentage</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5%</td>
<td>Quantity</td>
<td></td>
<td>12500</td>
<td>4500</td>
<td>700</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>Percentage</td>
<td></td>
<td>70%</td>
<td>25%</td>
<td>4%</td>
<td>1%</td>
</tr>
<tr>
<td>10%</td>
<td>Quantity</td>
<td></td>
<td>15000</td>
<td>6000</td>
<td>1800</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>Percentage</td>
<td></td>
<td>64%</td>
<td>26%</td>
<td>8%</td>
<td>2%</td>
</tr>
<tr>
<td>15%</td>
<td>Quantity</td>
<td></td>
<td>16000</td>
<td>8000</td>
<td>3000</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>Percentage</td>
<td></td>
<td>57%</td>
<td>28%</td>
<td>11%</td>
<td>4%</td>
</tr>
<tr>
<td>20%</td>
<td>Quantity</td>
<td></td>
<td>17000</td>
<td>9500</td>
<td>4000</td>
<td>1500</td>
</tr>
<tr>
<td></td>
<td>Percentage</td>
<td></td>
<td>53%</td>
<td>30%</td>
<td>12.5%</td>
<td>4.5%</td>
</tr>
</tbody>
</table>

The thermo-grams of DSC for the selected samples of the foamed epoxy with siloxane content from 0% to 20% show two or three transitions in the glassy state at a certain interval. This is because the transition temperature is extremely structure-sensitive due to steric effects and also due to intra- and inter-molecular interactions. However, it should select the one which has highest gradient in the heat value [46]. Figure 7 represents the variation of glass-transition temperature with the siloxane content for the selected specimen. The results show that transition temperature of the epoxy has increased from 375 K (102 °C) for the neat specimen until reached to 396 K (123 °C) for the specimen of 20% siloxane content, thus the overall increment is 20%. This means that the foamed epoxy has a tendency to be a glassy material more than the neat one. This is because the increasing in foaming agent means an increase in the crosslinking, which decreases the molecular mobility and hence rises the polymer's glass-transition temperature [47].
The current results have similar behavior to that obtained by the studies [33, 38, 39, 48]. However, the transition temperature for the samples introduced in the mentioned studies has increased by 4-12 K. Figure 8 represents the variation of thermal conductivity with the siloxane content for the selected specimen. The results show that the relationship between the coefficient of thermal conductivity and the addition of siloxane is reciprocating, where the thermal conductivity of the epoxy has decreased from 0.2 W/m.K for the neat specimen to 0.14 W/m.K for the specimen of 20% siloxane content, thus the overall reduction is 30%. This is due to the air presented in the foamed samples, where the thermal conductivity of air is less than that of polymer, thus the overall conduction of the composite tends to decrease [49]. This means that the foamed epoxy has a tendency for thermal insulation more than the neat one. The current results have similar behavior to that obtained by the studies [18, 19, 21, 26, 34, 50]. However, thermal conductivity for the samples introduced in the mentioned studies has less value by 30-50%. Figure 9 represents the variation of thermal expansion with the siloxane content for the selected specimen. The results show that the relationship between the coefficient of thermal expansion and the addition of siloxane is reciprocating, where the thermal expansion of the epoxy has decreased from 16x10^{-5} 1/K for the neat specimen to 3.6x10^{-5} 1/K for the specimen of 20% siloxane content, thus the overall reduction is 75%. In other words, thermal expansion coefficient of the composite has decreased due to the combined effect of pores and corresponding crosslinking happened, which leads to increase the glass-transition temperature of the material. Thus, the material exhibit higher stiffness [51, 52]. This means that the foamed epoxy is more rigid material and can resist at high temperatures more than the neat one. Table 4 shows a comparison between the current results and those obtained from other resources.
Table 4. Comparison between current results and those obtained from other resources for convergent conditions

<table>
<thead>
<tr>
<th>Property of the epoxy</th>
<th>Current results</th>
<th>Other results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>Decreased by 50%</td>
<td>Decreased by 60% [53, 54]</td>
</tr>
<tr>
<td>Glass-transition Temp.</td>
<td>Increased by 20%</td>
<td>Increased by 10% [39, 48]</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>Decreased by 30%</td>
<td>Decreased by 40% [34]</td>
</tr>
<tr>
<td>Thermal expansion</td>
<td>Decreased by 75%</td>
<td>-</td>
</tr>
</tbody>
</table>

4. Conclusions

The current study investigated the thermo-physical properties of foamed epoxy, as LWE using a blowing agent of siloxane (1,1,3,3-tetramethyldisiloxane). The results show that the foaming the neat epoxy resin using siloxane blowing agent has a direct influence on the thermo-physical characteristics due to the presence of pores, their sizes and distribution. These factors have direct influences on the resultant bulk density thus the corresponding thermo-physical properties. It is noticed that as the blowing agent added by 20% to the epoxy (am maximum), the density has decreased by 50%, the glass-transition temperature has increased by 20%, the thermal conductivity has decreased by 30% and the thermal expansion has decreased by 75%.

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Conflict of interest

The authors confirm that the publication of this article cause no conflict of interest.

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