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Research Article

Synthesis and Characterization of Epoxy/Boron Nitride Composite for Aerospace Applications

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Abstract

Beside extensive successful use of epoxy resins in many applications such as electronic packaging, insulation, adhesives and laminate technologies with various advantages; their low thermal conductivity and high CTE (thermal expansion coefficient) limit their performance. However, the addition of the particles into this material can significantly improve the constitutive and thermal properties. In this context, this study aims to develop an adhesive material where the epoxy resin is considered as the matrix material which is filled with Hexagonal Boron Nitride (h-BN) particles. Moreover, we characterize thermal behavior of the developed composite structure. A facile synthesis method was developed for minimizing the void formation while achieving a homogenous distribution of h-BN particles. SEM analysis has been employed to study the effect of the h-BN particles on the microstructural morphology. In addition, DMA (Dynamic Mechanical Analysis) and DSC (Differential Scanning Calorimeter) techniques were employed to examine the glass transition and viscoelastic mechanical behavior. The obtained results are consistent with the existing ones in the literature.

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Havacılık Uygulamaları için Epoksi/Bor Nitrür Kompozitinin Sentezi ve Karakterizasyonu

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Öz

Elektronik ambalaj, yalıtım, yapıştırıcı ve laminat teknolojileri gibi birçok uygulamada çeşitli avantajlara sahip epoksi reçinelerin kapsamlı başarılı kullanımı yanında; düşük ısı iletkenliği ve yüksek CTE (termal genleşme katsayısı) performanslarını sınırlar. Buna rağmen, çeşitli parçacıkların bu malzemeye eklenmesi, mekanik ve termal özellikleri önemli ölçüde artırabilir. Bu bağlamda, bu çalışma, epoksi reçinesinin, Altıgen Bor Nitrür (h-BN) partikülleri ile doldurulmuş matris malzemesi olarak kabul edildiği bir yapıştırıcı malzeme geliştirmeyi amaçlamaktadır. Ayrıca, gelişmiş kompozit yapının termal davranışı karakterize edilmiştir. H-BN parçacıklarının homojen bir dağılımını sağlarken, boşluk oluşumunu en aza indirmek için bir sentez yöntemi geliştirilmiştir. SEM analizi, h-BN partiküllerinin mikroyapısal morfoloji üzerindeki etkisini incelemek için kullanılmıştır. Ayrıca cam geçiş ve viskoelastik mekanik davranışları incelemek için DMA (Dinamik Mekanik Analiz) ve DSC (Diferansiyel Tarama Kalorimetresi) teknikleri kullanılmıştır. Elde edilen sonuçların literatür ile uygun olduğu gözlemlenmiştir.

1. INTRODUCTION

Epoxy resins have been a common material in various industries with different applications such as electronic packaging, insulation, adhesives and laminate technologies due to their low dielectric constant, high resistivity and effective production capability. Their excellent adhesion, electrical insulating and chemical behavior make them crucial in packaging of integrated circuits. On the other hand, low thermal conductivity and high coefficient of thermal expansion (CTE) of epoxy resins limit their use for such applications (see e.g. [1]).

Mechanical behavior as well as electrical and thermal properties of epoxy resins can be tailored by two main approaches to fulfill technical requirements for functional applications. First approach is to tailor the molecular design by altering flexible/rigid polymer chain configuration, cross-linking and functional side groups (see e.g. [2, 3]). The second approach is to employ the resin as the matrix material and to tailor its properties by adding different types of fillers (see e.g. [4, 5]). The second approach leads to functional composites having the benefit of incorporating different properties which are not observed at the same time in an individual material (neither matrix nor filler). Depending on the specific application, different types (organic or inorganic), size (micro, nano, etc.) and geometry (spherical, flake, fibre, etc.,) of fillers have been developed. Due to their proven durability and robustness inorganic fillers are preferred over organic ones. Typically, such inorganic fillers include graphite, carbon black [6], carbon fibers [7], ceramics [8] and various metal additives such as Al2O3 [9], AlN [10], ZnO [11], BN [1], powders of Cu [12], Ag [13], Ni [14], and Al [15].

Among others h-BN (hexagonal boron nitride) is one of mostly preferred filler materials to tailor mechanical as well as thermal behavior of epoxy resins without disturbing the electrical properties. Due to its two-dimensional structure hexagonal boron nitride exhibits significant implicit thermal conductivity on the basal plane. In contrast, h-BN is actually an electrically insulating material with a low dielectric constant. This makes h-BN superior in comparison to other Al2O3, SiO2 and AlN based fillers. In addition, high chemical and thermal stability make h-BN one of the mostly preferred filler material to modify epoxy resin matrix for electronic packaging applications.

In use of h-BN there are various factors which should be considered to achieve high performance. Filler content is one of main factors which needs to be addressed first. It defines maximum packing factor within the matrix material. Filling factor plays a major role for the formation of a conductive pathway. In addition, the thermal conductivity pathway is dependent on the shape, size and the size distribution of the particles. Filling content and the procedure followed during mixing influences the spread of epoxy resin to h-BN particulate agglomerates. In principle, an increase in the filler content results in an improvement of the thermal conductivity. Contrarily, very high content of filler may trigger the formation of highly agglomerated h-BN particulate networks which significantly reduce the effective contact area of the epoxy resin and the flexibility.

Custom adhesives have been formulated through different types of epoxy resins and h-BN particulates. Various studies report different approaches for getting an optimum filler content and a mixing process (see e.g. [16,17,18]) but still it is challenging to get effective and quick solution especially at industrial application level. In the current study, an epoxy based composite material with improved thermal behavior is obtained through the incorporation of h-BN as fillers for adhesion application in aerospace industry. The effect of filler content on both mechanical and thermal behavior of obtained composite material have been studied through the SEM analysis of the microstructure morphology as well as the DSC and DMA techniques applied on the material.

The paper is organized in the following way. First, in Section 2, the epoxy matrix material and synthesis and moulding of Epoxy/h-BN composites is presented with characterization method. Then, in Section 3, SEM and test results are summarized for different particle weight ratios by examining its effect on thermal properties of adhesive mixture. Finally, some concluding remarks are given in Section 4.

2. EXPERIMENTAL PROCEDURES

2.1. The filler and the matrix material

The filler, i.e. h-BN (Hexagonal boron nitride) having size <100 μm were purchased from Sigma-Aldrich. Loctite 9412 was chosen as the epoxy matrix. It is a material with low viscosity and flexible adhesive preferred in aerospace and aeronautical engineering. Its self-levelling and flow properties make it ideal especially for potting and encapsulating applications.

2.2. Synthesis and Moulding of Epoxy/h-BN Composites

Firstly, h-BN particulates were subjected a bake-out step at 120°C for 2 hours for the degas/moisture abatement. Such inorganic particulates contain high level of humidity (entrapped due to high surface area) which may result in the development of significant levels of porosity during incorporating them in an epoxy resin. Similar porosity problems may be observed due to the absorption of atmospheric moisture during the curing cycle, too.

Therefore, we applied two step degassing procedure to remove moisture, trapped air and volatiles from epoxy resin. First, a 40 kHZ sonication using ultrasonic bath was carried out for 30 minutes. Then, a vacuum conditioning at 4.2 Torr for an hour was applied. After adding baked-out h-BN particulates into the epoxy resin first a mild mechanical mixing was applied and afterwards ultrasonic sonication mixing was performed. Also we applied a second vacuum conditioning step to remove any trapped air induced by mixing procedure.

Trapped-air free epoxy resin filled with h-BN particulates were poured into custom PTFE (Teflon) moulds. Three different mould types were fabricated for Dynamic Scanning Calorimetry (DSC), Coefficient of Thermal Expansion (CTE) analysis and Dynamic Mechanical Analysis (DMA). Such moulds provide a minimum interaction with the sticky epoxy resin; which makes it easy to take-off after the addition of hardener to epoxy/ h-BN particulate mixture. A two stages curing was carried out; first at room temperature for 24 hours and additional 1 hour under 80°C. Finally, surface of cured samples was polished to remove any excessive material. Fig. 1 shows three different types of samples (epoxy filled h-BN) after moulding.

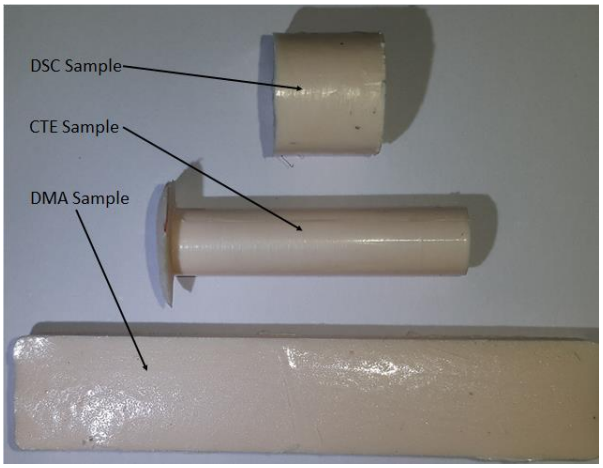


Figure 1. Samples repapered for DSC, CTE and DMA tests.

2.3. Characterization

The microstructural analysis was conducted and the dispersion of h-BN fillers in the epoxy matrix was studied through Scanning Electron Microscopy (SEM) (Plus Zeiss SEM). Prior to imaging samples were cut into several slices and their surfaces were covered with a thin gold layer using a PVD sputter-coater (Balzers). Imaging was carried out under an operating voltage of 7 kV.

Fourier Transform Infrared spectroscopy (FTIR) technique has been employed through Bruker Tensor 27 FTIR for 4000 – 400 cm-1 range to reveal the existence of dispersion of fillers in the matrix.

Differential scanning calorimetry (DSC) study was conducted through Q 200 (TA Instruments) to monitor epoxy matrix-h-BN interaction. Thermal conductivity analysis was done on 50×7.3 mm cylinder samples through guarded heat flow meter technique (DTC-300, TA Instruments).

Dynamic Mechanical Analysis (DMA) was conducted for prepared h-BN/Epoxy composites using ARES G2 (TA Instruments). A scanning tension mode was applied (30℃ - 100℃) at 5℃/min heating rate and 1 Hz frequency. Afterwards, loss factor, dynamic modulus, and Tg were determined.

3. RESULTS AND DISCUSSION

The morphology of neat epoxy and h-BN filled epoxy with 5, 10, 15 and 20 wt. % of Boron Nitride were studied through SEM and illustrated in Fig. 2. All samples including neat epoxy exhibited a typical morphology composed of holes and defects which might arise due to volumetric change at the curing stage. Especially composites exhibited a non-flat fracture surface, and the fillers were randomly distributed in the epoxy matrix. Such a fracture morphology may be explained by the matrix shear yielding after the addition of h-BN fillers. As one can see easily at high loading amounts (15 % and 20%), h-BN particulates form dense agglomerates due to high surface energy and poor wettability Boron Nitride. On the contrary, at low filling contents such as 5 % and 10 %, the recorded morphology reminded that of neat epoxy. At higher filler content, the poor dispersion may lead to a reduction in the mean free path of phonon owing to boundaries between filler and the matrix and the scattering of the defects, which may yield an inefficient heat transfer.

FTIR spectra for neat epoxy and 20% h-BN filled epoxy are illustrated in Fig. 3a and Fig3b. The peak shown explicitly at 1369.5 cm-1 in Fig. 3b may be attributed to the in-plane stretching vibration of B–N. Additionally, the peak around 811.9 cm-1 may refer to the out-of-plane bending vibration of B–N–B. In general, we observed a broad band around 2688 cm-1 at both neat epoxy and 20% h-BN filled epoxy samples. This broad band may be attributed to the hydroxyl amino groups at the edge planes of h-BN or the surface moisture of the matrix.

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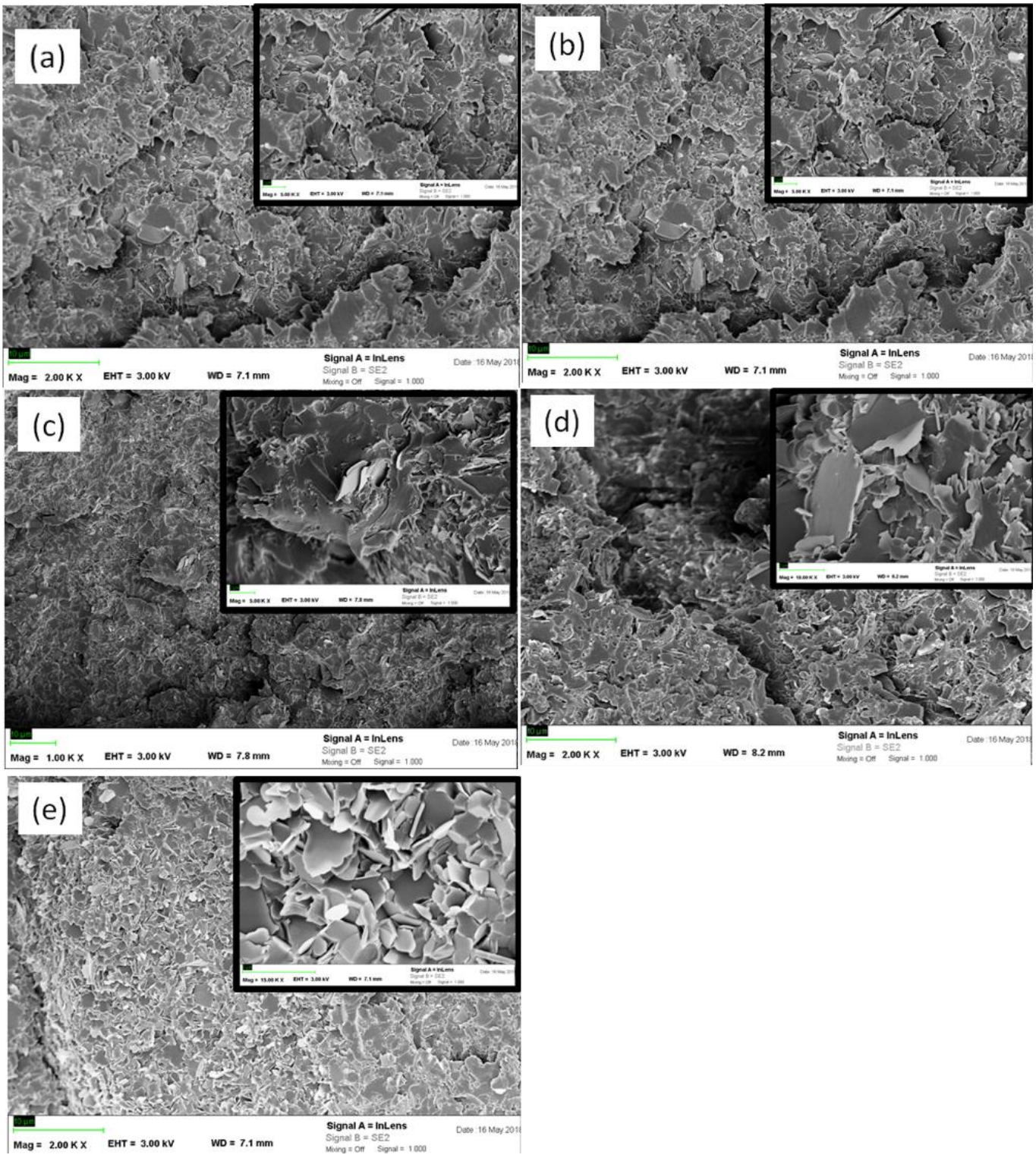


Figure 2. SEM image of BN reinforced epoxy adhesive with different BN amounts (a) neat epoxy (0 wt% BN) (b) 5 wt% BN (c) 10 wt% BN (d) 15 wt% BN (e) 20 wt% BN.

In general, we observed a broad band around 2688 cm-1 at both neat epoxy and 20% h-BN filled epoxy samples. This broad band may be attributed to the the surface moisture of the matrix Fig. 4 illustrates the thermal conductivity of composites at different temperatures as a function of h-BN content. Basically increasing the h-BN filler content results in an increase in the thermal conductivity of the developed composite. At higher temperatures thermal conductivity with high h-BN filling content (15% and 20%) became approximately 2 times higher than the conductivity of the neat epoxy. These results are consistent with the ones in the literature (see e.g. [1, 18]). Note that these studies obtain larger improvements due to the used surface agents such as Silane groups.

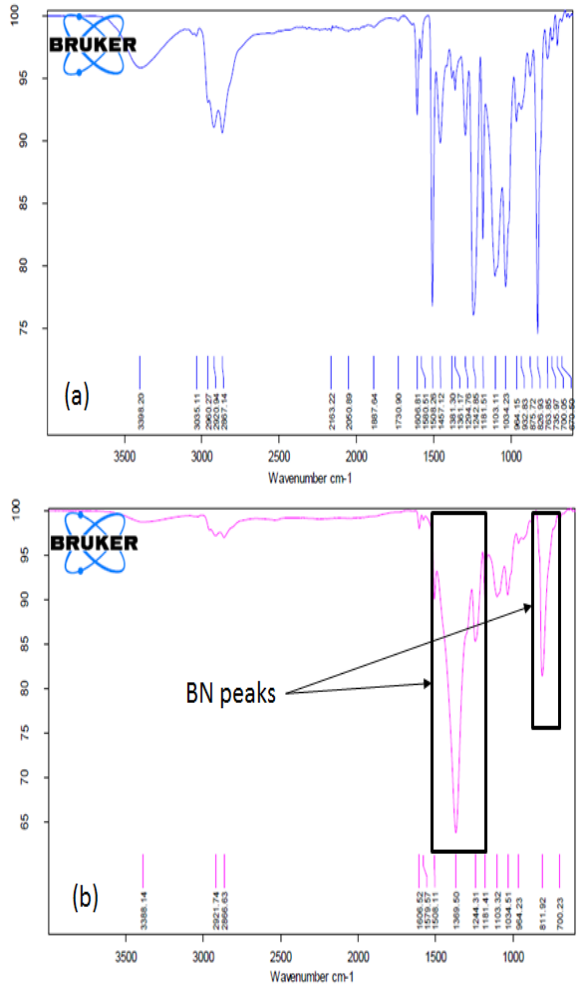


Figure 3. FTIR Results of BN reinforced epoxy adhesive with different BN amounts (a) neat epoxy (b) 20 wt%.

[1] states that that the 217% improvement of thermal conductivity is observed using silane groups and mixed mode particles (hBN and cBN (cubic Boron Nitride)). Another recent mixed mode study [19] develops electrically insulating BN/cellulosic fibre where 41% filler content has been used to obtain 387% improvement. In here the effect of single filler is illustrated at different temperature values upto 20% filler content. The increase in the current study can be interpreted through the formation of a thermally conducting network of h-BN particulates within the epoxy resin matrix, which leads to substantial improvement in the thermal conductivity of the developed composite. As previously shown Fig. 2 at higher filler content h-BN particulates were more heavily agglomerated in epoxy resin matrix. This increase in agglomeration may hinder uniform distribution of h-BN and this can disturb formation of an efficient thermal conduction network.

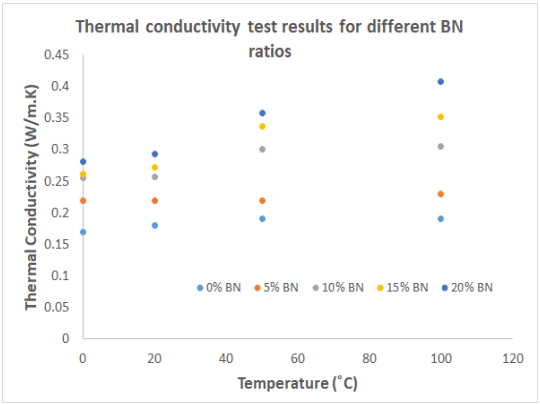


Figure 4. Thermal conductivity test results for different BN ratios.

Fig. 5 shows the dynamic-mechanical properties of the neat material and epoxy composites filled with h-BN particulates. There is a clear change in the storage modulus in glass as well as in rubbery regions at different h-BN filling contents, compared to that of neat epoxy (Fig. 5a). While G` stays around only 0.2 GPa for neat epoxy at 50°C, this value increased to 1.25 GPa which is a clearly indicating an enhancement of G` by five times. The effect of added filler on the storage modulus can be seen much easily in the graph given Fig.5 b. Besides the change in G`, the loss factor (tan δ, reveals the degree of crosslinking) of samples are also illustrated in Fig. 5b. The magnitude of tan δ helps estimating the effect of damping in polymer chains network, which could be obtained using Eq. (1):

$$\tan \delta = G``/G` \qquad (1)$$

where G`` shows the dynamic loss modulus indicating basically the energy dissipation associated with the movement of polymer chains. One can see that glass transition peaks of neat epoxy and h-BN filled epoxy composites seem to stay similar.

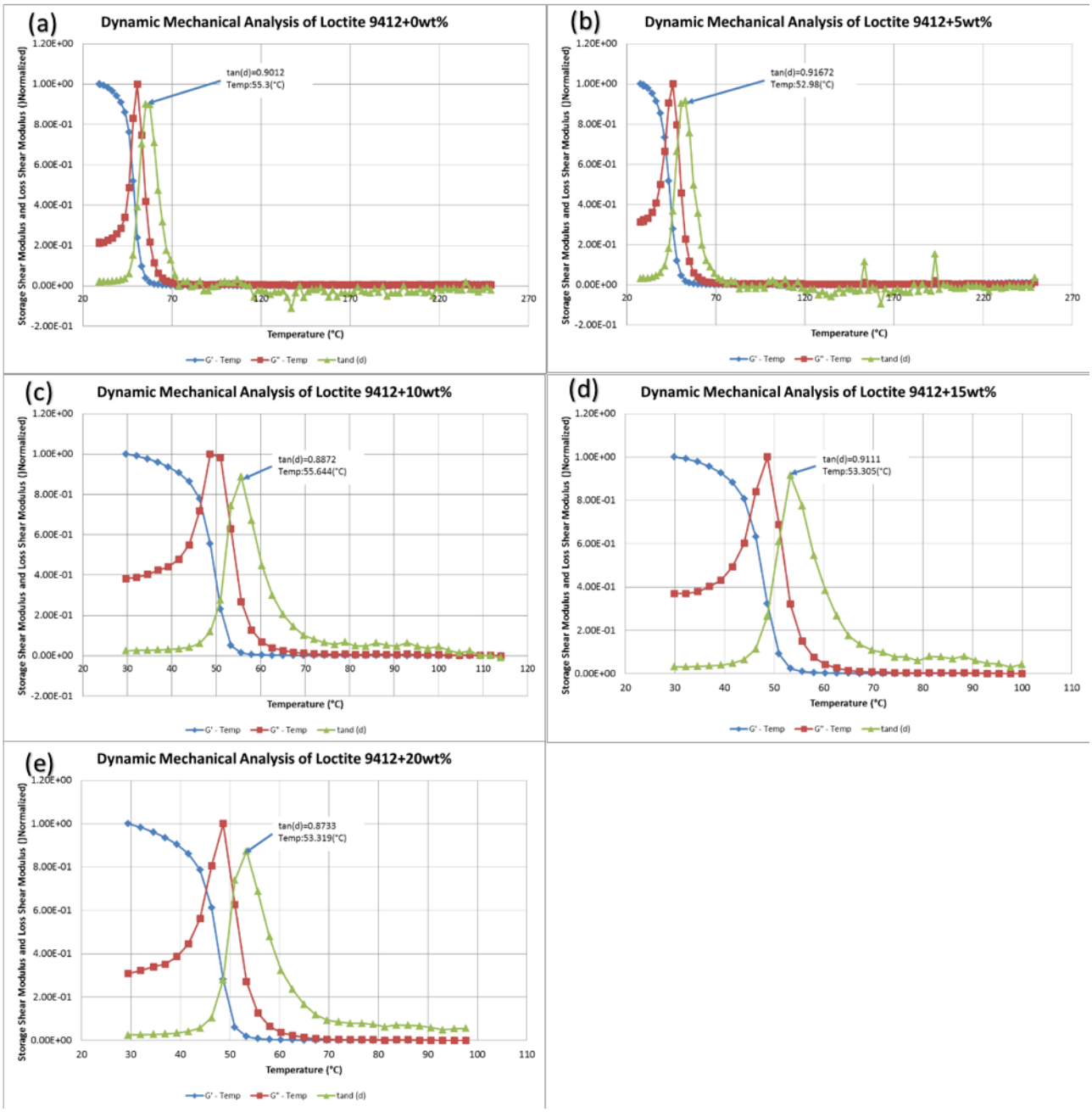


Figure 5. Dynamic-mechanical properties of the neat epoxy (a) and epoxy composites for different h-BN content (b-e).

4. CONCLUSION AND OUTLOOK

In this work, an epoxy based composite material is developed through reinforcement by h-BN particles (spheres and flakes) with distinct loading levels of 0, 10, 15 and 20 wt. %. At high filler content (15% and 20%) an inhomogeneous dispersion has been observed. On the other hand, contacting h-BN particulates formed conductive pathway in the epoxy matrix at these highly filling contents. The increase in the filler content also led to a significant change in the storage modulus. On the other hand, the Tg of all prepared samples stayed similar which indicates that the applied filler content was below the threshold. Basically we were successful to increase the thermal conductivity without altering the Tg. This may lead to preparation of thermally conductive epoxy composite with a flexible nature as neat epoxy exhibits. The results presented in the current work shows agreement with the ones in the literature (see e.g. [1, 18, 19]). As discussed previously it is important to note that these studies use surface agents and mixed mode particles to obtain improved results.

This methodology will be used in our future investigations as well for comparison reasons. Currently we illustrate the effect of single filler at different temperatures. Moreover, further work focusing on different fillers is required. More systematic study is planned on using h-BN particulates with a multimodal size distribution (micro and much finer nanoscale particulates) and different fillers. The current study illustrates clearly the effect of single filler for different temperatures without surface agents.

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