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Performance Analysis of Epoxy/Aluminum Borate Composite

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Abstract

Integration of micro fillers is an effective approach to enhance the mechanical and thermal properties of epoxy. In the current work, aluminum borate has been incorporated into epoxy to modify the dynamic mechanical properties, thermal expansion, thermal stability and solvent resistance of the matrix. Dynamic mechanical analysis (DMA) gave evidence of cure acceleration ability of aluminum borate and constrains imposed on the neighboring polymeric chains by aluminum borate. A uniform dispersion of microparticles of aluminum borate in epoxy as evident from scanning electron microscopic (SEM) analysis facilitates superior dimensional and thermal stability to the epoxy matrix. The solvent uptake study showed that aluminum borate effectively hinders the diffusion of water molecules through the epoxy matrix.

Keywords: Epoxy, Composite, Thermal stability, Thermomechanical properties

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1. Introduction

Epoxy resins are a group of thermosetting polymers having wide range of applications as surface coatings, adhesives and matrix for structural composites [1, 2]. They are well known for their mechanical strength and modulus, excellent electrical and thermal insulation, superior solvent and moisture resistance. The combination of distinct characteristics of epoxy and fillers results in unique physicochemical properties of epoxy composites [3]. The introduction of rigid nanoparticles with large surface area into the epoxy matrix eventually increases the particle-matrix interactions. In the vicinity of inorganic fillers, the polymer chain dynamics is entirely different as compared to bulk due to polymer filler interactions [4].

In power electronics, high thermal conductivity of adhesives is necessary to remove the excess heat [5]. This can be achieved by incorporating conductive fillers into epoxy matrix and effectively addressed the heat dissipation problems in such devices. Developments have been constantly done in the designing and fabrication of polymer composites by exploiting the thermally conductive fillers [6, 7]. Studies have shown that the addition of metal powders such as aluminum, copper, silver etc. improved the mechanical, thermal and electrical properties of polymer composites [8-12]. Ceramic materials including silicon carbide (SiC), alumina (Al_2O_3), boron nitride (BN), zinc oxide (ZnO), and aluminum nitride (AlN) and thermally conducting lightweight carbon derivatives such as carbon nanotubes (CNTs), carbon blacks (CBs), carbon fibers (CFs), graphite, and reduced graphene oxide (rGO) have been employed to enhance the thermal conductivity of polymer matrix [13-16]. Aluminum borate has been used as filler in many polymer matrices to enhance the thermal and mechanical properties [17, 18]. It is important to maintain least thermal expansion and high thermal stability upon achieving superior thermal conductivity in composites. Moreover, epoxy composites used in automobiles and electronic structures are susceptible to solvent and moisture attack. Hence, attempts were made to fabricate solvent resistant epoxy composites with some specialty fillers [19].

Herein, epoxy matrix has been modified with aluminum borate (AB). The developed morphology was investigated and correlated with their performance. Dynamic mechanical properties, solvent resistance, thermal stability, thermal expansion behavior of epoxy/AB composites were investigated.

2. Materials and Methods

2.1. Materials

Epoxy water clear casting resin kit (Carbon black composites) was used to prepare the matrix. The hardener used to crosslink the epoxy resin is polyamidoamine. Aluminum borate ($AlBO_3$) was purchased from Sigma Aldrich.

2.2. Preparation of control epoxy

Epoxy samples were prepared by mixing 1:1 ratio of epoxy monomer and hardener. The mixture was then sonicated for 3-5 minutes to get homogenized mixture. Later, it was heated inside an oven to degas the sample. The mixture was poured in to the mold and cured at the preheated temperature of 80 °C for 1 hour.

2.3. Preparation of epoxy/aluminum borate (EP/AB)

About 3g of aluminum borate was added into 20 g of epoxy and mix manually for 5 min and then magnetically stirred for 1 hour. The obtained homogenous mixture was mixed with 10 g of hardener and sonicated for 15 min. Then the mixture was degassed inside the vacuum oven for 1 hour to eliminate air bubbles. The presence of trapped air bubbles in the composite will adversely affect the mechanical properties of the composite. The mixture was then poured in to the mold and cured inside the oven at the preheated temperature of 80 °C for 1 hour.

2.4. Experimental techniques

Scanning electron microscopic (SEM) images of the fracture surface of the samples were obtained using FEI Quanta 2000 instrument. DMA Q-800 (TA Instruments) has been used to study the viscoelastic behavior of the samples between 25 °C and 250 °C at a heating rate of 3 K/min and frequency of 1 Hz. The dimensions of the samples used for the analysis were $30\times10\times3$ mm^3. The thermo-mechanical analysis of the samples was carried out using TMA Q-400 (TA Instruments) to study the dimensional stability of samples between -50 °C and 250 °C, at a heating rate of 3 K/min. Samples of dimensions $10\times10\times3$ mm^3 were used for TMA analysis. Thermal stability of the samples was analyzed using TGA Q 5000 TA instrument using nitrogen as the purge gas. The samples were heated from room temperature to 800 °C at a heating rate of 10 K/min.

Samples of dimension $10\times15\times2$ mm^3 were used for the solvent uptake studies. The samples were immersed in different solvents such as water, ethanol and acetone. The weight of the samples was determined at suitable intervals by using an electronic microbalance with an accuracy of

0.001 g. The results of the solvent uptake experiments were expressed as M_t function of time ($t^{1/2}$), where M_t is defined as follows:

$$Mt(\%) = (w_t - w_0)/ w_0 \times 100 \qquad (1)$$

where w_t is the weight of the sample at time t and w_0 is the Initial weight of the sample.

3. Results and Discussion

Figure 1 represents SEM images of control epoxy and epoxy/AB composites. **Figure 1(a)** represents the micro structure of neat epoxy, while **Figure 1(b)** that of epoxy/AB composite. Micro- particles of aluminum borate are uniformly distributed in the matrix with rarely seen agglomerates. The microparticles are individually separated with well-defined particle boundaries. This well distributed microparticle is expected to contribute towards the enhanced performance of the composite.

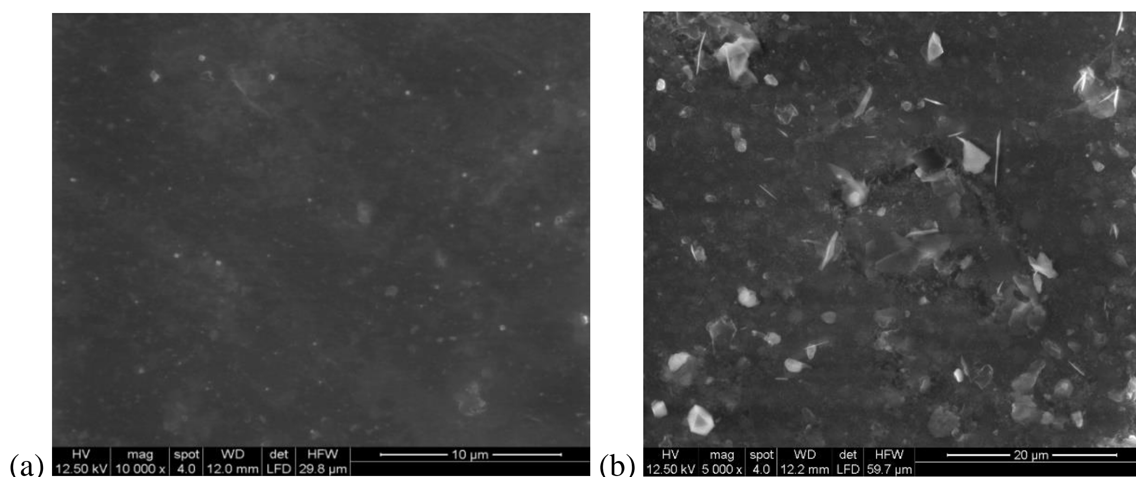

Figure 1. SEM images of a) control epoxy, and b) epoxy/AB composites

Dynamic mechanical analysis (DMA) is used to measure the viscoelastic properties of polymer samples. DMA curves of the epoxy and epoxy/AB composites showing the variation of storage modulus, loss factor (tan δ) and loss modulus with temperature are given in **Figure 2**. **Figure 2a** shows the variation of storage modulus with temperature for the samples. As the temperature increases, the storage modulus gradually decreases. At glass transition temperature (Tg) of the polymer, the storage modulus drops suddenly to a lower value. This is the region where the

polymer gets transformed to a high modulus glassy state to low modulus rubbery state. Below Tg, the storage modulus of EP/AB is lower than controlled epoxy. Above Tg, control epoxy and composite have almost similar storage modulus. The decrease in storage modulus below Tg in epoxy/AB may be due to reduced crosslink density of epoxy matrix in the presence of micro fillers. Glass transition temperature of different samples were determined from tan δ versus temperature (**Figure 2b**) and is tabulated in **Table 1.** The temperature corresponds to peak point in tan δ versus temperature curve denotes the Tg of the samples. It was found that, the presence of aluminum borate does not affect the Tg of the epoxy matrix. The polymer chain dynamics in the vicinity of inorganic fillers is different than that in bulk due to polymer-filler interactions. This indicates that the micro fillers would effectively constrain the polymeric chains neighboring them. The variation of loss modulus with temperature is shown in **Figure.2c**. The presence of multiple peaks in cured epoxy is due to the existence of regions having different crosslink density arises from incomplete cure during processing. However, only one major peak is observed for epoxy/AB composites, which indicates the assistance of uniformly dispersed aluminum in achieving proper curing of epoxy.

Table 1. The glass transition temperature (Tg) of epoxy and epoxy/AB composite.

Samples	**T_g (°C)**
Epoxy	73.60
Epoxy/AB composite	73.17

The dimensional changes in epoxy and epoxy/AB composites during heating were measured using thermomechanical analyzer (TMA) and TMA profile is given in **Figure 3**. The change in dimension increases with increase with temperature while heating from − 50 °C to 200 °C due to increased molecular vibration of the polymer chains upon heating. The coefficients of thermal expansion (CTE) were measured below T_g and above T_g for the epoxy, epoxy/AB composites. The CTE of control epoxy was measured as 62.0×10^{-6}/°C between − 45 °C and + 30 °C and those of the epoxy/AB composites is 58×10^{-6}/°C, respectively. As the temperature increases, the thermal mobility of the polymer chains intensifies and higher CTE values were found (169×10^{-6}/°C) between +75 °C and +200 °C for epoxy and 109.8×10^{-6}/°C between 80 °C and 130 °C.

A reduction of expansion coefficient in epoxy/AB composite when compared to neat epoxy matrix was detected. This result is in agreement with previously reported reduction in expansion coefficient in presence of metal oxide particles at the microscale [20].

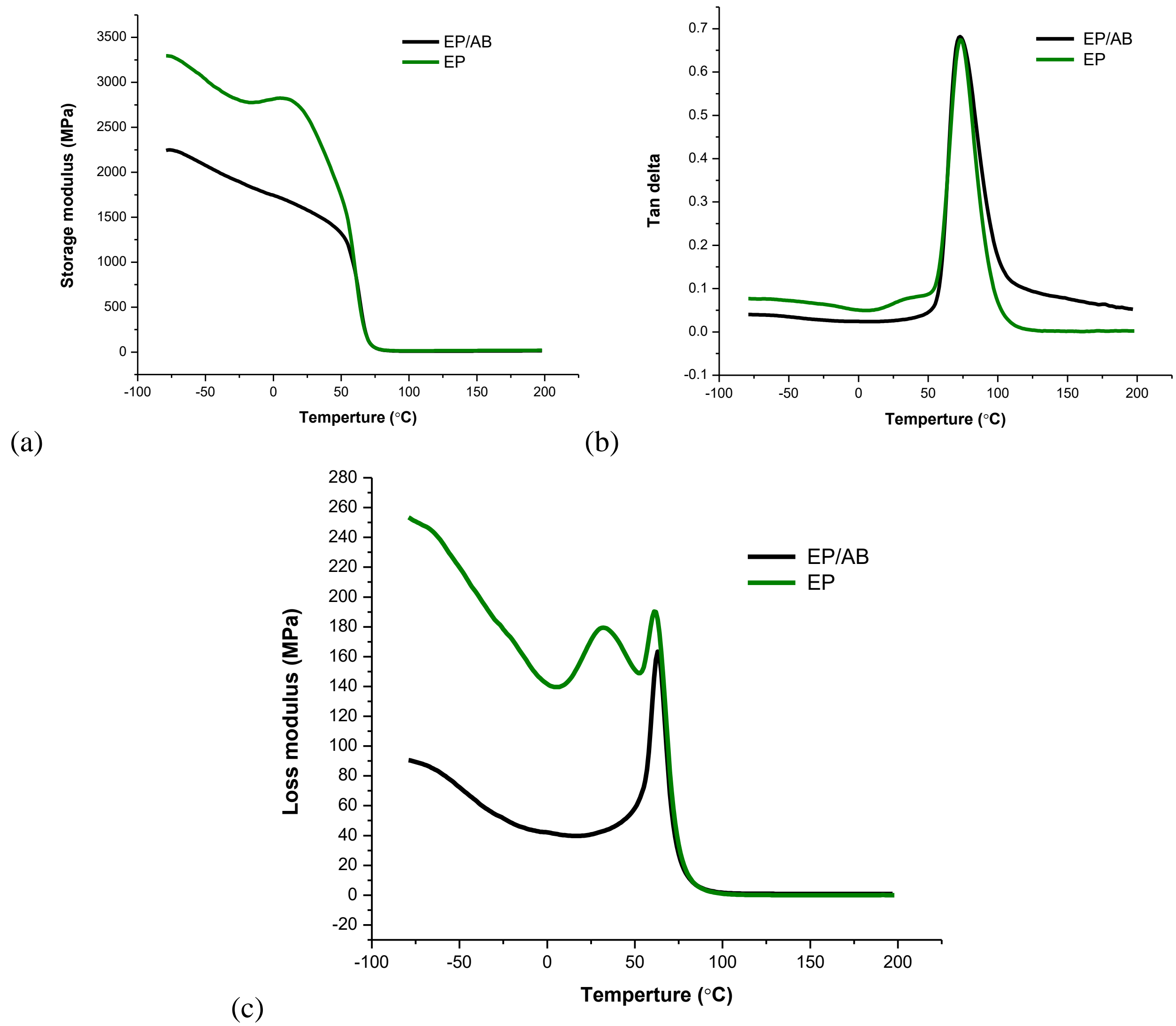

Figure 2. Variation of a) storage modulus b) tan δ and c) loss modulus with temperature for epoxy/AB and control epoxy.

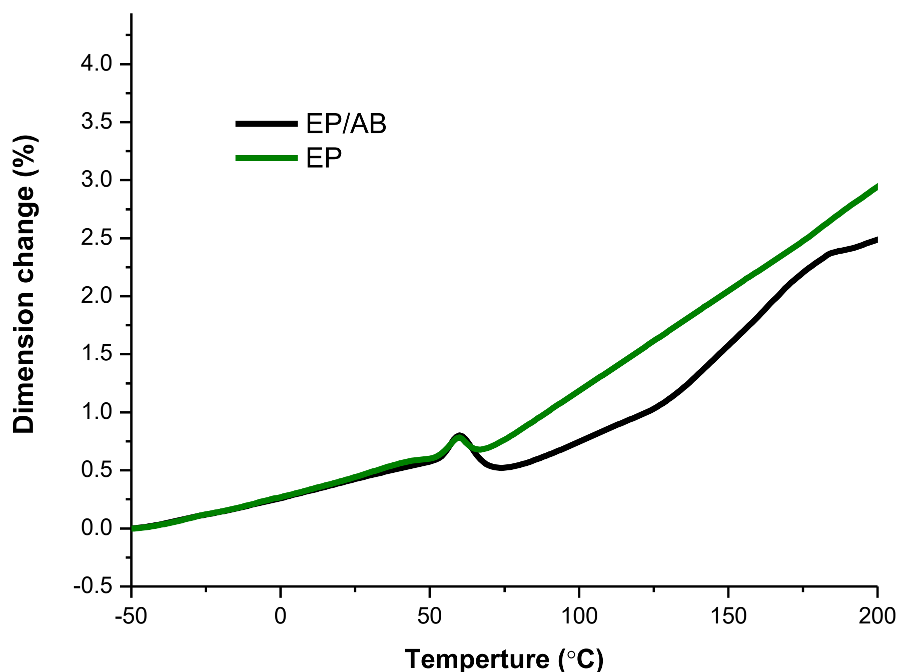

Figure 3. TMA profile for epoxy and epoxy/AB composite

It is important to evaluate thermal stability of epoxy composites used in automobile and electronic industry. Hence, thermal stabilities of epoxy and epoxy/AB composites were evaluated using thermogravimetric analysis (TGA). TGA and corresponding derivative thermogravimetry (DTG) curves of epoxy and epoxy/AB composites are given in **Figure 4**. A single step degradation profile has been observed for epoxy and its composites. The degradation begins above 340 °C. The degradation of the samples is due to the decomposition of the epoxy polymer matrix. However, a small hump in DTG graph is observed and it is due to the uneven crosslink density in control epoxy matrix. Both control epoxy and epoxy/AB composite have the same maximum decomposition temperature (MDT). MDT is the maximum temperature at which the degradation (T_{max}) occurred evaluated from the DTG graph. However, there is a significant difference in char residue of epoxy and epoxy/AB composite. The final char residue of control epoxy matrix at 800 °C is 3.74 wt%. The weight of the aluminum borate microfiller in the composite is 10 wt%, when it is added to the char reside of control epoxy, the total is 13.74 wt%. On the other hand, the char residue of epoxy/AB composite is 20.57 wt%, on subtracting the char reside with the calculated value, we will get 20.57–13.74 = 6.83. Thus, the results validate that the char residue of the epoxy matrix in epoxy/AB composite is more than the

control epoxy system. These results suggest that the incorporation of aluminum borate enhance the thermal stability of epoxy.

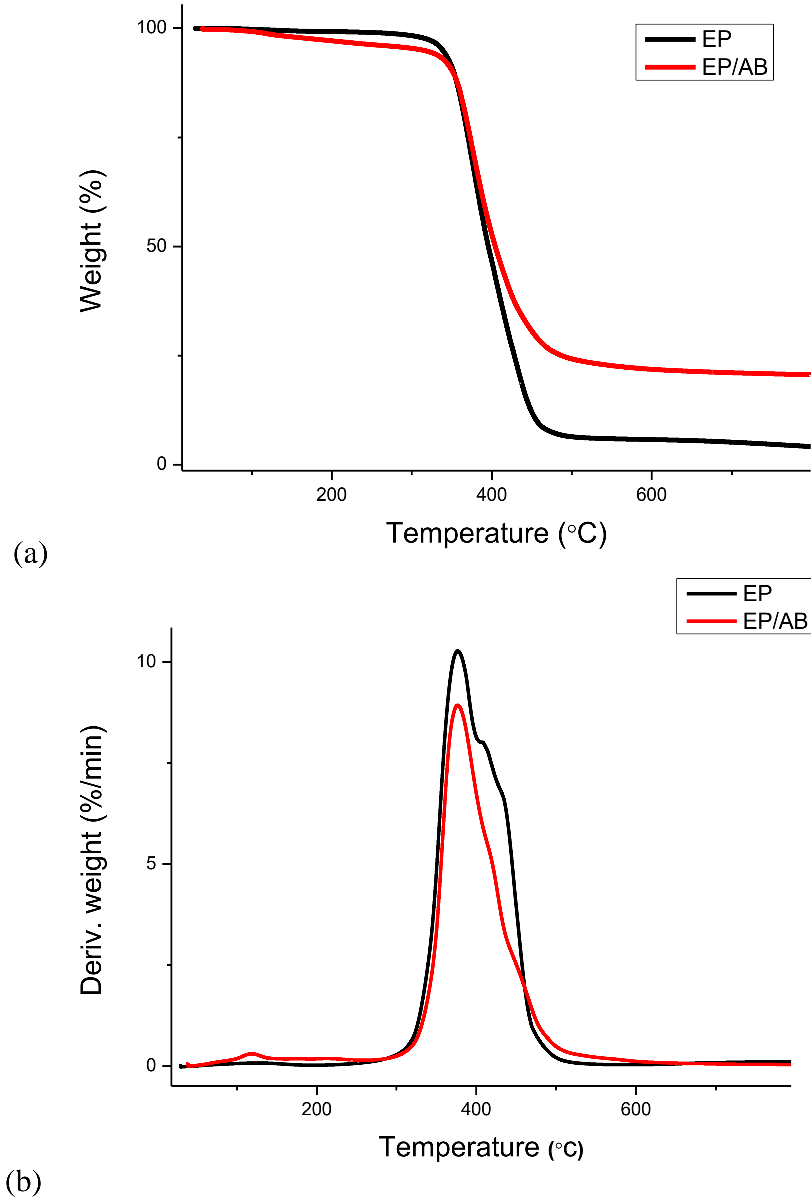

Figure 4. a) TGA and b) DTG curves for epoxy and epoxy/AB composite.

Figure.5 represents the solvent uptake study of control epoxy, epoxy/AB composites in water, ethanol and acetone. It is clear from the water uptake profile that aluminum borate hinders the diffusion of water molecules through the epoxy matrix. Unlike water, epoxy/AB composite is

easily prone to organic solvents which is expected due to undesirable chemical interaction of these type solvents with the matrix.

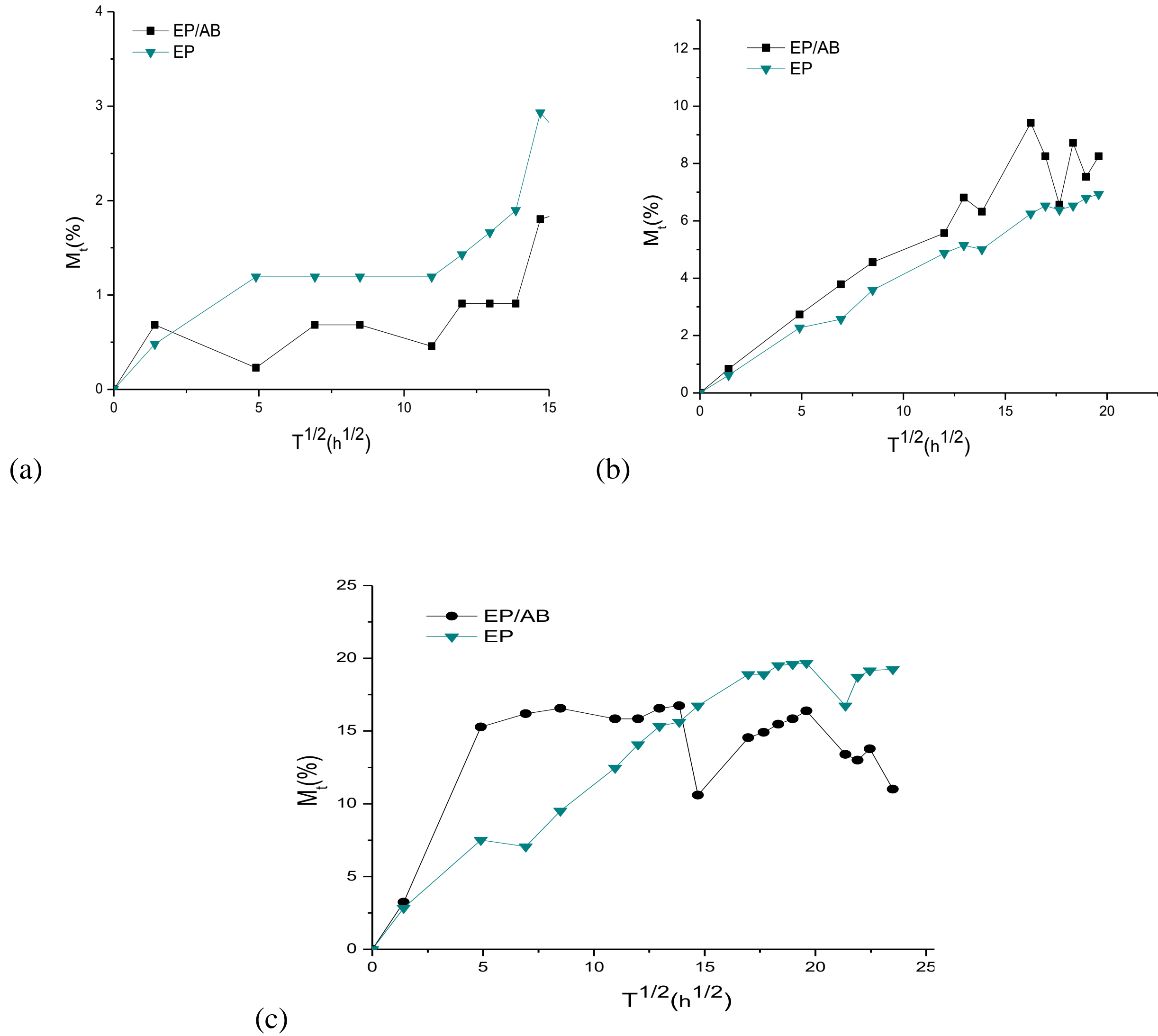

Figure 5. Solvent uptake profiles for control epoxy and epoxy/AB composite in a) water b) acetone and c) ethanol.

Conclusions

The experimental investigations on the effect of aluminum borate micro filler on the performance of epoxy have been done. The role of aluminum borate on dynamic mechanical properties, thermal expansion, thermal stability and solvent uptake behavior was detailed. From DMA studies, it was confirmed that the presence of aluminum borate decreases the crosslink density of epoxy which in turn reduce the storage modulus of the matrix. However, the Tg of the epoxy matrix remains unaltered in the presence of aluminum borate which would effectively constrain the polymeric chains. While multiple peaks in loss modulus curve of epoxy indicated incomplete cure and only one major peak in loss modulus profile of epoxy/AB composite confirmed the cure acceleration effect of aluminum borate. From the solvent uptake studies, it was found that aluminum borate has a strong effect on resisting the water uptake due to physical barrier created by the micro-filler.

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