DETERMINATION OF ELASTIC BEHAVIOUR OF SELF-HEALING COMPOSITES

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Abstract— **Present work consists of studies related to self-healing composites having encapsulated healing agent. Several research works have been conducted to prepare self-healing systems and for the identification of their mechanical properties. However, limited work has been done to evaluate elastic behavior of self-healing composites using different mathematical models. In this article we have used some well-known mathematical models to calculate elastic modulus of the capsules in particular and the overall composite. The experimental results from relevant research works are correlated with our theoretical predictions and some suitable analogy is drawn.**

Keywords—**polymer, composite, healing, elastic behaviour, mathematical modelling**

I. INTRODUCTION

The demand for composite materials in our day to day life has increased manifolds because of its superior mechanical, thermal and electrical performance. Researchers all over the globe are now working to design and develop better composite material to cater to high performance industrial demands. Thus, by changing the properties at the nano-scale, composites can be tailored to be used in high-end technological applications like aviation, aerospace and biomedical applications. Self-healing polymers and composites with microencapsulated healing agents are one of the class that offer tremendous potential for providing long-lived structural materials [1]. In this regard, scientists have formulated various ways through which a material can heal itself and bridge internal cracks. It has been found the healing with the help of encapsulated liquid healing agents has the maximum healing efficiency. Brown et al.[1] prepared dicyclopentadiene (DCPD) filled poly-urea-formaldehyde (UF) microcapsules for healing in composites. Microcapsules of 10-1000 µm diameter were prepared by varying the agitation rate. Micro capsule induced toughening was measured using tapered double-cantilever beam (TDCB). To cure the healing agent (DCPD), particles of bis(tricyclohexylphosphine)-benzylidine ruthenium (IV) dichloride (Grubbs') catalyst as curing agent is also used[2-8]. In most of the cases DGEBA was used as the base matrix, because of its compatibility with capsules and greater shelf life. Keller et. al.[10] extracted Elastic modulus of the capsule shell wall by comparison with a shell theory model for the compression of a fluid filled microcapsule [10]. Furthermore, several works have been done considering two different type of healing agents in microcapsules in a self-healing system for determination of relative healing efficiency. Jin et. al. [18, 19] prepared self-healing thermoset using encapsulated epoxy-amine. Diluted epoxy monomer EPON 815C was encapsulated in one type of capsules and curing agent EPIKURE 3274 was encapsulated in the other type. Qi Li et. al.[20] used poly(methylmethacrylate) (PMMA), as the encapsulating shell and amine as the healing agent. PMMA was chosen as a shell material instead of poly-urea formaldehyde because of it can encapsulate amines. The resulting microcapsules exhibit excellent thermal and curing agent storage stability. Maximum healing efficiency of 93.50% has been obtained with 15 wt.% epoxy containing microcapsules [13, 20]. In view of the above the present work has been planned in such a way as to understand the elastic behavior of self-healing composites and compare this with the different mathematical models available so that an optimized level of filler volume fraction in self-healing composites can be identified.

II. METHODS FOR PREPARATION OF SELF-HEALING COMPOSITES

Researchers now a day have been able to formulate a variety of self-healing composites. In this article we shall restrict our study to composites embedded with Dicyclopentadiene (DCPD) filled Poly-(urea formaldehyde) (UF) capsules. The capsules were prepared by *in-situ* polymerization of microcapsules encapsulating healing agent in an oil-in-water emulsion [1-3]. During crack propagation, the capsules get ruptured and the healing agent flows in the cracks as a result of capillary action [1]. In the presence of catalyst the healing agent solidifies thereby recovering the strength of the material. One of the standard methods of in-situ preparation of capsules is elaborately described in white et. al. 2001 [1]. Scientists have come up with new healing agents and better shell wall materials. Some researchers have used nano-capsules for self-healing by using ultra-sonication technique. The healing efficiency depends on factors like capsule content, shell wall thickness, capsule size etc. the healing efficiency of such composites ranges from 75-90%.

III. EXPERIMENTAL METHODS USED FOR CHARACTERIZATION

The capsules once prepared are dried and then mixed with epoxy resin and allowed to cure. Mechanical analysis is done with the help of tensile testing machine. The Dog-bone type samples are used for such test (ASTM D638 Type I). At least five numbers of samples were tested to failure in the tensile testing machine. The healing efficiency was measured by carefully controlled fracture experiments for both the virgin and the self-healed materials.

IV. THEORETICAL MODELS

A number of research works have been done to evaluate the elastic modulus of composite materials. However, not much analysis is done to evaluate the mathematical models that may define the elastic modulus self-healing composites. The problem that arises in case of self-healing composites is the nature of the filler. The aspect ratio of the filler primarily plays a significant role in determining the mechanical behavior of composite material. The strength of the filler shows a parabolic variation with the aspect ratio. Spherical fillers in this respect have an aspect ratio of 1. The strength of the composite also depends on the interaction between the fillers and composites. In this study, we have used some theoretical models to compare the elastic modulus with the experimental results obtained from research work done by others. We have used Rule of Mixtures [10], Halpin Tsai model [15], Guth model [14] to evaluate mathematically the expressions for Young's modulus of the composites as a function of volume fraction of fillers. There are other models used to predict the properties of composite with fillers, but not all of these are suitable for self-healing composites with micro or nanocapsules.

1. A. RULE OF MIXTURES

This model (often modified according to the type, shape and orientation of the reinforcement/filler) is commonly used to describe various properties of the composites. According to this rule the overall Elastic modulus of the composite depends on the elastic modulus of the individual constituents and also on the relative volume fraction as shown in equation (1). Mathematically,

$$E_c = V_f E_f + V_m E_m \quad \ldots\ldots\ldots\ldots\ldots 1$$

Where, E_c = Elastic modulus of the composite, E_m= Elastic modulus of the matrix, E_f = Elastic modulus of the filler material, V_f =Volume fraction of capsules and V_m =Volume fraction of matrix

$$V_f + V_m = 1 \quad \ldots\ldots\ldots\ldots\ldots 2$$

The concentration is expressed in terms of volume fraction and it follows equation (2). This model is quite simple and easy to understand.

B. HALPIN TSAI MODEL

This model describes the elastic modulus of composites based on the geometry and orientation of the fillers and the elastic modulus of the filler and matrix. The mathematical equation is given in equation (3 and 4)

$$\frac{E_c}{E_m} = \frac{1+\xi\eta V_f}{1-\eta V_f} \text{ ....3}$$

$$\eta = \frac{\frac{E_f}{E_m}-1}{\frac{E_f}{E_f}+\xi} \text{ ....4}$$

Where, E_c = Elastic modulus of the composite, E_m= Elastic modulus of the matrix, E_f = Elastic modulus of the filler material, V_f =Volume fraction of capsules, V_m =Volume fraction of matrix and ξ = Measure of reinforcement. The measure of reinforcement depends on the filler geometry, packing geometry and loading condition. In our case, for spherical particulate fillers the value of ξ is equal to 2.

C. GUTH MODEL

Eugene Guth [14] worked extensively on the mechanical properties of reinforced matrices and, in collaboration with Smallwood, Gold and Einstein, formed the Guth model to predict the Young's moduli, shear moduli and viscosity of composites. This model is formulated considering the reinforcement of rubber matrix with carbon black spheres. We have used this model since the fillers in our case resemble to that of carbon black spheres at nano scale. Thus for Young's modulus, the expression can be written as shown in equation (5).

$$E_c = E_m (1 + 0.67fV_f + 1.62f^2 V_f^2) \text{,.......5}$$

Where, E_c = Elastic modulus of the composite, E_m= Elastic modulus of the matrix, V_f =Volume fraction of capsules, V_m =Volume fraction of matrix, and f =The aspect ratio of filler particles. Since the particles in consideration are spherical, aspect ratio f is taken unity.

Also, for shear modulus

$$G_c = G_m\left(1 + K_E V_f + 14.1{V_f}^2\right) \text{........6}$$

Where, G_c = Shear modulus of the composite, G_m= Shear modulus of the matrix, K_E = Einstein's Coefficient. The Einstein's Coefficient, K_E, is can be calculated by knowing the Poisson's ratio of the matrix material. In case of DGEBA, the Poisson's ratio is found out to be around 0.3. So, the K_E value in this case is taken as 2.25

V. CORELATION BETWEEN THEORETICAL AND EXPERIMENTAL RESULTS

The experimental results of research done by others [11] have been correlated with the results calculated from the theoretical models [9 and 10]. The elastic modulus of a single capsule is evaluated using rule of mixture. The capsule consists of urea formaldehyde as shell material and DCPD as the healing agent. The volume fraction was calculated by considering average size of capsule as 185 µm and shell wall thickness as 170 nm. The elastic modulus of polymerized urea-formaldehyde was taken as 9.5 GPa [16]. And the elastic modulus of DCPD was calculated using equation (6). It has been found that the storage modulus of DCPD at 40 ^{0} C and 10 Hz is 1.49 GPa [17]. And the loss modulus of DCPD for the same parameters was evaluated using equation (7). Using equation (6 & 7), the elastic modulus of DCPD was calculated to be 3.81 GPa. So, using the Rule of Mixture the elastic modulus of a single capsule is found to be 3.825 GPa. Experimentally, the elastic modulus of the Poly-(urea formaldehyde) shelled capsule was calculated from compression of a single average sized capsule was found to be 3.5 -3.9 GPa [10]. This is well in justification with the results obtained from the membrane theory model. Therefore the Rule of mixture can be used to evaluate the elastic modulus of both micro capsules. For nano capsules we can also consider the same .

$$E_{DCPD} = \sqrt{(E')^2 + (E'')^2} \text{ ....6}$$

$$\tan\delta = \frac{E''}{E'} \text{.................................7}$$

Where, E_{DCPD} = Elastic modulus of DCPD, E' = Storage modulus, E''=Loss modulus, δ= phase lag between stress and strain.Putting the value of elastic modulus of capsules as 3.8 GPa [10] and that of the DGEBA matrix as 2.88 GPa in the Halpin Tsai equation, the variation of elastic modulus of the composite with the volume fraction of capsules is plotted (as shown in fig. 1). Experimental results reveal that elastic modulus of the composite remains almost constant or slightly increased with the increment of nanocapsule volume fraction from 0.5 to 2 vol.% (1.5 nm diameter). Whereas, a proportional decrease in modulus was observed for micro-capsules (180 µm diameter) with increase in capsule volume fraction [9]. The variation as obtained from Halpin Tsai equations show a steady rise in elastic modulus of composite with increase in the volume fraction of the capsules. This proves that Halpin Tsai equations are in direct correlation with the behavior of composites for nano-capsules. However, for micro-capsules the models of Halpin Tsai show contradictory predictions. The reason for such a behavior might be that Halpin Tsai model doesn't take into consideration the capsule content, bonding between fillers and the matrix. Moreover this beahavior can be attributed to the fact that the composite treats the capsules as voids and hence the overall modulus of the composite decreases.

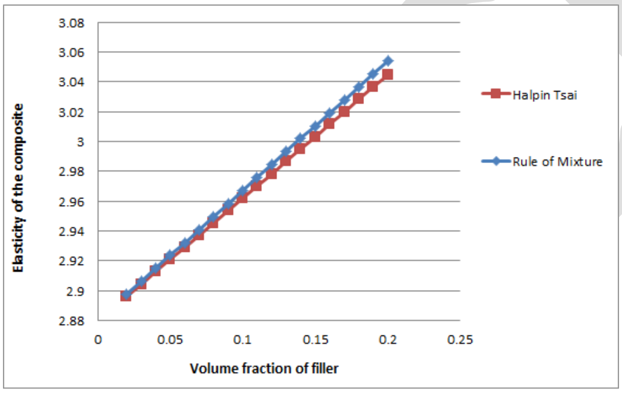
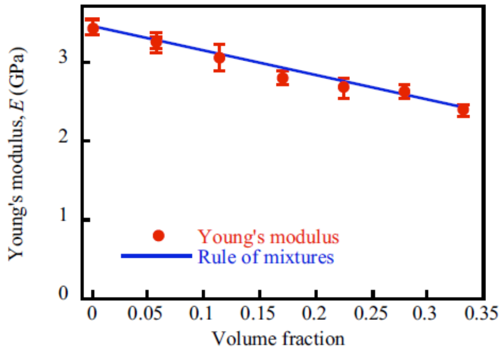


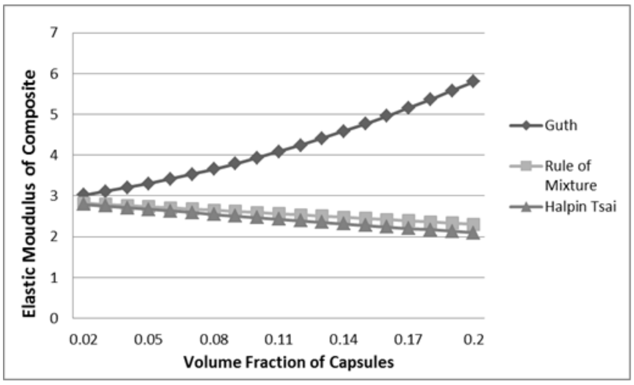
Fig (1): variation of elastic modulus of the composite with volume fraction of the capsules.

If the young's modulus of the capsules is taken as negligible, considering them as voids, then the results obtained using Rule of mixture model was identical to that of the experimental results [11] as shown in fig (2). But in principle there are no voids in the composite. The interaction between the capsules and composites is quite complex and hence remains our future aim of study. Also there is need of an optimum level of filler volume fraction beyond which the entire system will fail. Also, fig (3) shows the correlation between Guth model, Rule of mixture model and Halpin Tsai model. This graph is drawn considering the Young's modulus of capsules as negligible. The predictions of both Halpin Tsai model and Rule of Mixture models are found to be similar to that of experimental results as obtained by Rzeszutko et. al. [11]. However in case of Guth model the Young's modulus gradually increases. This may be because the Guth model doesn't take into consideration the Elastic modulus of the filler. It depends only on the elastic modulus of the matrix, volume fraction and aspect ratio of the filler. The aspect ratio of spherical fillers is unity and hence the curve has positive slope (as shown in fig. 3). Thus, Guth model couldn't predict the elastic modulus of the composite. Both Halpin Tsai model and Rule of Mixture model can accurately predict the elastic modulus of capsule reinforced composite only when the capsules are considered as voids. Thus, higher volume fraction of capsules means higher would be the porosity of the composite and as a result lower is its elastic modulus.



Fig(2): shows the variation of elastic modulus of the composite with the volume fraction of DCPD filled Poly-(urea formaldehyde) capsules[11]

This is the reason why the experimental results show a decrease in elastic modulus of the composite with increase in volume fraction of the fillers. We need to develop better models to precisely predict the behaviour of self-healing composites in particular taking all the parameters into consideration.



Fig(3): shows comparison of Guth model, Rule of mixture and Halpin Tsai when Elastic modulus of capsules is considered negligible.

VI. CONCLUSION

The following conclusions can be drawn from this research study:

a. Rule of mixture can be used to calculate the elastic modulus of both micro and nanocapsules
b. When elastic modulus of the capsules is taken into consideration, both Rule of Mixture and Halpin Tsai models give correct predictions for nanocapsules but not for microcapsules.
c. When elastic modulus is neglected, both Halpin Tsai model and Rule of Mixture give accurate predictions which are in direct correlation with that of experimental results.
d. Guth model couldn't predict the variation of elastic modulus of the composite with the volume fraction of embedded capsules and it deviates from experimental results.
e. We need better models to precisely predict the behaviour of self-healing composites in particular taking all the parameters into consideration.

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