Modified and Unmodified Graphite/Unsaturated Polyester Resins Composites: Thermal and Mechanical Behavior

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ABSTRACT

In this study, the unmodified graphite and graphite modified with a silane agent have been used to ameliorate the thermal conductivity coefficient and dynamical properties of unsaturated polyester resins. The effect of the addition of the unmodified graphite and modified graphite on the thermal conductivity coefficient and dynamical properties of unsaturated polyester resins in the graphite amounts of 0.02 % and 0.3 % by weight were studied using the solid thermal conductivity measuring device and DMA test. The results showed that the silane modifier could help to create strong covalent bonds between graphite particles and the unsaturated polyester resins network and cause changes in thermal and dynamic properties compared to unmodified graphite particles. Adding 0.3 % by weight of the unmodified graphite to the unsaturated polyester resins resulted in a 7 % raise in the storage modulus in the glassy region. However, adding the same amount of graphite modified using the silane agent increased the storage modulus by 33 % in the glassy region. The silane modifier caused a better dispersion of graphite particles in the resin structure. The superior dispersion of graphite particles caused more interaction between graphite particles and the resin network, which significantly increased the modulus of the unsaturated polyester resins. In contrast, the better dispersion of graphite particles because of the presence of the silane agent increased the thermal resistance at the surface of graphite particles, which reduced the thermal conductivity coefficient compared to the same regarding unmodified graphite.

1. Introduction

Unsaturated polyester resins are the most commonly used resins in the industry. They are used in the production of fiberglass pipes (GRP), transfer fluids, and in chemical marine, and automotive industries. Due to the miscellaneous uses of these resins, this research proceeds to improve their properties and eliminate their weaknesses.

The curing reaction of the polyester resins is exothermic, so in a thick sample a lot of heat is produced, especially in its center. The polyester resins have about 9 % shrinkage during the curing and until the final curing,

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and the amount of shrinkage during the curing depends on the degree of conversion. On the other hand, the rate of reaction depends on the temperature. Therefore, if in a thick sample there is a temperature difference at the different parts of the sample, the conversion degree at the center will be different from that at the wall of the sample (at a certain time) and ultimately the amount of shrinkage in different parts of the sample will not be the same. This causes internal stress in the chosen thick sample and thus causes cracks in the sample. The cracks act as stress concentration points and will significantly reduce the physical-mechanical properties of the sample. Instead, if the temperature in the center of the sample increases sharply, it can cause the thermal degradation of unsaturated polyester resins [1, 2].

The thermal conductivity coefficient in polymers is often about 0.1 to 1 $Wm^{-1}K^{-1}$. Considering the thermal conductivity coefficient of metals, it can be said that the thermal conductivity coefficient of polymers is very low. Therefore, polymers are often used as the thermal insulation. However, as stated earlier, the low thermal conductivity coefficient of polymers as well as the heat generated during the curing of unsaturated polyester resins can cause defects in the production of thick parts and ultimately lead to a significant reduction in their physical-mechanical properties [3, 4]. Thus, improving the physical-mechanical properties and enhancing the thermal conductivity coefficient of polymers are considered serious steps. The dynamic mechanical properties of epoxy resins containing nano and micron-TiO_2 particles were studied by Rajabi and colleagues. It was shown that the storage modulus for epoxy resins increased with the addition of particles compared with pure

resins [5]. The use of particles with a high thermal conductivity coefficient at the nanoscale and microscale can be useful for enhancing the thermal conductivity coefficient of unsaturated polyester resins. However, little research has been done on increasing the thermal conductivity coefficient of unsaturated polyester resins. In the performed studies, the mechanism of the heat transfer in unsaturated polyester resins has not been studied molecularly. Investigating the mechanism of the heat transfer at the molecular scale can mostly demonstrate the effect of added particles to raise the thermal conductivity coefficient of unsaturated polyester resins, as well as making the strategies for ameliorating the thermal conductivity coefficient clear.

The mechanism of the heat transfer in polymers is very different from that in metals. The heat transfer in polymers takes the form of phononic transfer. In simpler terms, the heat energy is propagated as waves in polymer chains, but in metals the heat transfer is done by free electrons. The phononic heat transfer in polymers causes the thermal conductivity coefficient in polymers to be highly dependent on several items such as the arrangement of polymer chains, the degree of crosslinking in the network of polymers, the crystallinity, etc. Also, the heat transfer in polymers with the phononic transfer mechanism depends on the amount of entanglement in the polymer chains, and the amount and shape of the branches in the polymer chain backbone.

Today, graphite, due to its abundance and high thermal conductivity coefficient, is used by researchers in improving the thermal conductivity coefficient of polymers. Graphite has a structure composed of carbon atoms with the sp^2 hybridization that are

linked together by covalent forces. Graphite has the thermodynamic stability and a high aspect ratio [6-8]. Due to the low cost, high thermal conductivity and uniform structure of graphite, and because it naturally exists in large quantities, it has a variety of applications, including in producing polymer composites, sporting goods, paints, pencils, etc., [9, 10].

In general, one of the main shortcomings of carbon nanoparticles is that they do not disperse well in the polymer, but modifiers can be used to make effective connections between polymer chains and particles [11, 12]. Therefore, due to the different nature of the heat transfer in polymers, and by using the surface modification of graphite, the thermal and mechanical properties of unsaturated polyester resins may be ameliorated.

So far, the effect of graphite on the heat transfer and mechanical properties of unsaturated polyester resins is not explored. There are a number of ingredients utilized to enhance the properties of polymers. In recent years, owing to the performance of graphite in improving the electrical and thermal conductivity of polymer composites, much attention has been paid to polymer/graphite composites [13-15].

Krupa and Chodak examined the thermal conductivity of HDPE and polystyrene composites containing graphite. In their study, they compared variations in the thermal conductivity of polymers in small and large sizes of graphite particles. They reported that the use of graphite increased the thermal conductivity. They found that the finer the graphite particles, the more superior the thermal conductivity [16].

Ganguli et al. prepared a composite of epoxy/graphite and identified that as the amount of graphite increased to 20 % by weight, the composite modulus reached approximately 6000 MPa, indicating a significant enhancement. They also showed that adding graphite to epoxy would increase its thermal conductivity. For instance, the thermal conductivity of the epoxy composite improved by 20 times with the addition of 20 wt % graphite [17].

Tu et al. investigated the changes in the thermal conductivity coefficient of polystyrene containing the colloidal graphite and graphite nanoparticles. They presented that adding graphite particles enhanced the thermal conductivity coefficient of the polystyrene composite nonlinearly. In their study, they found that the thermal conductivity coefficient of the neat polystyrene would increase considerably, by adding 34 % by volume of graphite, which could be as high as 400 % [18].

So far, no information has been published about the effect of the pure graphite and modified graphite in unsaturated polyester resins on the heat transfer coefficient from a molecular point of view and heat transfer mechanisms in this system. Also, the effect of temperature changes on the heat transfer coefficient in the mentioned systems has not been studied. Additionally, the effect of the pure graphite and modified graphite on dynamic properties from a molecular point of view and according to their role in the thermal conductivity coefficient has not been studied. In this study, the addition of graphite and modified graphite particles to unsaturated polyester resins and their effects on the thermal and mechanical properties of the composite have been examined. In addition, the effects of increasing the thermal flux on the thermal conductivity coefficient at

different weight percentages of the particles were also considered. A silane coupling agent was used to modify the graphite surface, which has a double bond in its structure, and can contribute to the radical reaction of curing unsaturated polyester resins and increase the bonding of graphite particles with unsaturated polyester resins. Also, the used particles were perfectly distributed throughout the resin matrix, creating a homogeneous mixture of unsaturated polyester resins and graphite. The chemical structures of the modified graphite and graphite particles were tested by the FTIR examination. In addition, thermal conductivity coefficient and DMA tests were used to study the thermal and mechanical properties of the polymer matrix.

2. Experimental
2.1. Materials
The unsaturated polyester resin applied in this work is Payapol 1500 ortho unsaturated polyester resin and supplied by Paya Zarand Company (Iran). The initiator used is methyl ethyl ketone peroxide from Pamokale Company (Iran). Cobalt naphthenate 1000 made by Chekad Company (Iran) has been used as an accelerator in resins. The silane is 3-(trimethoxysilyl) propyl methacrylate (g-MPS; Sigma-Aldrich, Germany). The mentioned silane with OH groups can be connected to OH groups on the graphite surface. On the other hand, the silane used in this research, due to having a double bond, can participate in the radical cure reaction of unsaturated polyester resins and create strong covalent bonds between the resin network and the modified graphite particles.

2.2. Silanization of the graphite particle surface
In order to modify the surface of graphite

particles using silane, a 70:30 solution of ethanol:water was first prepared. Then the acetic acid was gradually added to the solution so that the pH of the solution would be between 3 and 4. To reach 15-20 % by weight of graphite, first silane and then water-alcohol solution were added. The mixture was agitated for 24 h using a mixer and then, using a centrifuge, the modified graphite particles were separated.

2.3. Sample preparation method and curing of samples
The graphite in different percentages were added to the unsaturated polyester resin. Then each container containing the sample was placed in an oven at 40 ^{o}C. The sample was then stirred with a mixer for half an hour. Then 0.4 % by weight of cobalt naphthenate was added to it and the mixture was stirred more using a mixer. After the cobalt was completely uniform in the sample, 1.5 % by weight (based on total) of methyl ethyl ketone peroxide (MEKP) was poured into the container to start the curing reaction and mixed again for one minute. Due to the presence of 200 ppm of hydroquinone in the system, no curing reaction took place during that period. The sample was then transferred into a mold and placed at room temperature for 24 h. To postcure the samples, they were placed in a 120 ^{o}C oven for 2 h [3, 19].

2.4. Dynamic mechanical thermal properties
Dynamic mechanical thermal properties of graphite and modified graphite/unsaturated polyester resin composites were measured by the DMTA analysis with three bending points. Test conditions were: the frequency of 1 Hz, strain amplitude of 0.05 %, and temperature ranging from -30 to 200 ^{o}C.

DMTA specimens (30 mm long, 7.5 mm wide, and 2-2.5 mm thick) were cut from composite parts. All tests were performed by DMA1 Mettler Toledo (STARE SYSTEM). In this test, the storage module (E'), the loss module (E'') and the damping factor (tan δ) have been calculated.

2.5. Fourier transform infrared spectroscopy

The modified graphite and graphite particles were identified using a Fourier transform infrared spectrometer (Alpha, Bruker Co., Germany). This method allows functional groups of particles to be investigated. The spectrum was measured in the range of 400-4000 cm^{-1} and with a resolution of 4 cm^{-1}.

2.6. Conductive heat transfer properties

The P.A. HILTON LTD heat transfer device was applied to assess the thermal conductivity coefficient of composite samples. In this device, a sample is placed between two hot and cold elements. As the device is turned on and the constant heat flux is applied, the temperature rises in the hot part of the device. In the cold element, heat is taken from the sample using a water flow. When the temperature difference between the hot and cold parts of the sample is fixed, and the sample is stable, the thermal conductivity coefficient is calculated using the equation presented as follows:

$$Q = kA \frac{\Delta T}{\Delta X} \tag{1}$$

2.7. SEM test

The SEM test was performed using TESCAN model VEGA (Czech Republic).

3. Results and discussion

Before investigating the results of the thermal conductivity coefficient measurements and the results of the DMA test, it will be necessary to briefly examine the network made during the curing of the unsaturated polyester resin. It should also be noted that when mixing particles with unsaturated polyester resins, MEKP and the accelerator (cobalt naphthenate) had not been mixed with the resin, and then only after ensuring the proper mixing of the particles and curing of the mentioned system, the initiator and accelerator were added to the system.

In addition, 200 ppm of HQ (hydroquinone) was mixed with the resin to avoid the curing reaction during mixing. Hydroquinone is added to the unsaturated polyester resin to absorb free radicals and provide enough time for the initiator to mix with the resin. In this way, during the mixing period, the reaction will be prohibited. Therefore, the presence of hydroquinone at the time of the mechanical mixing means that there is no possibility of a reaction during this time period.

Alkyd chains and styrene are components of unsaturated polyester resins. The quantity of styrene in unsaturated polyester resins is estimated to be about 30 % to 40 % by weight. Decrease in viscosity and cross-linking of resins are among the functions of styrene in this resin system. Styrene double bonds are broken during the cross-linking reaction and react with the double bonds of alkyd chains to form strong covalent bonds. Free radicals, which in this study were created using MEKP as a peroxide compound, are required to break down the double bonds of alkyd chains and the double bonds of styrene molecules. By raising the temperature to about 80 to 85 °C, the MEKP decomposes and produces free radicals. However, using cobalt compounds that act as accelerators, the MEKP molecule can be broken down at low

temperatures and free radicals can be produced. The reaction of the radical generation in unsaturated polyester resins is as follows:

The fast decomposition of the peroxide using metallic ions (promoters) occurs at room temperature so that in the redox-oxidation initiation reaction, active radicals will be produced according to the reactions presented in Eqs. 2 and 3 [20]:

$$ROOR + Co^{2+} L_2 \rightarrow [ROOR\ Co^{2+} L_2] \rightarrow 2\ RO^{\bullet} + Co^{3+} L_3 \tag{2}$$

$$ROOR + Co^{3+} L_3 \rightarrow [ROOR\ Co^{3+} L_3] \rightarrow ROO^{\bullet} + R + Co^{2+} L_2 \tag{3}$$

In these equations, ROOR, Co^{2+} (Co^{3+}), $ROO^{\bullet}$ and L represent the initiator, promoter, free radicals, and ligand naphthenate respectively.

The crosslinking reaction of unsaturated polyester resins after the generation of radicals in the system starts according to the above reactions and then a network is formed as given in Figure 1.
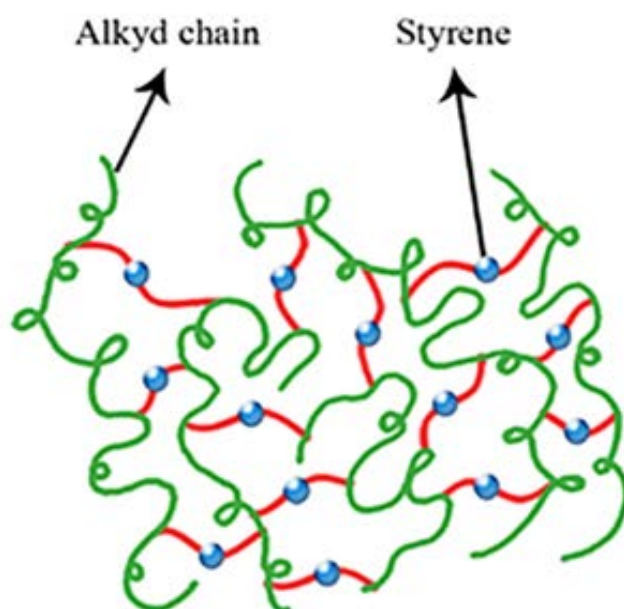

Figure 1. Schematic of the unsaturated polyester resin network formation.

Figure 2 displays the unsaturated polyester resin structure. As seen in Figure 2, in the unsaturated polyester structure, there are OH, COOH and ester groups in the alkyd chains of unsaturated polyester resins.
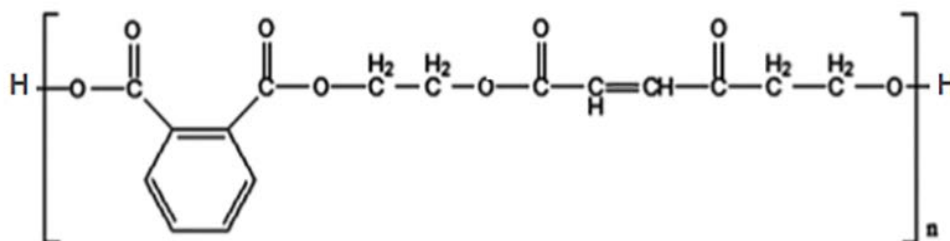

Figure 2. Structure of alkyd chain unsaturated polyester resins.

3.1. FTIR results

As previously mentioned, in the present work, the influence of the silane modifier on the thermal conductivity coefficient and dynamic properties (DMA) has been investigated. To modify the graphite particles, the silane agent shown in Figure 3 was used.
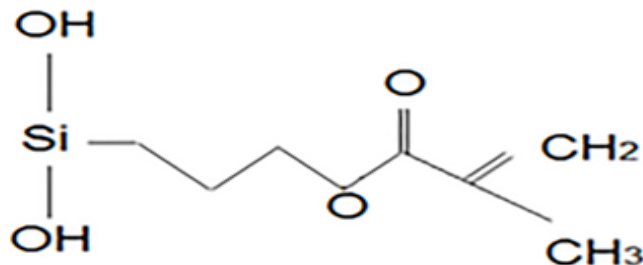

Figure 3. Chemical structure of the silane agent.

Figure 3 presents that there is a double bond in the silane agent structure that can participate in the radical reaction of the alkyd chains and styrene of unsaturated polyester resins and thus it helps to bind graphite particles and alkyd chains and improve the heat transfer and dynamic properties (DMA) of unsaturated polyester resins. Because of the modification of graphite by the silane agent, the silane group replaces the hydrogen in the graphite surface hydroxyl group and thus the -O-Si bond is formed in the graphite structure [21]. The way of binding the silane compound to graphite is shown in Figure 4.
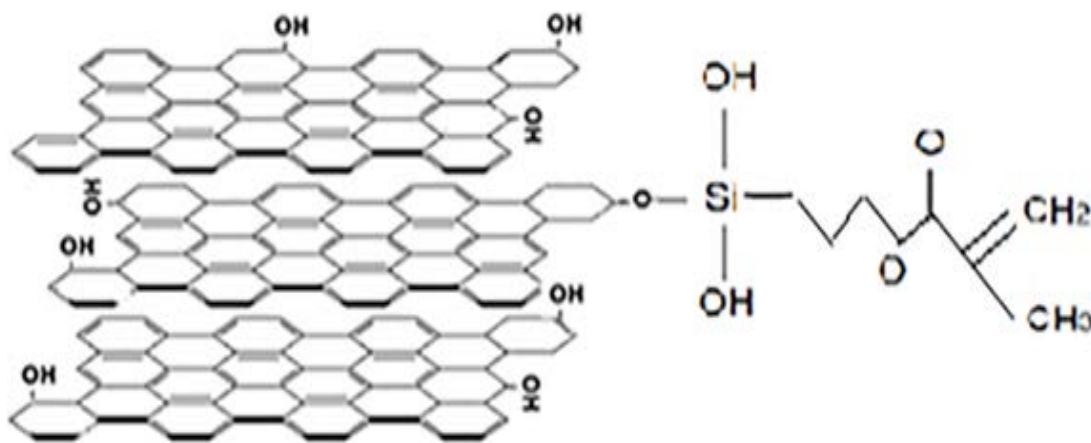

Figure 4. Modified graphite structure.

The FTIR spectrum for the unmodified graphite and graphite modified with the silane agent is displayed in Figure 5. According to Figure 5, a peak is observed at 3416 cm^{-1}, which belongs to the -OH bonds. The C=C structures found in the aromatic rings of graphite are also observed around 1622-1634 cm^{-1}.

As mentioned earlier, replacing the silane modifier with hydrogen in OH groups in graphite is estimated to lessen the number of OH groups in the graphite surface. This can be seen in Figure 5. Figure 5 shows that the peak intensity of OH groups in the modified

graphite (M-Graphite) sample has decreased significantly compared to the same in the non-modified sample, which indicates the replacement of a significant part of OH groups with the silane modifier.
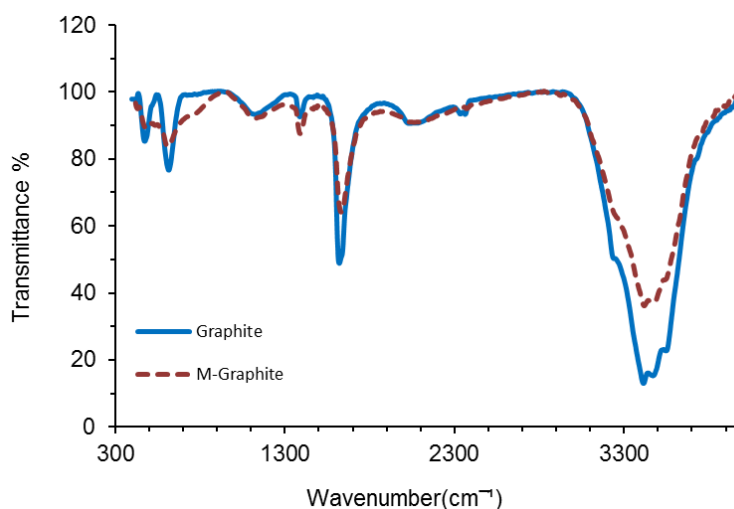

Figure 5. FTIR spectrum of graphite and the modified graphite (M-Graphite).

3.2. SEM results

The SEM test was used to better evaluate the graphite particle size. Figure 6 shows an image of the graphite particle size. As shown in Figure 6, most particles are larger than one micron in size. But particles smaller than one micron are also observed.
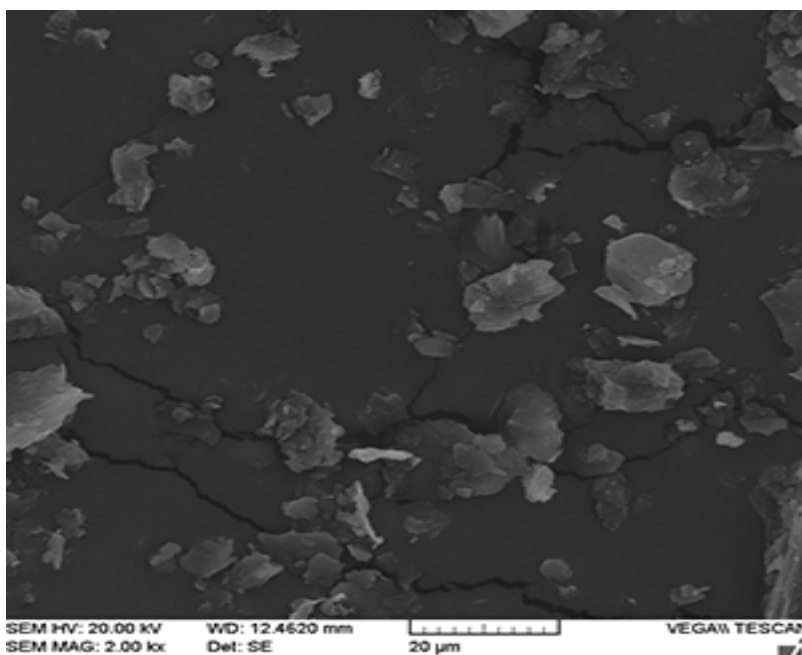

Figure 6. Image of the graphite particle size in the SEM test.

3.3. Dynamical and mechanical properties of composites

Figure 7 demonstrates the changes in the storage modulus in terms of temperature for neat unsaturated polyester resins, resins containing 0.02 % (UPG 0.02), and resins containing 0.3 % (UPG 0.3) by weight of the unmodified graphite. As seen in Figure 7, adding the unmodified graphite significantly increases the storage modulus of the

unsaturated polyester resin, which is much higher in the glassy region. Figure 5 illustrates that OH groups are present on the surface of graphite particles. In addition, due to the unsaturated polyester resin structure seen in Figure 2, there are OH, COOH and ester groups in the alkyd chains of unsaturated polyester resins. These groups in the structure of unsaturated polyester resins and OH groups on the graphite surface can attractively interact with each other and increase the storage modulus of unsaturated polyester resins containing graphite particles. However, as revealed in Figure 7, the increase in the storage modulus for unsaturated polyester resins containing 0.02 % of graphite (UPG 0.02) is higher than that for unsaturated polyester resins containing 0.3 % of graphite (UPG 0.3). The decrease in the storage modulus in the system containing 0.3 % of graphite compared to the sample containing

0.02 % of graphite can be caused by various factors. Latest research has shown that high filler loadings in unsaturated polyester resins can cause stress concentration points in the sample and ultimately reduce the storage modulus at high particle percentages. On the other hand, OH groups at the graphite surface can lessen the amount of free radicals created by the peroxide in unsaturated polyester resins by absorbing free radicals and converting them to radical oxygen species, and ultimately decreasing the network density. Investigation of the role of OH groups in the absorption of free radicals in the system involves further research using curing kinetics. Therefore, it can be stated that the reason for the lower storage modulus of the system containing 0.3 % of the unmodified graphite, compared to the system containing 0.02 % of the unmodified graphite is due to the above two factors.
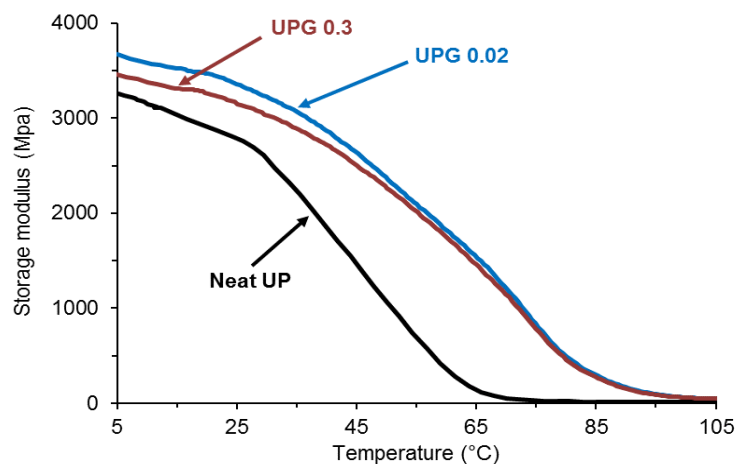

Figure 7. Storage modulus of the neat UP, UPG 0.02 and UPG 0.3.

According to Figure 7, it can be seen that the increase in temperature has reduced the difference between the storage modulus in the two UPG 0.02 and UPG 0.3 systems. Two phenomena can occur with increasing temperature in the DMA test in unsaturated polyester resin systems containing particles:

1. As mentioned earlier, there are attractive interactions between the OH groups present on the graphite surface and the OH and COOH groups present in the alkyd chains. Increasing the temperature can cause more movement of the mentioned groups and thus increase the distance

between the OH groups present on the surface of the graphite particles and the OH and COOH groups of the alkyd chains. This will reduce the attractive interactions between the groups, and therefore, the storage modulus will decrease with increasing temperature.

2. In the structure of the unsaturated polyester resin network, cooperative rearrangement regions (CRRs) play an essential role in determining the dynamic properties. As the temperature rises, enough energy is generated to move these regions. CRRs are not in the same size. In other words, there is a heterogeneity in the structure of the network, and this causes that in each temperature range, part of the CRRs to move and eventually reduce the storage modulus.

On the other hand, as mentioned in the article, OH groups at the particle surface can play the role of a radical scavenger. Therefore, it can be said that the network structures formed in the two systems of UPG 0.02 and UPG 0.3 are slightly different. Overall, it can be concluded that with increasing temperature, the small CRRs present in the UPG 0.02 system that react at low temperatures begin to move and eventually the difference between the two systems of UPG 0.02 and UPG 0.3 will be minimized, and finally at high temperatures the behavior of the two systems will be very similar.

Figure 8 displays the effect of the silane modifier on the storage modulus for systems containing 0.02 % and 0.3 % by weight of graphite. As it can be seen in Figure 8, the modification of graphite particles by the silane agent has increased the storage modulus in both systems of 0.02 % (UPMG 0.02) and 0.3 % (UPMG 0.3) by weight and this rise is particularly significant at temperatures below the glass transition point of the samples (glassy region). As mentioned earlier, due to the modification of the surface of graphite particles by the silane agent, the silane group replaces the hydrogen present in the hydroxyl group of the graphite surface and thus the -O-Si- bond is formed in the graphite structure. As it can be seen in Figure 3, there are double bonds in the silane agent structure. These double bonds can be broken by the radical reaction and then attach the unsaturated polyester resin and styrene to them.
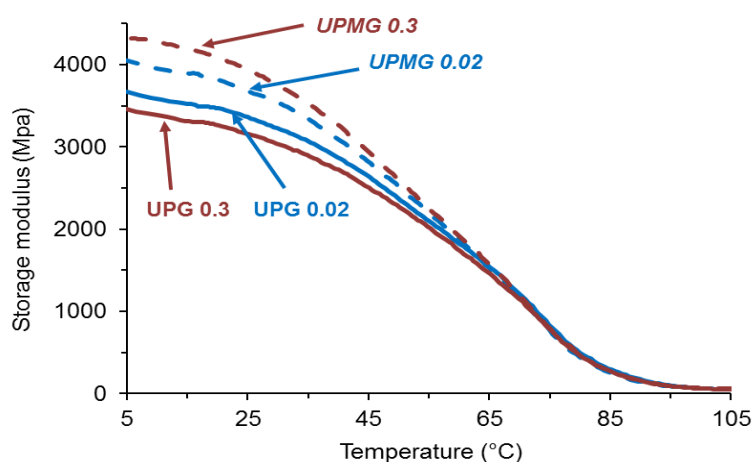

Figure 8. Storage modulus curves of UP containing 0.02 % of the unmodified graphite (UPG 0.02), UP containing 0.3 % of the unmodified graphite (UPG 0.3), UP containing 0.02 % of the modified graphite (UPMG 0.02), and UP containing 0.3 % of the modified graphite (UPMG 0.3).

Research conducted by Poorabdollah et al. has shown that the double bonds in the silane structure in the radical curing reaction of unsaturated polyester resins can be broken. The evidence of this is shown in the study of changes in curing kinetics in the studied system as well as in the study of the length of CRRs [21].

Thus, strong covalent bonds are formed between the graphite particles and the unsaturated polyester resin network. Such bonds can enhance the storage modulus of unsaturated polyester resins. These covalent bonds are more effective than Van der Waals attractive interactions between graphite OH groups and the OH, COOH and ester groups in the alkyd chains of unsaturated polyester resins.

On the other hand, as it can be seen in Figure 5, the silane modifier reduces the number of OH groups on the surface of graphite particles. As mentioned earlier, the OH groups present on the graphite surface can cause the adsorption of free radicals generated by the peroxide. This reduces the local presence of the peroxide in the unsaturated polyester resin during curing and reduces the amount of free radicals in the system. This phenomenon will cause the network density in the resin to decrease slightly and eventually reduce the elastic modulus and dynamic properties of the formed network. However, the replacement of OH groups by the modifier can reduce the intensity of the free radical adsorption in the system and reduce the negative impact of the free radical adsorption by OH groups on the dynamic properties of the system. Finally, it can be concluded that by modifying the graphite surface, the elastic modulus will increase.

However, according to Figure 8, it is realized that the influence of enhancing the storage modulus due to the modification of graphite particles in the sample containing 0.3 % of graphite is much higher than in the sample containing 0.02 % of graphite.

In addition to generating attractive interactions between particles and polymeric resins, modifiers can decrease the agglomeration in polymers. In thermoplastics, due to their high molecular weight compared to that of resins, the agglomeration of particles can be reduced by applying appropriate shear stresses. But because unsaturated polyester resins have much lower molecular weights than thermoplastics, the applied stresses cannot significantly reduce the agglomeration of the particles.

The influence of the polymer molecular weight on the exfoliation extent was studied by Fornes et al. They found that the stress resulted from the mixing of nanoclay platelets was increased by the high molecular weight of the polymer chains, which in turn enhanced their separation from the cluster structures. The stress applied by mixing devices on agglomerates when the molecular weight of the polymer is low is not large enough to cause the platelet separation and exfoliation [22].

Therefore, one of the best ways to prevent particles from agglomerating in resins, particularly unsaturated polyester resins, is to modify the surface of the particles with modifiers. According to Figure 8, it can be stated that the silane modifier, used to modify the surface of graphite particles, has caused better dispersion of particles in unsaturated polyester resins. This is obviously seen in the case of resins containing 0.3 % by weight of graphite. The effect of the silane modifier in

avoiding the agglomeration of particles has caused the increase in storage modulus in resins containing 0.3 % of graphite by about 10 % more than in the system including 0.02 % of graphite particles.

To better investigate the role of the interactions created in the resin containing the modified and unmodified graphite particles, it is superior to study the graphs of the loss modulus. In examining the effect of the particle size on the SBR polymer matrix containing silica particles, Robertson and colleagues determined that there were clear differences in the tan δ of samples containing silica particles. But by drawing the loss modulus curves, they observed that these curves were almost independent of silica particles. They noted that the significant differences in tan δ peaks were more associated with the increase in the rubber stiffness (polymer chain state) at high temperatures than with changes in the segmental relaxation of the polymer. Actually, if the objective is to study the segmental motion of the polymer, the loss modulus peak, which only specifies the segmental motion, should be used [23].

Loss module diagrams for samples of neat unsaturated polyester resins and unsaturated polyester resins containing weight percentages of 0.02 % and 0.3 % of the unmodified graphite and modified graphite are shown in Figure 9. As seen in Figure 9, the addition of the unmodified and modified graphite with a silane agent to the unsaturated polyester resin has resulted in structures with longer CRR (Cooperative Rearrangement region) regions. These regions are seen at temperatures above 75 ^{o}C. In Figure 9, two factors contribute to the increase in the length of the CRR region in this study. The first factor is the Van der Waals interaction. As revealed earlier, OH groups at the graphite surface and OH, COOH, and ester groups at the structure of alkyd chains can cause attractive interactions and these interactions increase the length of part of the CRR regions and lead them to higher temperatures. On the other hand, modifying silane groups can also direct some of the interactions to higher temperatures by making strong covalent interactions. The diagrams in Figure 9 approve the above results.
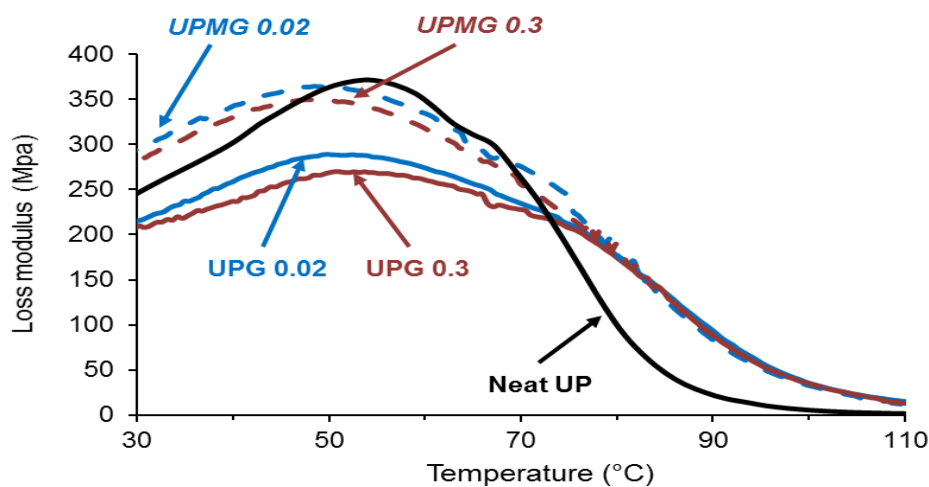

Figure 9. Loss modulus curves of the neat UP, UP containing 0.02 % of the unmodified graphite (UPG 0.02), UP containing 0.3 % of the unmodified graphite (UPG 0.3), UP containing 0.02 % of the modified graphite (UPMG 0.02), and UP containing 0.3 % of the modified graphite (UPMG 0.3).

3.4. Influence of graphite on the thermal conductivity coefficient

As mentioned earlier, the low thermal conductivity coefficient in unsaturated polyester resins can lead to heat trapping in the sample during curing. This increases the alteration in the amount of shrinkage during the curing of thick parts made with unsaturated polyester resins and finally, stresses are created during the curing of the resin in the thick samples and lessen the physical-mechanical properties of the desired part. Therefore, the use of high thermal conductivity particles in unsaturated polyester resins can be useful in this regard. In the following, we study the influence of graphite particles on the thermal conductivity of unsaturated polyester resins.

Figure 10 shows a comparison between the thermal conductivity coefficient of neat unsaturated polyester resins and unsaturated polyester resins containing 0.02 % and 0.3 % of the unmodified graphite in different heat fluxes. Figure 10 shows that at the same heat flux, composites containing 0.02 % (UPG 0.02) and 0.3 % (UPG 0.3) by weight of the unmodified graphite have a higher thermal conductivity coefficient than the ones containing neat unsaturated polyester resins, indicating the positive effect of graphite particles on the thermal conductivity coefficient of neat unsaturated polyester resins. The increase in the thermal conductivity coefficient of the composite with 0.02 % of graphite at a heat flux of 0.24 W/(mK) compared to neat resins was 59 % and in samples containing 0.3 % of graphite this increase was 64 %. As seen in Figure 10, the thermal conductivity coefficient in all systems has decreased with increasing heat flux. Increasing the heat flux causes more thermal energy to pass through the sample and therefore the sample reaches a steady state at higher temperatures. To better investigate this issue, the changes in thermal conductivity coefficient according to the temperature of the final steady state of the samples in the thermal conductivity measurement test have been investigated and the obtained results have been shown in Figure 11.
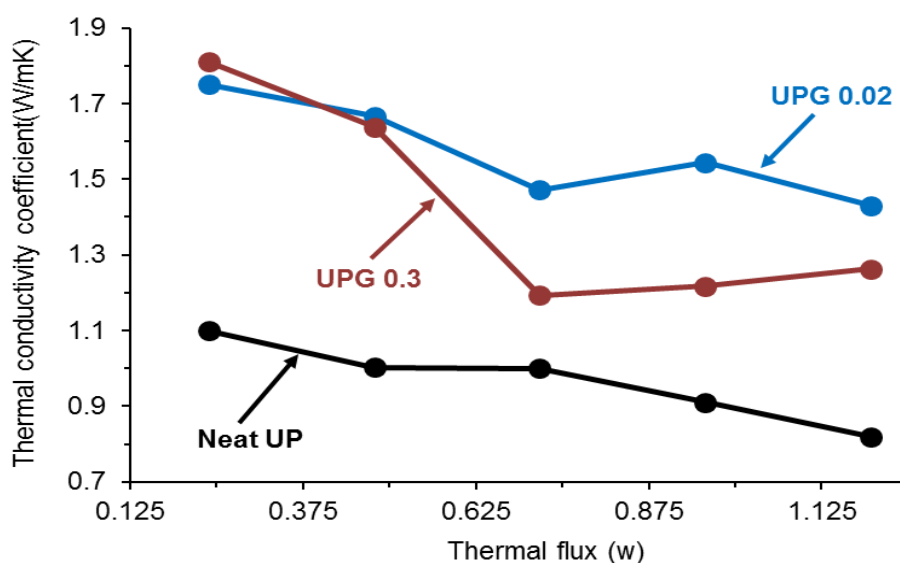

Figure 10. Thermal conductivity of the neat UP, UP containing 0.02 % of the unmodified graphite (UPG 0.02), and UP containing 0.3 % of the unmodified graphite (UPG 0.3).
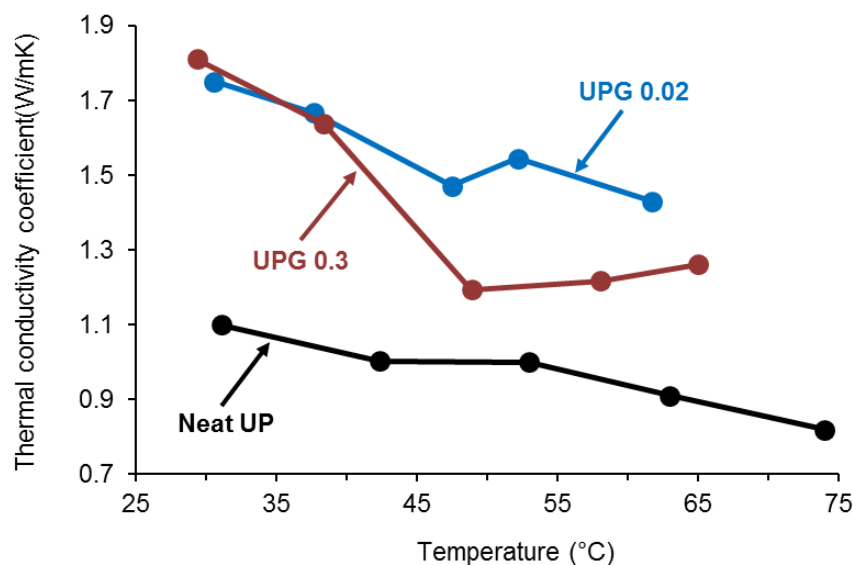
Figure11. Thermal conductivity of the neat UP and UP resin containing 0.02 % (UPG 0.02), and 0.3 % (UPG 0.3) of the unmodified graphite with increasing temperature.

As seen in Figure 11, increasing the temperature of the sample reduces the thermal conductivity coefficient in all three systems of neat unsaturated polyester resins, unsaturated polyester resins containing 0.02 % (UPG 0.02) by weight of graphite and resins containing 0.3 % (UPG 0.3) by weight of the unmodified graphite. Zhang and his colleague explored the effect of temperature on the thermal conductivity coefficient of polyethylene. They showed that increasing the temperature reduced the order in the polyethylene structure, which would significantly reduce the thermal conductivity coefficient of the sample. In their study, with raising temperature and approaching the glass transition temperature, the thermal conductivity coefficient reached about one-fifth of the thermal conductivity coefficient of polyethylene in the glassy mode [24]. Therefore, the role of polymer structure order in the thermal conductivity coefficient is very significant. As mentioned earlier, in all three systems described in Figure 11, a significant decrease in the thermal conductivity coefficient is observed with enhancing temperature. Increasing the temperature reduces the order in the structure of the resin network and makes the phononic transfer difficult.

As mentioned earlier, the heat transfer mechanism in polymers is based more on the phononic transfer. But in the meantime, the phononic scattering plays an essential role in reducing the amount of the heat transfer in polymers and causes a sharp decrease in the thermal conductivity coefficient of polymers. The order in the polymer structure improves the phononic transfer. On the other hand, decreasing the order increases the share of the phononic scattering and decreases the thermal conductivity coefficient. On the other hand, temperature increases the mobility of chains and network structures in polymers, and therefore, increases the free volume in polymers. Increasing the free volume in polymers and decreasing the existing order in the structure of the polymer network increase the share of the phononic scattering and ultimately lead to a significant reduction in the heat transfer coefficient [22].

It can also be expressed that in samples with

graphite particles, enhancing the temperature decreases the amount of attractive interactions between OH groups of the graphite surface and OH, COOH and ester groups of alkyd chains of unsaturated polyester resins, and therefore, the reduction of these attractive interactions disrupts the thermal conductivity by the phononic transmission mechanism.

Figure 11 illustrates that a slight enhancement of the thermal conductivity coefficient of some systems has been created by an increase in their temperature. For example, we can refer to the sample containing 0.02 % by weight of graphite in Figure 11. As the temperature in the system increases from about 47 $^\circ$C to about 52 $^\circ$C, there is a slight enhancement of the thermal conductivity coefficient.

Kikugawa et al. in examining the effect of the degree of crosslinking on the thermal conductivity coefficient in amorphous polymers indicated that heat in these networks can be transmitted by three mechanisms. (i) Energy transfer related to molecular movements, (ii) transmission of energy by non-bonded interactions, and (iii) transmission of energy by bonded interactions. As mentioned earlier, rising temperatures can disrupt non-bonded interactions and can also reduce the order in the resin network structure, thus negatively affecting the energy transfer by non-bonded interactions [25]. But on the other hand, raising the temperature can increase the molecular mobility and improve the energy transfer caused by the molecular movements (transition) and thus increase the thermal conductivity coefficient, albeit slightly. Therefore, it may be claimed that a slight enhancement of the thermal conductivity coefficient by raising temperature in some

samples could be due to the improved heat transfer due to the increased molecular motion.

Kikugawa et al. in examining the influence of the crosslinking degree on the thermal conductivity coefficient in amorphous polymers stated that the share of bonded interactions in the heat transfer was much higher than that of non-bonded interactions [25]. On the other hand, it has been previously stated that the heat transfer between graphite particles and the resin network is the result of non-bonded attractive interactions. These interactions are because of the OH groups present on the graphite surface and the OH, COOH, and ester groups present in the alkyd chains of unsaturated polyester resins. Therefore, it is predictable that if the surface of graphite particles is modified with modifiers such as silane, which has the ability to create a covalent bond between the surface of graphite particles and alkyd chains, it can increase the thermal conductivity coefficient.

Figure 12 shows the effect of the graphite particle surface modification using the silane agent on the thermal conductivity coefficient for two samples of unsaturated polyester resins containing 0.02 % and 0.3 % by weight of graphite. But as it can be seen in Figure 12, contrary to expectations, the modifier has a negative influence on the thermal conductivity coefficient. As observed in the study of the influence of the modifier on the dynamic properties of samples containing modified graphite particles, the silane modifier has caused better dispersion of particles in unsaturated polyester resins and has also improved properties such as Young's modulus. Better particle dispersion in unsaturated polyester resins means more contact surface of graphite particles with the

resin network. This can enhance the surface heat resistance of the graphite particles. A research has been done on the effect of the particle size on the thermal conductivity coefficient. The study found that tiny particles had high surface areas, which caused the phononic scattering. Also, the reduction in the particle size will reduce the amount of heat transferred by the phononic transmission mechanism and ultimately reduce the thermal conductivity [26]. Therefore, it can be concluded that the silane modifier can decrease the thermal conductivity coefficient by enhancing the contact surface of particles and polymers. As an alternative, the silane modifier can increase the thermal conductivity coefficient by providing strong

covalent bonds between the graphite particles and the resin network. According to the results observed in Figure 12, it can be concluded that the effect of increasing the surface resistance of particles in order to reduce the thermal conductivity coefficient has overcome the formation of covalent bonds in order to increase the thermal conductivity coefficient, and finally, has reduced the thermal conductivity coefficient of the samples modified by the silane agent. This decrease in the sample containing 0.3 % by weight of graphite is much larger and about 19.5 % decrease in the thermal conductivity coefficient has been observed because of the modification of the graphite surface.
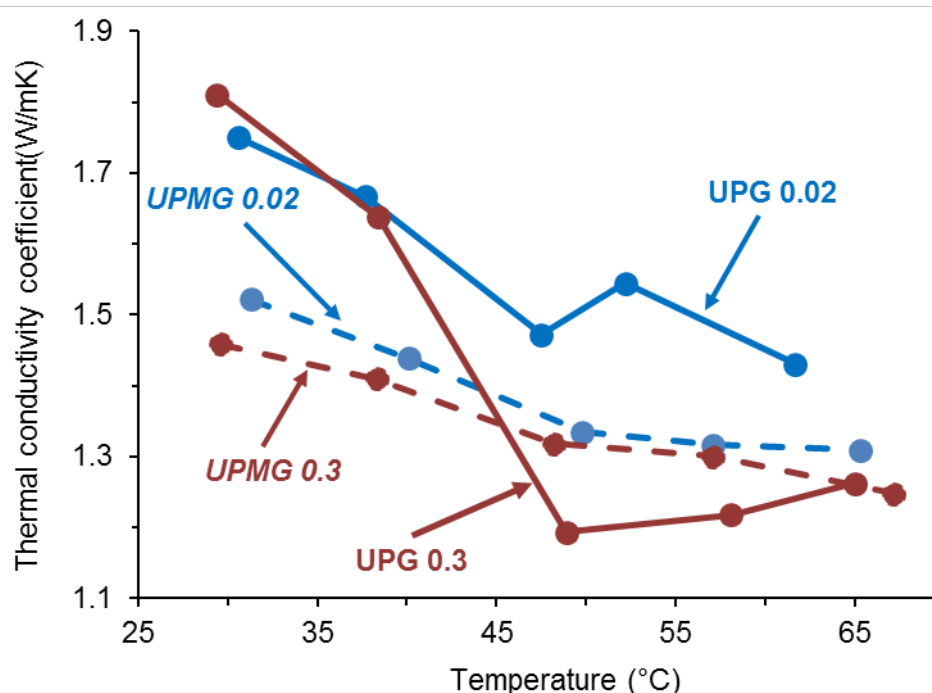

Figure 12. Thermal conductivity of UP resins containing 0.02 % of the unmodified graphite (UPG 0.02), 0.3 % of the unmodified graphite (UPG 0.3), 0.02 % of the modified graphite (UPMG 0.02), and 0.3 % of the modified graphite (UPMG 0.3).

Examining the effect of the crosslinking degree on the thermal conductivity coefficient in amorphous polymers, Kikugawa et al. said that by forming a network of crosslinks and creating strong covalent bonds, the thermal

conductivity coefficient increased due to a better phononic transfer [25]. On the other hand, Ni et al. stated that crosslinking, even in small amounts, reduced the thermal conductivity due to the phononic scattering

[27]. To study the influence of crosslinking on the thermal conductivity coefficient of unsaturated polyester resins, samples of unsaturated polyester resins as well as composites containing 0.02 % and 0.3 % by weight of the unmodified graphite in both postcured and non-postcured modes were compared together. As stated in the previous section, to postcure, samples were placed at 120 °C for 2 h. The postcuring operation is to overcome the dominance of the diffusion in the ending steps of the reaction. Therefore, it can be said that non-postcured samples have a much lower crosslinking degree than postcured samples. A comparison between the results of the thermal conductivity coefficient in the two postcured and non-postcured modes for neat polyester resins and resins with 0.02 % and 0.3 % by weight of the unmodified graphite in Figure 13 has been reported.
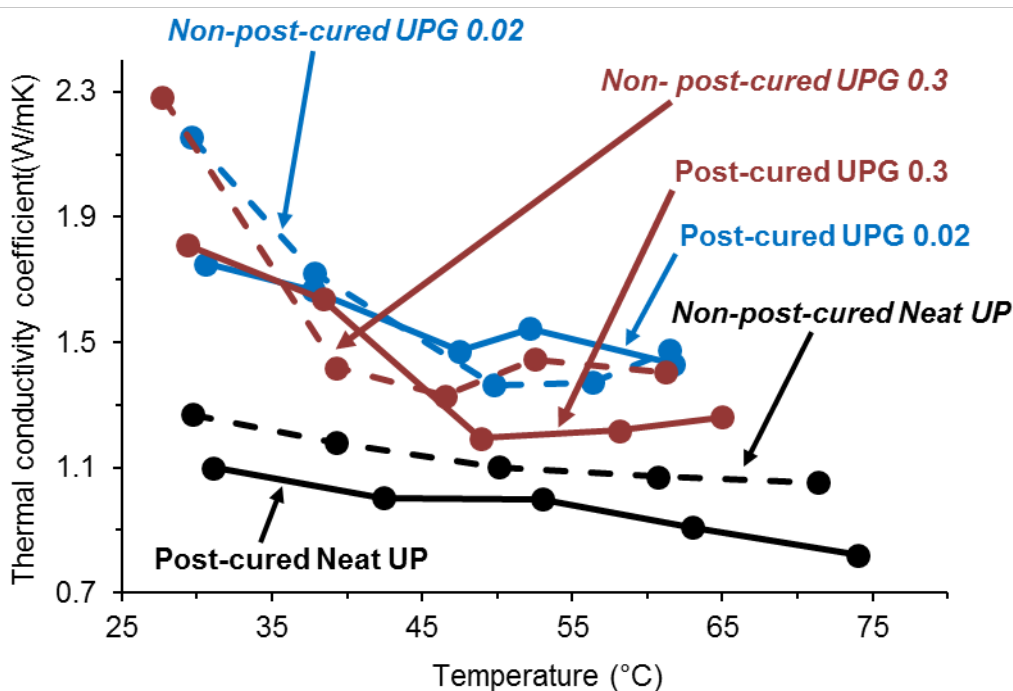

Figure 13. Thermal conductivity coefficient of the postcured neat UP, non-postcured UP, postcured UP containing 0.02 % of the unmodified graphite (Postcured UPG 0.02), Non-postcured UP containing 0.02 % of the unmodified graphite (Non-Postcured UPG 0.02), Postcured UP containing 0.3 % of the unmodified graphite (Postcured UPG 0.3), and Non-Postcured UP containing 0.3 % of the unmodified graphite (Non-Postcured UPG 0.3).

As it can be seen in Figure 13, by applying the postcuring process, the thermal conductivity coefficient in all of the above samples is reduced. As mentioned earlier, increasing the crosslinking can both increase and decrease the thermal conductivity coefficient. Therefore, according to Figure 13, the decrease in thermal conductivity coefficient due to the phononic scattering overcame the increase in the thermal conductivity coefficient due to the phononic transmission through strong covalent bonds and finally reduced the overall thermal conductivity coefficient. As a result of Figure 13, it is seen that the decrease in thermal conductivity coefficient due to the temperature increase is more severe in non-postcured samples and has also occurred at

lower temperatures. Non-postcured samples have a lower Tg temperature due to lower cross-links, as well as a lower intra-network order than postcured samples. Therefore, as the temperature increases, their intra-network order decreases more rapidly, and therefore the heat transfer through the phononic transmission mechanism is disrupted and the thermal conductivity coefficient decreases. Therefore, by enhancing temperature, the thermal conductivity coefficient in non-postcured samples decreases more sharply than in postcured samples.

4. Conclusions

The purpose of this research work was to investigate the influence of using graphite on dynamic properties and the thermal conductivity coefficient. With the aim of the superior disperse of the graphite particles in the unsaturated polyester resin network as well as the stronger connection of the graphite particles to the resin network, the graphite particles were modified by the silane agent. Unsaturated polyester resin composites were made with loading values of 0.02 % and 0.3 % by weight of the unmodified graphite and modified graphite. By adding unmodified graphite particles to the resin, the storage modulus increased, nevertheless, the increase in the storage modulus of the sample containing 0.3 % by weight of the unmodified graphite was less than that of the sample containing 0.02 % by weight of the unmodified graphite. The decreased storage modulus at 0.3 % by weight of the unmodified graphite can be associated with the agglomeration of graphite particles in unsaturated polyester resins, which causes a stress concentration in the part and reduces its mechanical properties. The use of a silane agent to modify graphite particles creates

covalent bonds between graphite particles and unsaturated polyester resin chains. The formation of covalent bonds creates strong interactions between graphite and resin particles, thus increasing the storage modulus significantly. By adding 0.3 % by weight of the modified graphite to unsaturated polyester resins, the storage modulus increased by about 8 % compared to composites comprising 0.02 % by weight of the modified graphite. The examination of the graphs of the loss modulus in neat resins and resins containing graphite showed that adding graphite particles increased the length of some CRR regions compared to neat resins, which was due to the attractive interactions between OH, COOH and ester groups of alkyd chains and OH groups on the graphite surface.

Examining the changes in the thermal conductivity coefficient of composites containing 0.02 % and 0.3 % by weight of the unmodified graphite showed that adding graphite particles improves the thermal conductivity coefficient of unsaturated polyester resins. The thermal conductivity coefficient of resins containing 0.3 % by weight of graphite was higher and increased by approximately 64 % compared to neat resins. Increasing the heat flux passing through the sample while measuring the thermal conductivity coefficient decreased the thermal conductivity coefficient. Increasing the heat flux stabilized the sample at higher temperatures, and increasing the sample temperature caused changes in the free volume of the sample and increased mobility of the polymer chains, which increased the phononic scattering. The particle modification with the silane agent resulted in better particle dispersion in the resin matrix and increased the contact surface of the particles with the

resin network. Enhancing the contact surface of graphite particles increased the surface thermal resistance and reduced the thermal conductivity coefficient of the modified graphite samples compared to those of the unmodified graphite.

References

[1] Al-Khanbashi, A., El-Gamal, M. and Moet, A., "Reduced shrinkage polyester-montmorillonite nanocomposite", *Journal of Applied Polymer Science*, **98** (2), 767 (2005).

[2] Beheshty, M. H., Vafayan, M. and Poorabdollah, M., "Shrinkage control and kinetics behaviour of clay-unsaturated polyester nanocomposites", *Iranian Polymer Journal*, **15** (10), 841 (2006).

[3] Beheshty, M. H., Vafayan, M. and Poorabdollah, M., "Low profile unsaturated polyester resin-clay nanocomposite properties", *Polymer Composites*, **30** (5), 629 (2009).

[4] Xu, L. and Lee, L. J., "Effect of nanoclay on shrinkage control of low profile unsaturated polyester (UP) resin cured at room temperature", *Polymer*, **45** (21), 7325 (2004).

[5] Rajabi, L., Mohammadi, Z. and Derakhshan, A. A., "Thermal stability and dynamic mechanical properties of nano and micron-TiO_2 particles reinforced epoxy composites: Effect of mixing method", *Iranian Journal of Chemical Engineering (IJChE)*, **10** (1), 16 (2013).

[6] Yasmin, A. and Daniel, I. M., "Mechanical and thermal properties of graphite platelet/epoxy composites", *Polymer*, **45** (24), 8211 (2004).

[7] Sadasivuni, K. K., Ponnamma, D., Thomas, S. and Grohens, Y., "Evolution from graphite to graphene elastomer composites", *Progress in Polymer Science*, **39** (4), 749 (2014).

[8] Li, J., Kim, J. K. and Sham, M. L., "Conductive graphite nanoplatelet/epoxy nanocomposites: Effects of exfoliation and UV/ozone treatment of graphite", *Scripta Materialia*, **53** (2), 235 (2005).

[9] Erol, M. and Celik, E., "Graphite-flake carbon-black-reinforced polystyrene-matrix composite films deposited on glass-fiber woven fabrics as plane heaters", *Mater. Technol.*, **47**, 25 (2013).

[10] Cai, W., Piner, R. D., Stadermann, F. J., Park, S., Shaibat, M. A., Ishii, Y., Yang, D., Velamakanni, A., An, S. J., Stoller, M. and An, J., "Synthesis and solid-state NMR structural characterization of 13C-labeled graphite oxide", *Science*, **321** (5897), 1815 (2008).

[11] Kim, M. T., Rhee, K. Y., Park, S. J. and Hui, D., "Effects of silane-modified carbon nanotubes on flexural and fracture behaviors of carbon nanotube-modified epoxy/basalt composites", *Composites Part B: Engineering*, **43** (5), 2298 (2012).

[12] Ma, P. C., Siddiqui, N. A., Marom, G. and Kim, J. K., "Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: A review", *Composites Part A: Applied Science and Manufacturing*, **41** (10), 1345 (2010).

[13] Ezquerra, T. A., Kulescza, M. and Balta-Calleja, F. J., "Electrical transport in polyethylene-graphite composite materials", *Synthetic Metals*, **41** (3), 915 (1991).

[14] Navarro, J., Roig, A., Noguera, P.,

Vicente, F., Vilaplana, J. and López, J., "Electrochemical behaviour and electrical percolation in graphite-epoxy electrodes", *Journal of Materials Science*, **29** (17), 4604 (1994).

[15] Blaszkiewicz, M., McLachlan, D. S. and Newnham, R. E., "The volume fraction and temperature dependence of the resistivity in carbon black and graphite polymer composites: An effective media-percolation approach", *Polymer Engineering & Science*, **32** (6), 421 (1992).

[16] Krupa, I. and Chodak, I., "Physical properties of thermoplastic/graphite composites", *European Polymer Journal*, **37** (11), 2159 (2001).

[17] Ganguli, S., Roy, A. K. and Anderson, D. P., "Improved thermal conductivity for chemically functionalized exfoliated graphite/epoxy composites", *Carbon*, **46** (5), 806 (2008).

[18] Tu, H. and Ye, L., "Thermal conductive PS/graphite composites", *Polymers for Advanced Technologies*, **20** (1), 21 (2009).

[19] Poorabdollah, M., Beheshty, M. H. and Vafayan, M., "A study on the kinetic behaviour and thermo-mechanical properties of nanoclay reinforced unsaturated polyester resin prepared under high shear conditions", *e-polymer*, **12**, 1 (2012).

[20] Weatherhead, R. G., FRP Technology: Fibre reinforced resin systems, Springer Science & Business Media, (2012).

[21] Poorabdollah, M., Beheshty, M. H. and Atai, M., "Investigating curing kinetics and structural relaxation phenomena of unsaturated polyester resin containing silanized silica", *Journal of Composite Materials*, **50** (18), 2459 (2016).

[22] Fornes, T. D., Yoon, P. J., Keskkula, H. and Paul, D. R., "Nylon 6 nanocomposites: The effect of matrix molecular weight", *Polymer*, **42** (25), 09929 (2001).

[23] Robertson, C. G., Lin, C. J., Rackaitis, M. and Roland, C. M., "Influence of particle size and polymer-filler coupling on viscoelastic glass transition of particle-reinforced polymers", *Macromolecules*, **41** (7), 2727 (2008).

[24] Zhang, T. and Luo, T., "Morphology-influenced thermal conductivity of polyethylene single chains and crystalline fibers", *Journal of Applied Physics*, **112** (9), 094304 (2012).

[25] Kikugawa, G., Desai, T. G., Keblinski, P. and Ohara, T., "Effect of crosslink formation on heat conduction in amorphous polymers", *Journal of Applied Physics*, **114** (3), 034302 (2013).

[26] Chen, H., Ginzburg, V. V., Yang, J., Yang, Y., Liu, W., Huang, Y., Du, L. and Chen, B., "Thermal conductivity of polymer-based composites: Fundamentals and applications", *Progress in Polymer Science*, **59**, 41 (2016).

[27] Ni, B., Watanabe, T. and Phillpot, S. R., "Thermal transport in polyethylene and at polyethylene-diamond interfaces investigated using molecular dynamics simulation", *Journal of Physics: Condensed Matter*, **21** (8), 084219 (2009).