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THERMAL AND DIELECTRIC BEHAVIOUR OF SILANATED CHITOSAN BIO CERAMIC PARTICLES REINFORCED EPOXY RESIN BIO COMPOSITE

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In this research work the effect of silane treatment over the bio ceramic Chitosan particles were studied. The principal aim of this work is to explicit the importance of silanation of particles dispersion in high denser matrix. Particle dimension of 3μm was used as filler. The fillers were surface treated by using an amino silane. The thermal properties were revealed by TGA and thermal conductivity behaviour. The dielectric results shows that the addition of silanated Chitosan particles not altered the dielectric constant and loss tangent to maximum level whereas additions of as-received Chitosan particles formed cluster and tends to conduct more charge. Similarly additions of silanted chitosan particles of 5wt% improved the thermal stability to maximum level by absorbing more energy. Scanning electron microscopy results revealed even dispersion of silanated particles in epoxy matrix.

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Keyword: PMC; Epoxy; Chitosan; Thermal properties; dielectric properties; SEM

1. Introduction

The particulate composites have attractive application in thermal, electromagnetic and spectra electronic applications due to their ability of possessing high resistance, durability and reliability [1]. Thermally and dielectrically strengthened epoxy composites have attractive features like EMI shielding, Thermal interfacing and high thermal stability behaviour [2]. The filler could be surface modified buy an amino silane to improve the dispersion of filler in matrix. The Chitosan particles could be used to make bio composites which may harm less for environment [3]. Adding conducting or semi conducting filler may improve thermo-mechanical properties at the same time they may affect the supreme insulation quality of thermo-set plastics.Surface modification of fillers mat reduces the clustering effect and not affecting the real characteristics of epoxy resin. The surface modified fillers may not response to external frequency hence the real dielectrical parameters could be unaltered [4]. While adding the Chitosan particles in as-received condition into hydrophobic epoxy resin the formation hydroxide may initiate the Di-polar activation of particles. This activation may lead formation of active polarity at lower frequencies itself. Adding Chitosan into epoxy resin, the tensile, flexural, impact, and thermal properties could be improved. In this way the Chitosan is a bio ceramic which never affects the insulation behaviour of epoxy resin. Hand layup technique of composite making could be more adaptive technique where low process parameters were employed.

Arun prakash et al [5] has confirmed that additions of Iron(III)oxide particles into epoxy resin increased the mechanical and thermal behaviour at the same time it affects the insulation behaviour. The dielectric constant was increased near 60% which may lead the dielectric to lose its supreme insulation.

Viswanathan et al [6] has concluded that reinforcing of conductive fillers into epoxy resin increased the dielectric constant and also conduction behaviour. But there could be a problem of

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losing the insulation properties.Saravanan et al [7] has confirmed that adding surface treated MWCNT not altered the conduction behaviour epoxy much. This effect is attributed because of non polar nature of fillers in epoxy matrix. The surface treatment process fetched positive polarity in outer surface of the particles which can't response properly for external frequency.

The thermal and dielectric properties of Chitosan reinforced epoxy could be evaluated by TGA, DSC and Lee's disc method. The electrical conductivity behaviour of composite could be evaluated by LCR Hi-tester with variable frequencies. The dispersion morphology of fillers in epoxy matrix could be revealed by field emissive scanning electron microscopy.

2. Experimental

2.1 Materials

The epoxy resin used here was having the grade of LY556 an equivalent product of araldite. The curing catalyst used for curing was HY951 an aliphatic hardener having low viscosity 0.9Cp. The Chitosan particles were prepared from costal area of southern Tamil Nadu India. The surface modifier used for this study was 3-Aminopropyletrimethoxylane from Sigma Aldrich. Ethanol and aqua solutions were purchased from Merk India Ltd. All the chemicals were used in as received form without any post process treatments.

2.2 Preparationon of Chitosan

The typical chitosan particles were collected from sea waste and get dried off in a hot oven to remove the moisture. The resulting product was then ball milled for 8 hours to convert the substance as a fine powder of 3µm [8]. The Figure 1 shows the SEM image of 8 hour ball milled chitosan particles. It shows rough surface morphology due to random formation of polysaccharide.

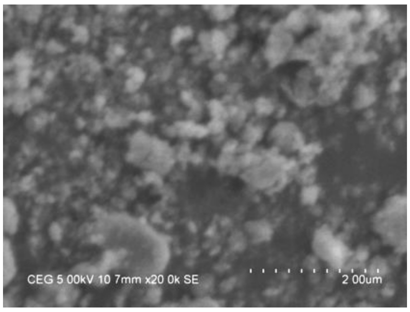


Fig. 1. SEM image of Chitosan particles

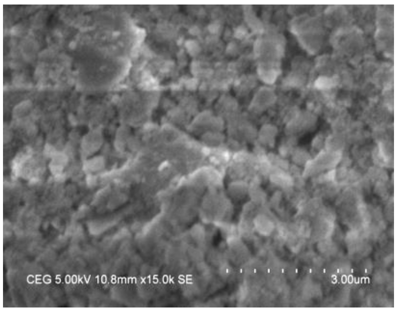


Fig. 2. SEM image of calcinated Chitosan particles

The ball milled chitosan particles have been calcinated around 2hrs at 700ºC to convert the carbonate phase as oxide phase to become more strength micro particles [9]. Figure 2 shows the SEM images of calcinated chitosan particles after 2 hours.

2.3 Surface treatment of Chitosan

The ball milled and calcinated chitosan particles were surface treated by an amino silane via aqueous solution method. In this ethanol of 90% added with water of 10% combined together forms aqua solution resulting acid hydrolysis process with the presence of acetic acid. The silane solution was then added drop by drop to form Si-O structure by eliminating methanol. The fine chitosan particles then briefly spread over the solution to activate the surface with silica molecules [10]. Figure 3 shows the typical reaction of surface modification process.

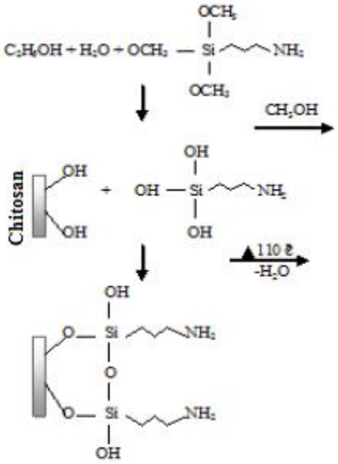


Fig. 3. Silane surface treatment of chitosan particles

2.4 Specimen preparation

The surface treated chitosan particles were dispersed in epoxy matrix as 1wt%, 3wt% and 5wt% at elevated temperature 80ºC for better mixing of filler into matrix. The curing catalyst generally 10wty% added with resin at room cooled condition and stirred continually to get homogenous solution. The resulted epoxy-chitosan solution get poured in to a mould to get final shaped composites. The test specimens of ASTM standards were cut using an abrasive water jet machine with following parameters. The machining was done with SOD of 3mm, abrasive flow rate of 35gm/min, and jet velocity of 220psi and nozzle diameter of 1.1mm.

3. Result and Discussion

3.1 Thermal properties

Table 1 shows the thermal properties of as-received and surface modified chitosan reinforced epoxy composite. The thermal stability behaviour was tested by using a thermo gravimetric analyzer (NETZSCH STA Jupitar 409 PL Luxx, Germany) under N_2 atmosphere). The results revealed that additions of bio ceramic filler into epoxy resin increased the onset temperature in initial degradation of epoxy resin. The initial onset temperature of pure epoxy resin measures 323ºC. The remarkable mass loss of 4.18% was observed in this stage. The middle decomposition stage get starts at the temperature around 366ºC and end up with 417ºC. The final mass loss stage was get starts from 417ºC and end up with 560ºC. The additions of 1, 3 and 5wt% of Chitosan reinforcements improved the onset and offset temperatures of initial, middle and final decomposition stages. The additions of ceramic Chitosan increased the heat absorption behaviour of epoxy resin by acquiring more heat energy. Table 1 shows the values of TGA of different samples.

Table 1 TGA results of composites.

Epoxy %/ As-rec filler%/ Sil filler %	Initial degradation		Middle degradation		Final degradation	
Temperature (ºC)	On	Off	On	Off	On	Off
100/0.0/0.0	323	366	366	417	417	560
100/1.0/0.0	328	372	372	423	423	566
100/3.0/0.0	331	376	376	431	431	573
100/5.0/0.0	338	387	387	440	440	580
100/0.0/1.0	333	376	376	430	430	563
100/0.0/3.0	338	376	376	437	437	570
100/0.0/5.0	340	395	395	446	446	586

Sil- Silane treated

It is observed that additions of 1, 3 and 5wt% of as-received chitosan particles reinforced epoxy composite gives improved initial thermal stability of 1.4, 2.6 & 4.5% than neat epoxy resin. It is because of high thermal absorption coefficient of bio chitosan particles in epoxy matrix. These particles may observe maximum het thereby increasing the initial thermal stability of epoxy resin. It is observed that the surface modified chitosan particles reinforce epoxy resin increase the initial thermal stability than as-received chitosan particles reinforced epoxy resin. The improved thermal stability of 3, 4.4 & 5% were noted for 1, 3 & 5 wt% of silane modified chitosan particles reinforced epoxy resin composite. This improvement is because of addition of surface treated particles disperse on epoxy matrix very uniform thereby increasing the thermal stability [11]. The improved dispersion of particles on epoxy matrix facilitates the heat absorption resistance due to ceramic nature of chitosan micro particles. The applied heat is not received directly by the epoxy molecules and they may observe by the ceramic fillers directly. Hence the intimate contact of micro particles is maximum which leads improvements in thermal stability [12]. Similar improvements were observed in middle and final decomposition stages of surface treated chitosan particles reinforced epoxy resin composite. The rate of thermal stability is little decreased in middle and final decomposition stages compare than initial thermal stability zone. This is because of above the glass transition temperature of polymer the sample behave different and the conversion polysaccharides at elevated temperature [13]. The presented polysaccharides may undergo a kind of phase change thus resulted decrement in thermal stability. Any way the additions of surface treated micro chitosan particles reinforced epoxy resin composite gives better results in thermal stability in as-received particle reinforced epoxy composite.

The thermal conductivity results show that improved results for filler loaded epoxy resin composite. Figure 4 shows the graph of thermal conductivity of as-received and surface treated particles reinforced epoxy system. The surface treated particles shows very high thermal conductive resistance. This is because of additions of ceramic chitosan arrest the heat conduction of matrix. The as-received particles reinforced epoxy composite gives average result in thermal conductivity. Near 60% of improvement is observed in lower thermal conductivity for surface treated chitosan particles in epoxy resin matrix [14]. The maximum dispersion of 5wt% surface modified filler gives very lower thermal conductivity of 0.17W/mK.

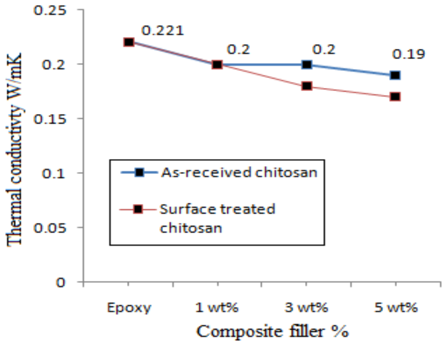
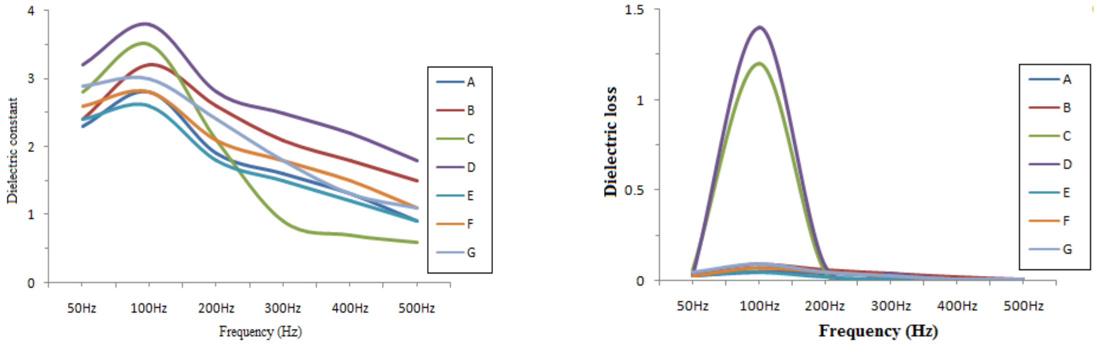


Fig. 4. Thermal conductivity values of composites

3.2 Dielectric properties

The Fig.5 (A, B) shows the dielectric constant&loss, of as-received and surface treated Chitosan reinforced epoxy resin composite. The dielectric test was taken with the help of LCR Hi-Tester, HIOKI, JAPAN. The operating frequency ranges various from 50Hz to 50GHz. Circular specimens of dia 13mm and thickness of 3mm was used as sample measurements. The additions of Chitosan micro particles into epoxy resin increased the dielectric permittivity of composite. This effect is because of additions of ceramic bio chitosan parties may react with epoxy resin via OH group transition and thus polar molecular structure gets developed. These formed polar groups may acts as a Di-pole and response heavily to external frequency thereby increasing the charge conductance. But it is observed that additions of surface modified 1, 3 and 5wt% chitosan particles in to epoxy resin not altered the dielectric values much. This phenomenon get happen due to the reaction of chitosan particles in to epoxy resinwith more uniform manner. The particle cluster was significantly reduce by surface treatment thereby no much difference in dielectric properties were observed [15].

It is observed that the dielectric constant and loss were increased by increase of frequency. This is because of when frequency is in optimal level all the Di pole molecules will response properly. The moment frequency is increased the Di-polar molecules cannot response to high frequency finally they may converted as heat as per Joule’s effect. It is noted that the dielectric values were unaltered much for surface treated composites. In this even though the frequency increased the charge jumping will not be promoted [16, 17]. The amount of fillers is directly proportional to the dielectric values. Among 1, 3 & 5wt% of fillers the 5wt% gives improved result. As more dipoles more charge carrier propagates which may increased the charge transfer. Among all samples the 5wt% chitosan gives very high improvement in constant and loss. But anyway the silane modified composites gives relatively low change in dielectric properties.



(a) *(b)*

Fig.5 (a) Dieletcric constant and (b) Dielectric loss of composites where: (A) pure epoxy, (B) 1wt% as-received filler, (C) 3wt% as-received filler, (D) 5wt% as-received filler, (E) 1wt% surface treated filler, (F) 3wt% surface treated filler, (G) 5wt%surface treated filler.

3.3 Morphology

Fig.6 shows the scanning electron microscopy images of as-received and surface treated chitosan bio particles reinforcements in epoxy hard matrix. The images explicated that addition of as-received particles formed cluster in most of the places and shows reacted phase in epoxy matrix. Whereas additions of surface treated chitosan particles dispersed neatly in the epoxy matrix due to NH_2 functional group reaction [18, 19]. The reacted chitosan particles never formed cluster and shows uniform dispersion. Figure 6(A) shows particle cluster in epoxy matrix. The as-received particles on high denser matrix gives clustered portions. Figure 6(B) shows the enhanced view of chitosan particles in epoxy matrix. It reveals that reacted phase in matrix medium. Figure 6(C) shows the finely dispersed chitosan particles in epoxy matrix. the particle functionalization helped to improve the dispersion of fillers uniformly on matrix. Figure 6(D) reveals the enhanced view of particles dispersion on matrix. It explicit uniform order with base matrix which indicates particle surface treatment give better adhesion with matrix which leads better performance [20].

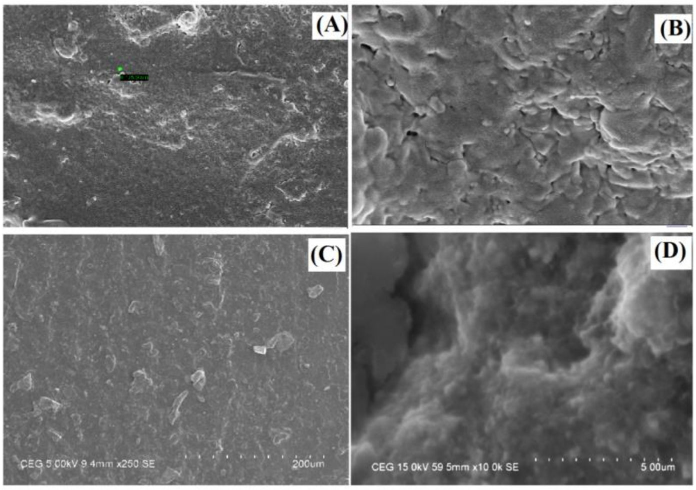


Fig.6. SEM images of (A, B) as-received chitosan particles in matrix and (C, D) surface treated particles in matrix

4. Conclusions

The following conclusions were made from this study. The preparation and functionalization of bio chitosan particles render better application in polymer matrix composites. The additions of chitosan particles into epoxy matrix altered the thermal and dielectric properties. The additions of 5wt% of chitisan particles into epoxy matrix greatly increased the thermal degradation stability of epoxy resin. Among two categories the surface modified reinforcements gives optimal output in thermal properties. The addition of filler altered the dielectric properties much. Whereas additions of surface treated filler not changed the dielectric properties to the maximum level. The SEM morphology shows fine dispersion for surface treated chitosan particles whereas as-received particles show cluster. Hence, additions of chitosan particles improved high thermal performance materials but at the same time they may change the supreme insulation properties. The surface modified particles reinforced epoxy composite not altered the insulation behaviour much.

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