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Preparation and Properties of Graphene/Nanocopper Reinforced Epoxy Resin Composites

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This work describes a novel epoxy resin (EP) composite which is reinforced by graphene/nanocopper composites. Nanocopper is supported on the layer of the graphene by thermal reduction method, forming the graphene/nanocopper composites (graphene/Cu) and by the emulsion dispersion method to make the graphene/Cu homogeneously dispersed among the epoxy resin, respectively, to achieve the enhancement of the mechanical property and the heat resistance of this novel epoxy resin. The result shows that the modified resin has more excellent mechanical property and the heat resistance compared with most of the epoxy resin samples that are unmodified. The best modified research in the work shows the mechanical property and heat resistance of the modified epoxy resin are different when changing the content of graphene/Cu in the modified epoxy resin. By the scanning electron microscope method, it is found out that when the content of graphene/Cu is within 1.9 wt%, the graphene/Cu in the epoxy resin has good dispersion, it is found out that the mechanical tensile strength, elastic modulus and shearing strength of modified epoxy resin will be enhanced, however, the excess of graphene/Cu can cause a decline in the mechanical properties of epoxy resin. In addition, in the dynamic thermodynamic analysis, it is discovered that when the content of graphene/Cu is changed within limits, the glass transition temperature of modified epoxy resin gradually rises. Finally, the excellent mechanics capability and heat resistance of EP/graphene/Cu composites will add immensely to the development and research of the modification of epoxy resin.

1. Introduction

Epoxy resins are well established as thermosetting matrices for adhesives, rigid components and fabricating advanced composites due to their good mechanical, chemical, heat-resistant, dielectric and flame-retardant properties (Motahari,et al., 2013). On the one hand, because of these excellent performances, epoxy resin has been commonly used as matrix and nanostructured fillers that are suitable to modify the material properties. However, on the other hand, the applications of epoxy resin are dramatically limited by its intrinsic brittleness and poor resistance to the crack propagation. In general, the properties of epoxy resin are determined by its own structure. With the addition of the hardeners and the fillers, the cross-linked network forms after curing (Rosu,et al., 2012). In order to make up the weaknesses of epoxy resin and get some more excellent properties, the various nanometer particles can be used to enhance the properties of epoxy resin (Shin,et al., 2009). However, the epoxy resin which is enhanced by nanometer particles also has a poor fracture resistance because the addition of nanometer particles cannot effectively enhance the mechanical properties of the matrix (Wilson,et al., 2009). Recently, the graphene has been used in order that it can enhance the mechanical properties of the matrix (Kim,et al., 2010).

The graphene has attracted more and more attention due to its unique electrical, optical, mechanical and thermal properties (Berger,et al., 2006), since the successful exfoliation of graphene flake into two-dimensional graphene in 2004 (Novoselov,et al.,2004). In recent years, graphene has been widely used as reinforcing nanofiller for polymer to form functional and structural composites (Gopiraman,et al., 2013), such

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as expanded graphite, graphite nanometer platelets, graphene oxide and graphene nanometer ribbons. However, due to π-π aromatic stacking interaction and strong attraction between graphene sheets, direct aggregation of two graphene nanometer sheets was observed, limiting the applications of graphene (Kuilla,et al., 2010). In order to avoid the above problems, the graphene is sonicated for dozens of minutes. By the above method, the space of graphene layers can be effectively increased. And with the increase of ultrasonic frequency, the space of graphene layers will be gradually increased. And the feature of the sonication is easily manipulated and the product processed by sonication is pure (Sreedhar and Reddy, 2007). In this paper, the graphene will be the reinforced material for the mechanical properties of epoxy resin. The reason why the graphene can enhance the mechanical properties of epoxy resin is that the graphene nanometer piece will present the gossamer and crapy layer structure, which is mutually intertwined together. This kind of structure plays an important role in enhancing the mechanical interlocking effect and the load transfer of composite material (Xie,et al., 2012).

In this work, the composite material is prepared first which contain the graphene and nanoparticles. In order to enhance the mechanical property of composite materials, the nanometer copper and graphene oxide are chosen as the reactants that have a thermal reduction reaction. There are two reasons why the nanocopper are chosen. One is that the nanocopper can effectively enhance the heat resistant property of composite material, the other is that the nanocopper are cost-effective. The addition of graphene and nanocopper effectively enhances the mechanical property and the heat resistance of epoxy resin. This modified epoxy resin has a good prospect in the production and research.

2. Experimental

2.1 Preparation of graphene oxide (GO)

The preparation of graphene oxide from natural graphite powder was following the modified Hummers-Offeman method. In short, the graphite powder (9.8g) was dispersed in concentrated sulfuric acid (230 mL, 98%) cooled in an ice bath. Then the potassium permanganate ($KMnO4$, 30g) was gradually added with stirring. We should pay attention to avoid the temperature of the mixture from exceeding 293 K by cooling. After that, the ice bath was removed and replace with a water bath and the mixture was heated to 307 K under the continuous stirring in 40 min. After 40 min reaction, we slowly added the deionized water (480 mL) caused a rapid increase in solution temperature up to the maximum of 372 K. In order to make the graphite powder fully react, the reaction was maintained at 372 K for 40 min. A bright yellow suspension was obtained by the addition of distilled water (240 mL) and a solution of hydrogen peroxide (30%, 250 mL) respectively. The precipitate was separated by centrifugation at 3000 r/min, and then washed with hydrochloric acid several times. The solid was washed five times with acetone and dried 24 h in a vacuum oven.

2.2 Synthesis of nanocopper supported on graphene

Firstly, in order to allow the graphene oxide (GO) to fully react in the reaction process, the prepared GO was transformed into GO sheets by sonication for 30 min at 308 K. At the same time copper sulfate was dissolved in distilled water and sonicated for 30 min. Secondly, the above-mentioned $CuSO4$ solution and GO were put into the three-necked flask and also sonicated at room temperature for about 40 min in order to make it uniformly dispersed. After sonication, the mixture was heated and stirred at room temperature in a water bath. When the temperature of water bath rose to 343 K, the sodium hydroxide solution was added in order to make the solution become alkaline and the hydrazine hydrate solution was added as a reducing agent and the mixing was continued for 2 h in a water bath. After reacting for 2 h, the product was cooled to room temperature, filtered and then washed with copious amounts of distilled water and anhydrous ethanol. The wet product was dried in vacuum oven for 24 h.

2.3 Preparation of EP/graphene/Cu composites

Firstly, epoxy resin (70 g) and a certain quality of hardeners, whose quality is half of the epoxy resin (about 35 g) were weighted. And then, preheated the hardeners and the PTFE mold whose surface was coated with release agent at 333 K for 2 h. Secondly, epoxy resin and a fixed amount of graphene/Cu (1.1, 1.3, 1.5, 1.7, 1.9, 2.1, 2.3 and 2.5 wt%) were mixed using the high-shear emulsifying machine for 6 min at 8000 r/min followed by the compositions that were placed in a vacuum oven at 323 K for 6-7 d to remove the bubbles and the remaining solvent. And then the hardeners were mixed with the compositions and stirred for 5 min until forming a evenly composite mixture. Finally, the mixture was poured into the preheated PTFE mold and cured at 348 K/2 h + 398 K/2.5 h + 423 K/1 h. After that, we got the final wanted product.

3. Result and discussion

Figure 1(a)-(f) is the SEM images showing the morphology of epoxy resin with different content of graphene/Cu, which are 0 wt%, 1.1 wt%, 1.3 wt%, 1.5 wt%, 1.7 wt%, 1.9 wt% respectively. From the Figure 1(a), it can be observed that the section of pure epoxy resin is tidy, on which the distribution of crack is uniform with clear river-like lines. It can be seen from the above characteristics that the typical brittle fracture occurs in the pure EP. So add the graphene/Cu into the EP in order to enhance the mechanical property. From the Figure 1(b) to Figure 1(f), it can be observed that with the increase in the content of graphene/Cu, the newly generated surfaces are increasing a lot.

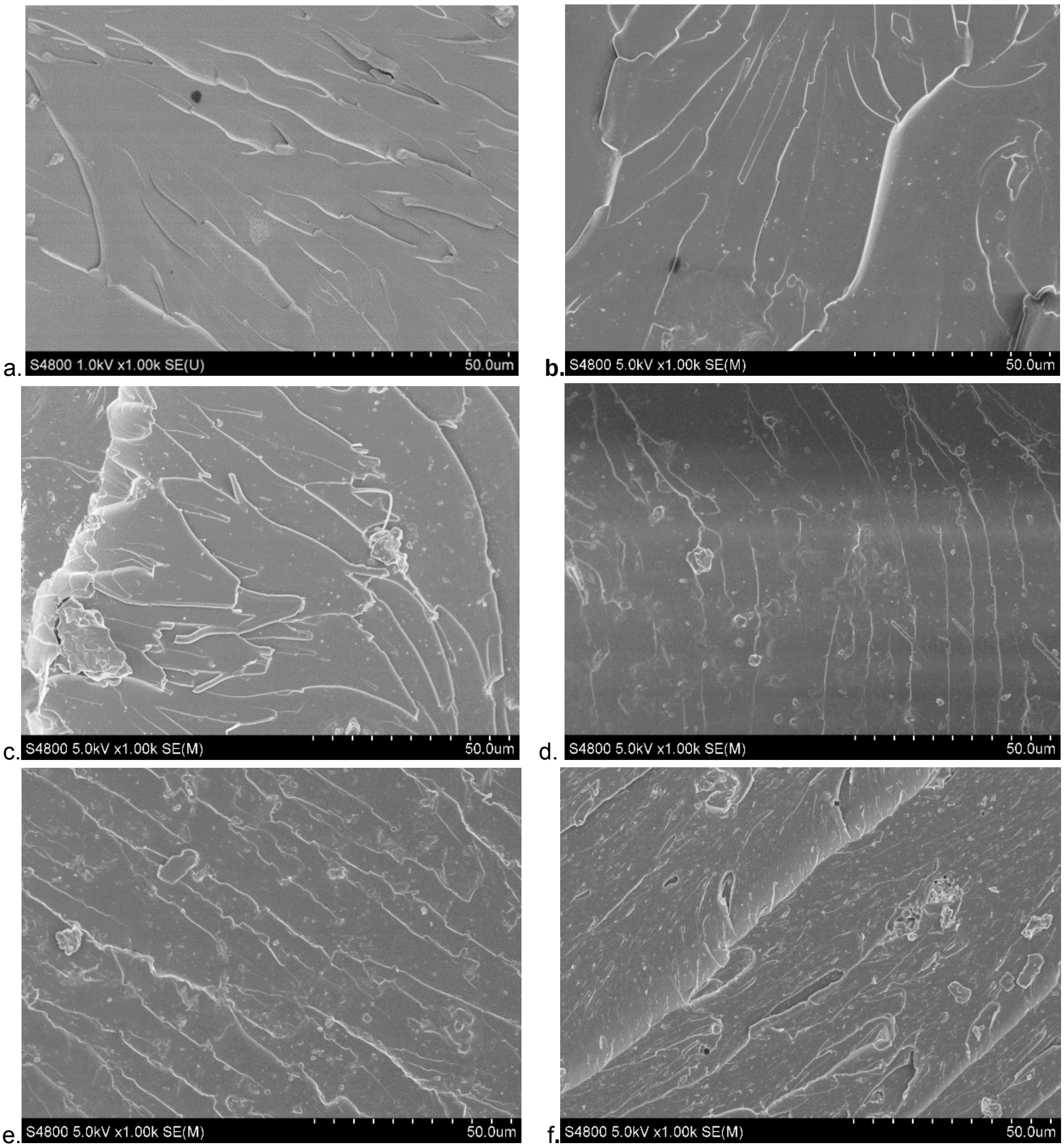


Figure 1: SEM images of different contents of the graphene/nanocopper in the epoxy resin.

This kind of phenomenon is because with the increase in the content of graphene/Cu, the chemical bonds that are formed by the graphene/Cu and epoxy resin are increasing, which can enhance the mechanical property of the epoxy resin. As can be seen from the comparison of Figure 1(e) and Figure 1(f), when the content of graphene/Cu within 1.9 wt%, it can be seen from figures that the surface of epoxy resin is relatively smooth, this phenomenon proves that the graphene/Cu has a good dispersion in the epoxy resin. And then continue to increase the content of graphene/Cu to 1.9 wt%, it can be seen from the figure that the graphene/Cu has an uneven distribution on the surface of the epoxy resin, which can shows that the graphene/Cu are not fully

dispersed in the epoxy resin. So we can only get a moderate content of graphene/Cu that can effectively enhance the mechanical properties of the epoxy resin. However, if too much graphene /Cu are added to, it will cause the mechanical properties of the modified epoxy resin to decrease.
In order to enhance the mechanical properties of EP, the graphene is added into the epoxy resin. Figure 2 show that with the increase of the content of graphene/Cu, the tensile strength and modulus of elasticity of the EP/graphene/Cu composites have a trend of increase before reduction, and reach the maximum when the content of graphene/Cu is 2.1 wt%. The reason for the above phenomenon is that the content of the graphene/Cu is increased within a certain limit. The tensile strength and modulus of elasticity of EP/graphene/Cu composites are higher and higher until the content of graphene/Cu is 2.1 wt%. And then if we continue to increase the content of graphene/Cu, we can see from the Figure 2 that the tensile strength and modulus of elasticity of composites will get lower. This is because, in general, when there is external stress in composites, the composites can produce crazing, which will be further developed into the crack. The effect of graphene/Cu on the properties of epoxy resin is that the graphene/Cu goes into the internal crack of the material. A variety of surface functional groups thus easily form ‘filamentous connection’ structure together with the epoxy resin, and then change the cracks into crazing. Through the above processes, the mechanical properties of the composites have been improved. And when the content of graphene/Cu increases to a certain extent, the graphene/Cu will tend to gather, the dispersion in the substrate becomes uneven, and it cannot form a good interface either, even forming defect in the substrate and causing stress concentration, which leads to the decline of mechanical properties of the composites.

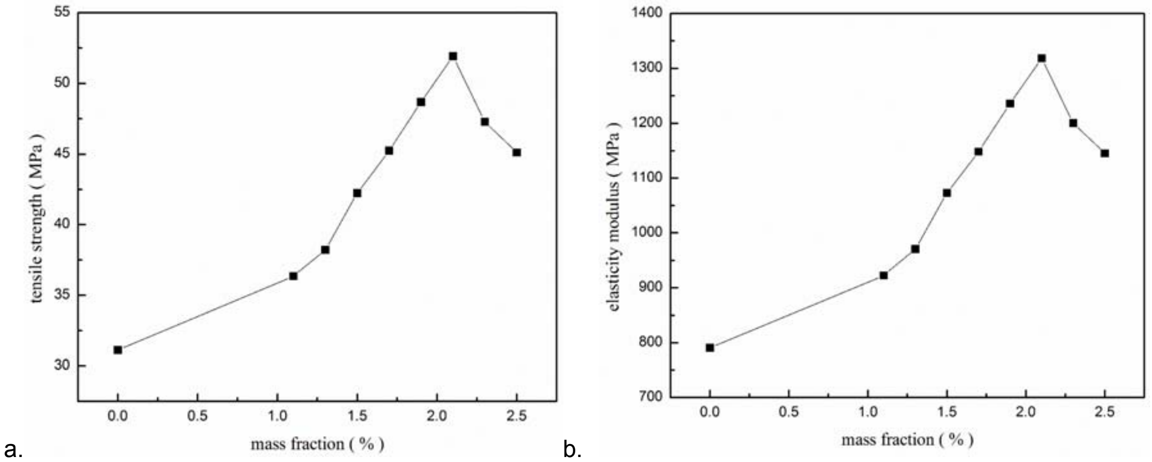
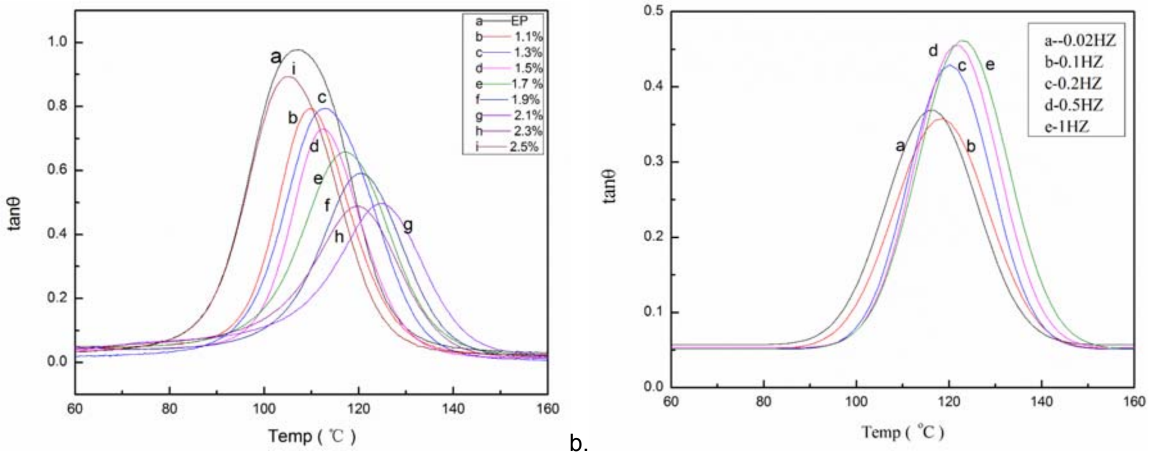


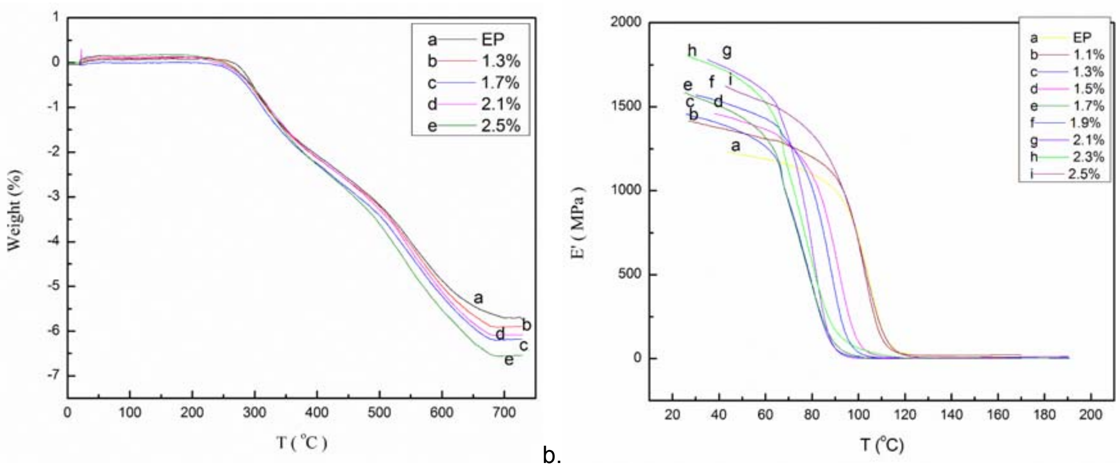
Figure 2: a) The tensile strength and b) the elasticity modulus curve of EP/graphene/nanocopper composites

Figure 3(a) shows that compared with the pure epoxy resin, the position of the loss factor peak of EP/graphene/Cu composites is clearly moving in the direction of high temperature, which proves that the addition of graphene/Cu reinforced the glass transition temperature of epoxy resin. On the one hand, it is because the graphene/Cu have strong surface energy and chemical reactivity, which can be polymer chains. With the increase, the crosslinking density increases and make chemically bonded with the epoxy resin and form chemical junction. On the other hand, with the addition of graphene/Cu, rigid particles in epoxy system are introduced, whose surface is advantageous to the epoxy resin chain tangles and form the physical junction with the polymer chains and this makes the free volume of the system decrease, the athletic ability of chain segment decline, and the flow resistance of molecular chain increase, improving the glass transition temperature of composites. The above analysis shows that the addition of graphene/Cu improves the heat resistance of epoxy resin substrate obviously. We can also see from the picture when the content of graphene/Cu is more than 2.3 wt%, the initial capacity loss temperature is reduced and the position of the peak moves to the low temperature. The reason for this phenomenon is that the crosslinking density decreases.Figure 3(b) shows that with the increase of frequency, the position of loss factor peak of material moves to the high temperatures, so the glass transition temperature of composites also move to the high temperatures. It is because when the frequency is low, the polymer chain segment motion completely keep up with the change of the external force, and the internal friction of the material is small, so the motion of molecular chain segment is blocked small and the glass transition temperature is small. At a high frequency, the polymer chain segment motion completely failed to keep up with the change of the external force, so the internal friction of the material is large, which greatly limits the movement of molecular chain segments, and the polymer shows rigidity and the glass transition temperature is large.



a. b.

Figure 3: The curve of a) pure EP and different contents of EP/graphene/nanocopper composites and b) different frequencies have effect on the glass transition temperature of composites



a. b.

Figure 4: The curve of different contents of the graphene/nanocopper have effect on a) the thermo-gravimetric of composites and b) the energy storage modulus

From the Figure 4(a), it can be seen that the interval of weightlessness is from 533 K to 953 K. Below 533 K, the main reasons for the hot weightlessness are the evaporation of water in the samples, the decomposition of a small amount of epoxy resin and the volatilization of low molecular weight materials. The main interval of the weightlessness is from 533 K to 953 K. The main reason for hot weightlessness at the interval is the decomposition of epoxy resin molecular. At a lower temperature, the thermal weight loss of composites, which contain the different contents of graphene/Cu, makes no big changes. But compared with the pure EP, by the thermal decomposition method, the residual amount of the composites, which contain a certain content of graphene/Cu, is obviously small. And with the increase in the content of graphene/Cu, the residual amount of thermal decomposition of composites decreases. Although the nanocopper can improve the heat resistance of epoxy resin, its dosage is still smaller than that of graphene. And then compared with epoxy resin, the decomposition temperature of graphene is lower, so at a high temperature, compared with the same quality of epoxy resin, the graphene can absorb less heat. So the Figure 4(a) will indicate a phenomenon that the thermo-gravimetric is larger.The Figure 4(b) shows us that when the content of graphene/Cu is less than 2.1 wt%, with the increase in the content of graphene/Cu, the energy storage modulus constantly increase, but the energy storage modulus begins to decline until the content of graphene/Cu is 2.3 wt%. The reason why this kind of change appears is that there are many carboxyl, hydroxyl and epoxy groups on the surface of graphene/Cu. In the process of experiment, these surface groups react with the epoxy resin, so the energy storage modulus constantly increases. When the content of gaphene/Cu is too much, although the interaction between the epoxy resin and surface groups is strong, its surface groups will hinder the crosslinking reaction between the epoxy resin and hardeners, thus reducing the crosslinking density and mechanical properties of epoxy resin. So the phenomenon appear that the energy storage modulus of composites decreases consequently.

4. Conclusions

In conclusion, the approach demonstrated in this study effectively reinforce the mechanical properties and heat resistance of epoxy matrix. The main highlight in this experiment is that we prepare the modified epoxy resin which contain the different contents of graphene/Cu. Based on the study of the morphology and properties of modified epoxy resin, it can be found that when the graphene/Cu disperses evenly in the epoxy resin within the scope of right amount, the glass transition temperature, strength, toughness, hardness and heat resistance of the epoxy resin are reinforced. Based on the study of the data in the article, we can come to the following conclusions: Firstly, it can be seen from the data that a certain content of graphene/Cu composites have a good dispersion in the epoxy resin that can effectively reinforce the mechanical properties and heat resistance of epoxy resin. Secondly, comparing the dynamic mechanical properties of the epoxy resin with the different contents of graphene/Cu, we can find that with the increase in the content of graphene/Cu, the glass transition temperature of composites gradually increases. The glass transition temperature of the modified epoxy resin containing 1.9 wt% of graphene/Cu increases by about 14□, compared with the pure epoxy resin. Thirdly, the addition of graphene/Cu has a great effect on the mechanical properties of epoxy resin. From the data, it can be seen that when the content of graphene/Cu is 2.123 wt%, the tensile strength and elastic modulus reach the maximum. when the content of graphene/Cu is 2.1 wt%,the shear strength of composites reach the maximum value of 34.78 Mpa, which is about 69% higher than that of shear strength of epoxy resin. Fourthly, the addition of graphene/Cu has a great impact on the thermal stability of cured epoxy resin and with the increase in the content of graphene/Cu, the thermal endurance properties of composites have a significant improvement.

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