VARIATION OF MECHANICAL PROPERTIES DUE TO HYGROTHERMAL AGEING AND PERMANENT CHANGES UPON REDRYING IN CLAY/EPOXY NANOCOMPOSITES

By

SALAH UDDIN AHMED HAMIM

Bachelor of Science in Mechanical Engineering
Bangladesh University of Engineering and Technology
Dhaka, Bangladesh
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Thesis Approved:

Raman P. Singh
Thesis Advisor

Kaan A. Kalkan

Sandip P. Harimkar

Mark Payton
Dean of the Graduate College

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CHAPTER 1

INTRODUCTION

Thermosetting polymers, such as epoxy resins and unsaturated polyesters are highly cross-linked and are very important class of advanced materials. Their main distinction from other types of polymers lies in their densely cross-linked molecular structure. This cross-linking leads to a number of favorable thermal and mechanical properties including high strength and modulus, high creep resistance, high glass transition temperature, low shrinkage, good resistance to chemicals, etc. These properties in conjunction with ease of processing have made epoxy resins an attractive choice for use in many engineering components and structures. They have found huge applications in aerospace, automotive, packaging, coating and micro-electric industries. In recent years, researchers have developed and investigated polymer nanocomposites based on a wide variety of nano-scale fillers including clay particles [1, 2], aluminum particles [3], TiO_2 particles, carbon nanotubes, etc.

1.1 Water epoxy interactions

Epoxy polymers are characteristically hydrophilic, which means they have strong affinity towards water. This nature of epoxy resins make them susceptible to high moisture absorption; in general, depending on the nature of the epoxy resin the equilibrium moisture uptake can be in the range of 1–7% [4]. Various factors influences the water uptake rate in epoxy polymers, such as the number of hydroxyl groups, the glass transition temperature of the epoxy, and the presence of secondary dispersed phase [5]. Carfagna *et al.* investigated the effect of hardener ratio on the moisture absorption behavior of epoxy resins and found that equilibrium moisture uptake for epoxy systems with higher hardener ratio is higher than stoichiometric ratio epoxy systems [6]. Three different modes for water absorption in epoxy systems were proposed by Apicella *et al.*: (a) bulk dissolution of water in the polymer network; (b) moisture absorption onto the surface of hole that define the excess free volume of the glass structure; and (c) hydrogen bonding between hydrophilic groups of the polymer and water [7]. Moy and Karasz studied the interactions between water and epoxy and found that water can exists in two forms inside the epoxy: micro-void or free volume filling free water, and strongly bound water trapped at polar sites which is usually bonded to hydroxyl groups in the epoxy network [8]. Study conducted by Diamant *et al.*, and Maggana and Pissis also supported this observation [9, 10]. The free water that fills up the nano-voids does not cause swelling, while the hydrogen bonded water directly play effects on the polymer chain, causing swelling of the polymer.

Effects of moisture absorption on epoxy resins are being extensively studied using various techniques [4, 11, 12]. Absorbed moisture usually degrades the functional, structural and mechanical properties of the polymer matrix [13, 14, 15, 16]. It is reported that, mechanical and thermal properties of epoxy-based systems are more severely affected by moisture absorption in comparison to other matrix materials, such as as bismaleimide (BMI), polyetheretherketone (PEEK), cyanate ester, etc. [17].

Water absorption into a polymer matrix leads to change in both the chemical and physical characteristics and it affects the mechanical properties primarily through three different mechanisms: plasticization, crazing, and hydrolysis. Plasticization is the most important physical change that occurs through the interaction of the water molecules with polar groups in the matrix and it can severely depress the glass transition temperature [6, 15, 18]. For example, high moisture absorption capability of TGDDM/DDS epoxy resin, which is about 7% reduces the system T_g from 260℃ to 130℃ [19, 20, 21]. In general, for most epoxy systems T_g is reduced by 20℃/1% of moisture intake [22]. Plasticization can also lead to decrease in modulus. Several studies have attributed the decrease in modulus due to the plasticizing effect of the water on the epoxy polymer [23, 24, 25, 26]. Once absorbed in the system, the water spreads the polymer molecules apart and reduces the polymer-polymer chain secondary bonding. This action provides more space for the polymer molecules to untangle and move, which results in a softer, more easily deformable mass [27]. Other studies show the decrease in epoxy modulus after moisture absorption resulting from crazing [28, 29, 30], where the absorbed water can act as a crazing agent continuously decreasing the mechanical strength of epoxies with exposure time in water [29]. This is supported by SEM micrographs of epoxies, which have shown cavities and fractured fibrils that could only be explained by a moisture induced crazing mechanism [31]. The chemical changes mainly include chain scission and hydrolysis [18, 32]. However, plasticization is considered reversible upon drying, while crazing, chain scission and hydrolysis is not.

Absorbed moisture can create hydrostatic pressure at the crack tips and speed up the crack propagation. In the materials, the areas with defects and pre-cracks are the most adversely affected due to moisture absorption and more likely to fail during mechanical loading. Reduction in properties due to temperature and moisture has been observed by various researchers [33, 34, 35]. In hygrothermal conditions, leaching of unreacted monomer can also happen due to moisture absorption in to epoxy polymers.

1.2 Effect of moisture absorption on the properties of epoxy polymer

. Clay has been widely used as reinforcing agent to fabricate polymeric nanocomposites because it can provide improved properties, such as enhanced tensile and thermal properties, high heat distortion temperature and better flame retardency, etc. over neat polymer. Clays are available in micron-sized tactoids where a few hundreds of individual plates having a dimension of 1μm x 1μm x 1μm are stacked together with the help of electrostatic forces. Naturally found clays are organophobic, and to make them well dispersed inside epoxy polymer, they need to be organophillic and hence, needs to be surface modified. Complete exfoliation can only be achieved in the systems with high polarity. Clay layers possess hydroxyl groups which restricts the entrance of any non-polar species inside the galleries [36]. Structurally clay has two fused silica tetrahedral sheets and in between these two sheets there is an edge-shared octahedral sheet. Isomorphous substitutions of Si^{4+} for Al^{3+} in the tetrahedral lattice and of Al^{3+} for Mg^{2+} in the octahedral sheet results in an excess of negative charges within the layers, and can be counterbalanced by cations such as Ca^{2+} and Na^{+} situated between the clay layers. By exchanging the cations for alkylammonium ions, it is possible to make the clay organophilic and only then it is possible for organic species to diffuse inside the layers and eventually separating them.

Once these individual platelets are exfoliated inside the epoxy matrix, large aspect ratio and surface of exfoliated clay can act as efficient barrier against moisture transport into the nanocomposites. Researchers have found diffusivity to have reduced to half when clay is incorporated into epoxy systems. Such improvement is attributed to tortuosity effect - increase in path length for molecules diffusing through the polymer [37]. Among the various micro/nano-sized reinforcements such as talc, glass fibers, and glass beads, large aspect ratio layered silicates are especially attractive for enhancing the barrier properties and hence the resistance to environmental degradation. Furthermore, nano-clays are readily available, are cheaper than other nano-scale fillers, and have well understood intercalation chemistry [38].

Toyota researchers were the first to discover that polymer-clay nanocomposites can provide significant reduction of water absorption rate, which was 40% for the nylon 6-clay nanocomposite compared with the neat polymer [39, 40]. Hoa *et al.* [41] reported similar results for Epon 828/Epikure epoxy-clay nanocomposites. An 80%

decrease in water absorption was also reported for poly (ϵ - caprolactone) nanoclay composites [42]. Decreasing trend of moisture diffusivity for nanocomposites was also observed by Glaskova and Aniskevich, which was attributed to tortuosity effect [43]. However, it is reported by Peter and Anne [44] that, addition of clay provides no significant improvent on moisture absorption for Epon 828/Jeffamine D 230 epoxy system. Massam and Pinnavaia [45] studied the barrier properties of epoxy-clay nanocomposite for organic solvents and water; the absorption of organic solvents in nanocomposites is faster than in pristine epoxy resins. However, in the case of water, there is no significant change in equilibrium moisture uptake; the rate of moisture absorption is reduced. It was further observed that the resistance to water uptake is more in the nanocomposites with exfoliated clay structure than intercalated clay structure.

Effect of clay loading on mechanical properties of epoxy polymers has been studied at depth. Lan and Pinnavaia found linearly increasing trend for tensile strength and modulus with increasing in clay loading. Based on their investigation they have concluded that, reinforcement provided by the exfoliated clay is much more significant for low glass transition temperature epoxy systems [46]. Yasmin *et al.* used shear mixing technique and studied the effect of clay content on mechanical properties. According to their report, tensile strength decreases with higher clay loading, while in case of elastic modulus they found increasing trend [47]. Kornmann *et al.* studied the effect of clay loading on flexural properties of epoxy polymer and found that flexural modulus increases with clay loading % [48]. Similar increase in modulus for glass-bead epoxy system requires more than three time the reinforcing content [49]. Kornmann *et al.* also reported that largest improvements in modulus (higher degree of exfoliation) with clay content can be obtained for an epoxy resin cured with an aliphatic curing agent with relatively low reactivity. Kim *et al.* investigated the effect of clay on coefficient of thermal expansion and found that it decreases as the clay content increases [50]. As the amount of clay increases in an epoxy system restriction to the polymer chain mobility starts to increase, which in turn results in lower coefficient of thermal expansion.

Zainuddin *et al.* reported 48% decrease in weight gain in case of 2 wt% samples over neat samples conditioned at 80 °Cfor 90 days. Yellowish discoloration on the surface of the samples were observed after hygrothermal aging [51]. For elevated temperature aging, similar discoloration of epoxy based composite materials immersed in distilled water is reported by Ellyin and Maser. Once epoxy resins are hydrolyzed, the ester bonds are broken. With less bonding between and within the polymer chains, the chains will slide past each other with greater ease; thus, inelastic deformation is achieved at smaller loads and a loss in stiffness results. [34]. Zhao *et al.* reported tensile strength and modulus decreased for both neat epoxy and nanocomposites upon moisture absorption, while the tensile strain increased significantly for moisture absorbed samples. Scanning electron micro-graphs showed smooth surface and evident brittle failure for these samples. Although, effect of plasticization was found as images showed shear yielding for both neat epoxy and nanocomposite samples [52]. Similar observation of strength and modulus decreasing upon moisture absorption has been reported by Glaskova and Aniskevich [53]. Wang *et al.* investigated the effect of hydrothermal effects on mechanical properties such as tensile strength, modulus and fracture toughness with immersion duration [54]. For DGEBA epoxy systems, fracture toughness and modulus was not influenced much with immersion time, while strength decrease for nanocomposites. According to the study conducted by Buck *et al.* at elevated temperature, combination of moisture and sustained load can significantly reduce ultimate tensile strength of E-glass/vinyl-ester composite materials [33]. A study on elastic modulus of epoxy polymer after a absorption-desorption cycle showed recovery of property from wet condition, although modulus remains at a lower value than as-prepared samples for lower filler volume. For higher volume fraction of reinforcement, elastic modulus improves to a value which is more than the elastic modulus of as-prepared samples [16]. Ferguson and Qu [55] also reported recovery of elastic properties from moisture saturated state after a desorption cycle. However, DeNeve and Shanahan [18] did not observe any recovery of elastic modulus after a absorption-desorption cycle at elevated temperature. It is evident from the published works that moisture absorption can severely alter mechanical properties of epoxies by decreasing the elastic modulus [23, 28], shear modulus [24, 25], yield stress [26] and ultimate stress [26] as water uptake increases.

1.3 Objective

Most of the research on polymer-clay nanocomposites has focused on investigating the effect of various parameters on mechanical properties such as modulus and strength. Although fracture toughness is a very important property for these nancomposites to be used in various structural applications, it has not been studied adequately and the results reported in the literature are inconclusive. Furthermore, the effects of moisture absorption on fracture toughness of polymer-clay nanocomposites has not been studied extensively and to our best knowledge no study was conducted to investigate the recovery of fracture and flexural properties after a absorption-desorption cycle. Durability of polymer/clay nanocomposites are still needed to be studied in depth, particularly for hygrothermal aging in which the degradation of the mechanical properties and loss of integrity of these nanocomposites occur from the simultaneous action of moisture and temperature.

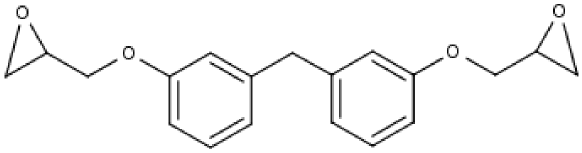
This study on epoxy/clay nanocomposites is designed to investigate the effect of hygrothermal ageing on mechanical properties of these nancomposites. A drying cycle is employed to quantify the recovery of the properties after hygrothermal ageing. This would be helpful to understand the extent of permanent damage occurred by the combined action of elevated temperature and moisture. Fracture toughness, flexural strength and modulus are the properties that were studied. Two structurally different clays are used as reinforcement in epoxy matrix in order to aid comparison between clays. Scanning electron microscopy was done to elucidate the underlying fracture mechanisms of these preconditioned specimens.

CHAPTER 2

MATERIALS AND EXPERIMENTS

2.1 Materials

The epoxy resin used for this study is a diglycidyl ether of bisphenol F (Epon 862, Miller-Stephenson Chemical Company, Inc., Dunbury, Connecticut, USA). The curing agent used for this resin system was a moderately reactive, low viscosity aliphatic amine curing agent (Epikure 3274, Miller-Stephenson Chemical Company, Inc., Dunbury, Connecticut, USA).



EPON 862

Figure 2.1: Chemical structure of Epon 862/DGEBF epoxy system

For mixing the clay with epoxy, a high-speed shear disperser was used (T-25 ULTRA TURRAX with SV 25 KV25 F dispersing element, IKA Works Inc., North Carolina, USA).Two different nanoclay particles were used for this study. First one is surface modified Montmorillonite based layered silicate (Nanomer I.28E, Nanocor, Inc.,Arlington Heights, IL). It is a natural montmorillonite (MMT) modified with a quaternary amine. The other one is synthetic fluorine mica modified with di-methyl di-tallow quaternary ammonium (Somasif MAE, Co-op Chemicals, Japan).

2.2 Sample preparation

Epoxy was preheated to 65℃ before desired amount clay was introduced and mixed using mechanical mixer for 12 hours. To reduce the viscosity of the mixture and facilitate mixing, temperature was maintained at 65℃ for the entire duration of mixing using a hot plate. To remove entrapped bubble from the mixture degassing was done for around 30 minutes. Bubble-free mixture of clay and epoxy was then shear mixed at 13000 rpm for 30 minutes. During this process, temperature was maintained at 65℃ using an ice bath. Subsequently, the mixture was then degassed until it was completely bubble-free. Curing agent was added to the mixture at 100:40 weight ratio and carefully hand mixed to avoid introduction of any air bubble. After it was properly mixed, the final slurry containing epoxy and clay was poured in to an aluminum mold and cured at room temperature for 24 hours followed by post-curing at 121℃ for 6 hours. The final outcome has a nominal dimension of 7 in. × 6 in. × 0.25/0.125 in. The weight fraction of the clay was varied from 0.5 - 2.0 % to study the influence of clay on mechanical properties of nanocomposites after degradation.

2.3 Environmental pre-conditioning

After specimens were cut into final required dimension, they were subjected to degradation. Specimens from each nanocomposite were taken and submerged in purified boiling water for 24 hours. It was experimentally found that 24 hours time was enough to ensure saturation of water uptake into the specimens. Water saturated specimens were dried in an oven at 110℃ for 6 hours to remove void-filling moisture from the samples leaving only permanent degradation in form of bonded water.

2.4 Fracture Toughness, K_{Ic} determination

Mode-I fracture toughness was determined by Single Edge Notch Bend (SENB) test as per the ASTM D-5045 [56] on Universal Testing Machine (Instron 5567, Norwood, MA) in a displacement-controlled mode with fixed crosshead speed of 10 mm/min. Nominal dimension for the SENB test samples were 2.65 inch×0.6 inch×0.25 inch. For fracture toughness determination a notch was created using precision diamond saw (MK-370, MK Diamond Products Inc., Torrance, California, USA). A sharp pre-crack with ratio of $0.45<a/W<0.55$ was created by tapping a fresh razor blade into the notch. At least 5 specimens were tested for every condition and nanocomposite. Fracture toughness for the specimens were calculated in terms of critical stress intensity factor, K_{Ic} using the equation 2.1. The crack length, a was measured using an Optical Microscope (Nikon L150) which has a traveling plate with graduations.

$$K_{Ic} = \frac{P}{B\sqrt{W}}\, f\left(\frac{a}{W}\right) \tag{2.1}$$

where,

P = maximum applied force, N

B = thickness of the specimen, mm and

W = width of the specimen, mm

$f(\frac{a}{W})$ = geometry factor, and is given by the equation 2.2.

$$f\left(\frac{a}{W}\right) = \frac{3\frac{S}{W}\sqrt{\frac{a}{W}}}{2(1+2\frac{a}{W})(1-\frac{a}{W})^{3/2}} \times [1.99 - \left(\frac{a}{W}\right)\left(1-\frac{a}{W}\right)(2.15 - 3.93\left(\frac{a}{W}\right) + 2.7\left(\frac{a}{W}\right)^2)] \tag{2.2}$$

where,

S = support span, mm

a = length of the pre-crack, mm.

2.5 Flexural Strength and Modulus determination

Flexural Modulus and Strength was determined using Three Point Bend (3PB) test according to ASTM D790 [57] on Universal Testing Machine (Instron 5567, Norwood, MA). The nominal dimension for the flexural test specimens were 2.2 inch ×0.5 inch×0.125 inch. The crosshead speed for the test was calculated using equation 2.3. The crosshead speed was found to be 1.35 mm/min.

$$R = \frac{ZL^2}{6d} \tag{2.3}$$

where,

R = rate of crosshead motion, mm/min

L = support span, mm

d = depth of beam, mm and

Z = rate of straining of the outer fiber, mm/mm/min. Z = 0.01.

The Flexural Strength and Flexural Modulus were calculated using the equation 2.4 and 2.5 respectively.

$$\sigma_{f,max} = \frac{3P_{max}L}{2bd^2} \tag{2.4}$$

$$E_b = \frac{L^3 m}{4bd^3} \tag{2.5}$$

where,

$\sigma_{f,max}$ = flexural strength, MPa; E_b = flexural modulus, MPa

P_{max} = maximum load on the load-deflection curve, N; L = support span, mm

b = width of beam tested, mm and

d = depth of beam tested, mm

m = slope of the tangent to the initial straight-line portion of the load-deflection curve, N/mm of deflection.

2.6 Fracture surface morphology

Surface morphology of the fractured specimens from Single Edge Notch Bend (SENB) test were observed using Scanning Electron Microscopy (Hitachi S-4800 FESEM, Dallas, TX). As polymer materials are nonconductive to electrons, all fracture surfaces were sputtered with gold-palladium alloy before SEM imaging was done. For every samples at least two micrographs were taken; one in the slow sub-critical crack zone and the other one in the rapid or fast crack propagation zone.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Gravimetric measurements

Table 3.1 shows the relative weight changes occurred in the specimens after 24 hours of boiling water degradation and 6 hours of redrying. For both clays, the amount of water uptake increases as the clay loading percentage increases. Similar increase in equilibrium water uptake was observed by Glaskova and Aniskevich [43] for nanocomposites. As the clay content increases the interface area between the clay and the epoxy increases. The higher amount of water uptake in nanocomposites with higher clay loading is attributed to the higher interface area. Although, both clays are structurally different both nanocomposite systems absorbed almost same amount of water.

From the experimental data it is possible to see that, most of the absorbed water is free water, which can be driven out of the system by drying. For neat epoxy, the amount of water remaining after desorption cycle is more compared to the nanocomposites. This is possibly due to the fact that, presence of clay hinders the moisture diffusion process in an out of the epoxy polymers. It is important to note that, Somasif MAE clay nanocomposites retained more water than I.28E nanocomposites for all the clay loading.

Table 3.1: Weight changes in samples after pre-conditioning

Specimens	After absorption (%)	After drying (%)
Epon 862	2.97	0.69
2.0% I.28E	3.27	1.18
1.5% I.28E	3.21	1.12
1.0% I.28E	3.12	1.02
0.5% I.28E	3.05	0.87
2.0% Somasif MAE	3.31	1.27
1.5%Somasif MAE	3.25	1.15
1.0% Somasif MAE	3.17	1.04
0.5% Somasif MAE	3.15	1.02

3.2 Fracture Toughness

The critical stress intensity factor as a function of clay loading for I.28E and Somasif clay/epoxy nanocomposites are shown in figure 3.1 and figure 3.2, respectively. In these figures, fracture toughness of nanocomposites that were subjected to different conditioning were plotted and K_{Ic} values for as-prepared samples were also given as a reference.

Table 3.2: Fracture toughness of I.28E clay/epoxy nanocomposites

Clay loading (wt%)	As-Is	Moist	Dried
Epon 862	1.13±0.08	-	0.8±0.05
0.5	1.45±0.05	1.13±0.04	1.21±0.01
1.0	1.45±0.03	1.20±0.05	1.38±0.07
1.5	1.31±0.06	1.24±0.03	1.36±0.03
2.0	1.26±0.08	1.11±0.01	1.36±0.01

Table 3.1 and 3.2 shows the fracture toughness values for different I.28E and So-

Table 3.3: Fracture toughness of Somasif clay/epoxy nanocomposites

Clay loading (wt%)	As-Is	Moist	Dried
Epon 862	1.13±0.08	-	0.8±0.05
0.5	1.29±0.17	1.13±0.06	1.15±0.02
1.0	1.28±0.06	1.06±0.03	1.13±0.08
1.5	1.28±0.07	1.07±0.04	1.08±0.06
2.0	1.32±0.03	1.23±0.03	1.25±0.01

masif clay/epoxy nanocomposites respectively, that are subjected to different preconditioning. Fracture toughness of neat Epon 862 is also listed in the table as a reference. Critical stress intensity factor, K_{Ic} increases 28% for as-prepared 0.5wt% I.28E clay/epoxy nanocomposite compared to neat epoxy. But the toughening effect of clay on epoxy polymer starts to decrease with any additional clay reinforcement. This is a common behavior for clay/epoxy nanocomposites and has been reported in previous studies conducted on these nanocomposites. Depending on the processing technique and clay/epoxy interaction, there is optimum weight percentage for which the property enhancement can be maximized. Any further addition of clay would form agglomerates due to improper exfoliation of the clay platelets and result in stress concentration, which would force a material to fail in lower loads. Single-edge-notch-bend test for moisture saturated neat Epon 862 samples showed excessive plasticization. As linear elastic fracture mechanics does not hold for viscoelastic materials, fracture toughness of moisture saturated neat epoxy was not calculated. The effect of moisture on epoxy polymers were studied by various researchers, and it was found that water effectively plasticizes the polymer and degradation of the matrix involves hydrolysis and chain scission. As a result overall integrity of the entire system is undermined and fracture toughness is reduced. In case of moisture saturated clay/epoxy nanocomposites the physical effect of plasticization was absent and K_{Ic}

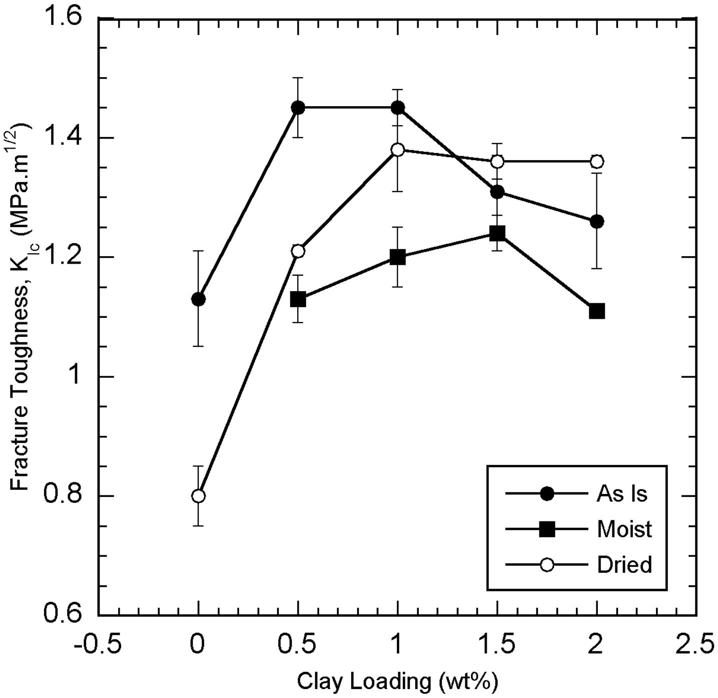


Figure 3.1: Mode-I Fracture Toughness as a function of clay loading percentage for Nanocor I.28E nanocomposite

is found to have decreased compared to as-prepared samples for all nanocomposites. This degradation of clay/epoxy nanocomposites and the reduction in fracture toughness reduces with increasing clay content. Dried neat Epon 862, free of void-filling water showed 29% reduction in fracture toughness from as-prepared neat Epon 862 samples. In case of I.28E clay/epoxy nanocomposite the degradation of property is significantly less compared to neat epoxy. For only 0.5wt% addition of clay results in 84% recovery of fracture toughness when compared to as-prepared samples. For 2.0wt% clay/epoxy nanocomposite, we have found that dried samples are more tougher than the as-prepared samples. But in this case, the standard deviation of the as-prepared samples are much higher and it is possible that, dried and as-prepared samples has no difference in toughness.

Figure 3.2 shows the critical stress intensity factor, K_{Ic} for Somasif clay/epoxy nan-

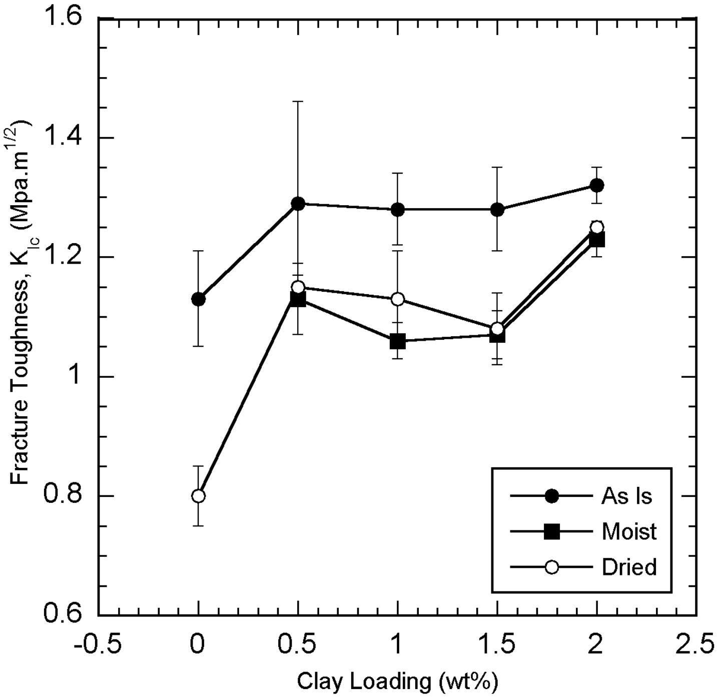


Figure 3.2: Mode-I Fracture Toughness as a function of clay loading percentage for Somasif MAE nanocomposite

composites. For as-prepared and moisture saturated samples Somasif and I.28E clay nancomposites showed similar trend. However, the degradation of fracture property due to hygrothermal aging is less in Somasif clay nanocomposites compared to I.28E clay nanocomposites. For 0.5wt% of Somasif MAE clay loading, fracture toughness decreased only 12% for moisture-saturated sample with respect to as-prepared sample. On the other hand, fracture toughness decreased 22% for same weight percentage of I.28E clay loading. This difference may have occurred due to the structural difference between the two clay used in the study. Both the clays used in this study has identical structures with only one difference. I.28E clay has hydroxyl ions present on the four corners of tetrahedral lattice. In Somasif MAE, which is a fluorinated mica, these -OH ions are replaced with fluorine ions. This hydroxyl ions may help the process of hydrolysis during hygrothermal ageing and as a result, I.28E clay nanocomposites may have been damaged more than Somasif MAE clay nanocomposites. This hypothesis is supported by the fracture property of dried nanocomposites. For 0.5wt% clay loading, Somasif MAE clay/epoxy nanocomposites provided 90% recovery of as-prepared samples' K_{Ic} value; whereas, for same clay loading I.28E clay/epoxy nanocomposites provided only 84% recovery to its as-prepared counterpart.

3.3 Flexural Properties

Flexural strength for the epoxy and clay/epoxy nanocomposites were determined using 3PB test and is plotted against clay loading percentage in figure 3.3 and 3.4 for I.28E and Somasif MAE clay, respectively. Table 3.3 and 3.4 lists the flexural strength values for different I.28E and Somasif clay/epoxy nanocomposites respectively, that are subjected to different pre-conditioning. Flexure strength of neat Epon 862 is also listed in the table as a reference.

Table 3.4: Flexural strength of I.28E clay/epoxy nanocomposites

Clay loading (wt%)	As-Is	Moist	Dried
Epon 862	101.84±2.77	65.32±3.17	98.08±0.94
0.5	106.54±2.15	87.96±2.46	110.83±5.58
1.0	108.80±1.27	74.38±4.01	103.09±1.57
1.5	104.44±3.28	81.49±0.55	95.16±1.59
2.0	95.68±3.81	86.68±3.06	108.90±1.38

Figure 3.3 shows that, 1.0 wt% I.28E clay nanocomposite provides the maximum improvement in flexural strength. Any further addition of clay results in reduction of property. Poor quality of dispersion may have resulted in formation of clay agglomeration, which can be a possible cause of reduction in property for higher clay loading nanocomposites. Agglomerates in a nanocomposite acts as stress concentration points and as a result these structures fail at lower loads; where as a properly

Table 3.5: Flexural strength of Somasif clay/epoxy nanocomposites

Clay loading (wt%)	As-Is	Moist	Dried
Epon 862	101.84±2.77	65.32±3.17	98.08±0.94
0.5	110.22±3.36	84.53±1.37	106.11±1.62
1.0	105.50±0.51	85.06±0.95	102.96±7.96
1.5	107.56±3.61	85.35±2.60	96.52±0.76
2.0	100.96±3.50	78.09±2.56	93.10±1.23

Table 3.6: Flexural modulus of I.28E clay/epoxy nanocomposites

Clay loading (wt%)	As-Is	Moist	Dried
Epon 862	3.04±0.08	2.43±0.03	2.94±0.07
0.5	3.14±0.17	2.71±0.06	3.11±0.11
1.0	3.21±0.06	2.75±0.06	3.18±0.07
1.5	3.40±0.06	2.89±0.04	3.16±0.14
2.0	3.60±0.12	3.07±0.08	3.22±0.08

exfoliated structure would fail at higher load. Moisture saturated nanocomposites show degradation in terms of flexural strength. For, 1.0wt% of I.28E clay/epoxy nanocomposites, reduction in flexural strength due to hygrothermal aging is 32%. In clay/epoxy nanocomposites moisture can diffuse into the interface between the clay and the polymer, which can result in reduced interfacial bonding between the clay and the epoxy. The reduction of flexural strength for moisture absorbed samples can be attributed to this interface property degradation. Furthermore, absorption of moisture can create hydrostatic pressure at the crack tips and hastens the crack propagation and damage in the system. In case of dried samples, as most of the moisture is driven out of the system, plasticization effect was not present and all the samples showed quasi-brittle failure in 3PB test. From the collected data, it is possible to conclude that flexural strength for samples that are pre-conditioned with absorption-

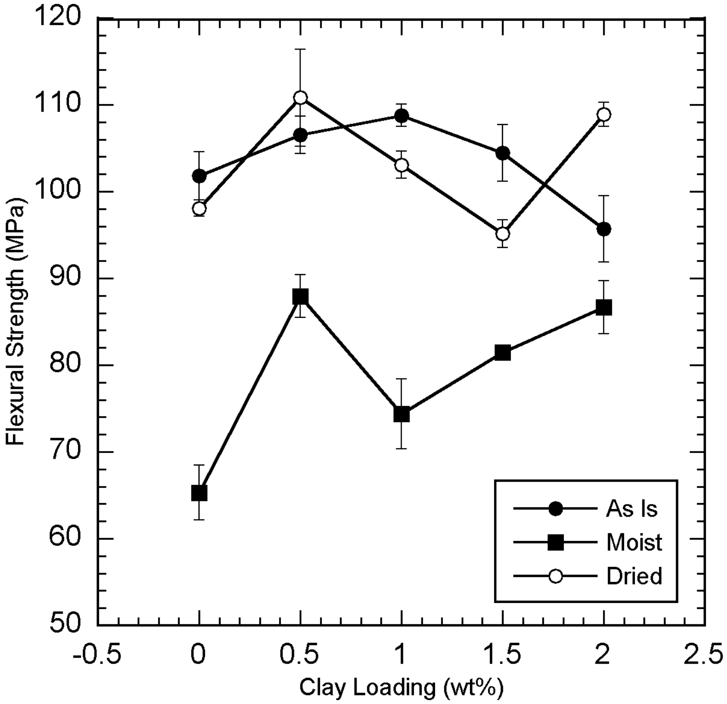


Figure 3.3: Flexural Strength as a function of clay loading percentage for Nanocor I.28E clay nanocomposite

desorption cycle recovers almost fully. For instance, flexural strength recovers to 95% of its original value for 1.0wt% of I.28E/epoxy nanocomposite.

Almost similar trend was observed for Somasif MAE clay/epoxy nanocomposites. Addition of clay resulted in increased flexural strength for these nanocomposites and after 24h of hygrothermal aging it was decreased, although the severity of degradation was much less compared to I.28E clay/epoxy nanocomposites. For 1.0wt% of Somasif clay flexural strength was reduced 19%, while it was reduced 32% for I.28E clay. The characteristic structural difference between the two clays is the main reason for this mismatch. Due to the presence of hydroxyl ions in the I.28E clay, it is possible that these nanocomposites might have damaged more after moisture absorption than the Somasif MAE clay/nanocomposites. For dried nanocomposites, similar trend was observed for both the clays and it was found that, flexural strength recovers almost

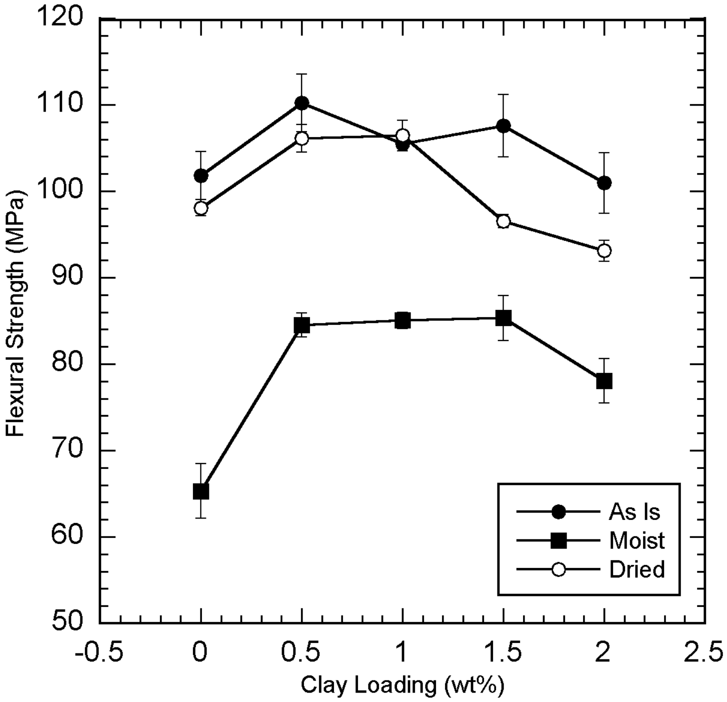


Figure 3.4: Flexural Strength as a function of clay loading percentage for Somasif MAE nanocomposite

fully. It is conclusive from the data that, permanent changes have very little effect on flexural strength for the epoxy system under investigation.

Flexural modulus for the epoxy and clay/epoxy nanocomposites were determined from 3PB test and is plotted against clay loading percentage in figure 3.5 and 3.6 for I.28E and Somasif MAE clay, respectively. Table 3.5 and 3.6 shows the flexural modulus values for different I.28E and Somasif clay/epoxy nanocomposites respectively, that are subjected to different pre-conditioning. Flexure modulus for neat Epon 862 is also listed in the table as a reference.

Flexural modulus increased almost linearly for both the clays with increase in clay loading. According to previous studies on epoxy polymers, incorporation of hard substance such as clay, alumina, etc. in polymer matrix results in higher modulus. When a load is applied on epoxy, the polymer chains slide past each other and deforms.

Table 3.7: Flexural modulus of I.28E clay/epoxy nanocomposites

Clay loading (wt%)	As-Is	Moist	Dried
Epon 862	3.04±0.08	2.43±0.03	2.94±0.07
0.5	3.33±0.06	2.96±0.10	3.08±0.09
1.0	3.40±0.11	3.02±0.03	3.15±0.07
1.5	3.44±0.04	3.11±0.05	3.15±0.07
2.0	3.46±0.08	3.13±0.05	3.14±0.05

This deformation is more in less cross-linked structure compared to higher cross-linked structures. Once layered silicates such as clay particle is introduced in a polymer system, it restricts the motion of the polymer chain sliding and make the matrix less pliable. As the clay content increases it is more difficult for the polymer chains to untangle and move. This increase in restriction of polymer chains is responsible for the increase in modulus as the clay percentage increases.

For hygrothermally conditioned specimens, the modulus is lower compared to the as-prepared specimens. This behavior observed is mostly due to the presence of water inside the epoxy system. Water acts as an effective plasticizer and water can diffuse into the clay-polymer interface and weaken the bonding between them. Other mechanisms effecting the polymer such as hydrolysis and chain scission is also responsible for lowering the modulus. Once hydrolysis and chain scission takes place, less bonding between the polymer makes it more deformable resulting in lower modulus for aged samples. For neat polymer, the effect of hygrothermal aging is more severe than in the nanocomposites.For neat Epon 862, flexural modulus decreased 20% after hygrothermal aging; where as, it is only 13% and 11% for 0.5wt% of I.28E and Somasif clay/epoxy nanocomposites, respectively. It was observed that, modulus increases almost linearly for moisture absorbed samples also.

For samples conditioned at 110℃ for 6h, almost full recovery of modulus is ob-

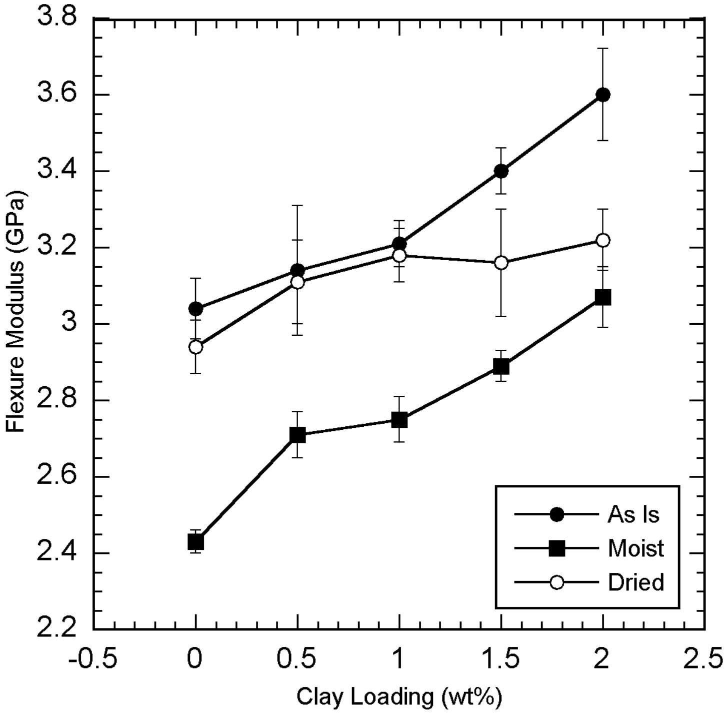


Figure 3.5: Flexural Modulus as a function of clay loading percentage for Nanocor I.28E clay nanocomposite

served in this study for both the systems. Once dried free water that is residing in the micro-voids is evaporated, and the effect of plasticization is not present anymore. As a result, the recovery of mechanical properties from moisture absorbed state occurs. From the collected data, it can be observed that permanent damage to the modulus of clay/epoxy nanocomposite is more for higher clay loading. The reason for this behavior can be attributed to the weakening of interfacial property. Interfacial area increases with increase in clay content. As a result for higher clay content nanocomposites, the damage to the interfaces would be more than lower clay content nanocomposites.

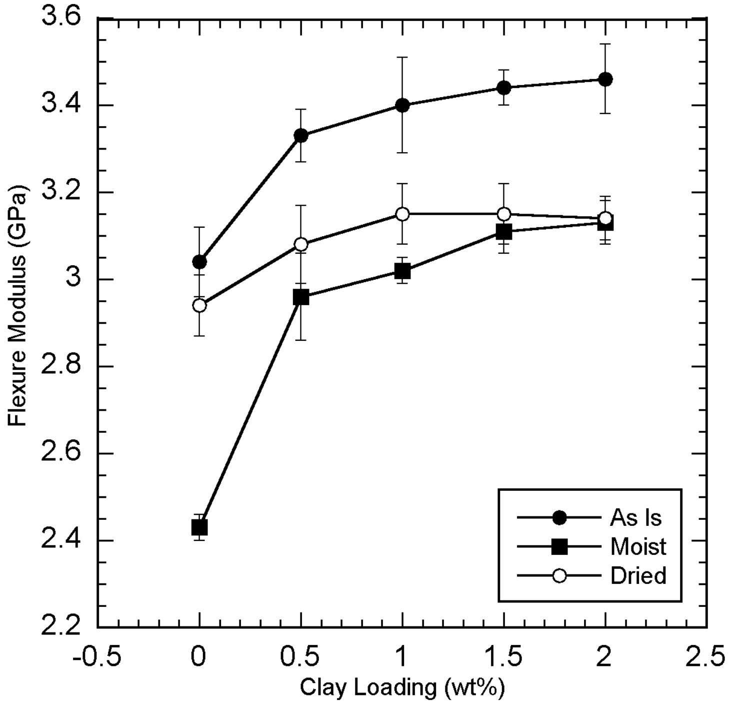


Figure 3.6: Flexural Modulus as a function of clay loading percentage for Somasif MAE nanocomposite

3.4 Scanning Electron Microscopy

The scanning electron micrographs of the fracture surface of tested neat polymer and clay/epoxy nanocomposites are shown in Figs. 3.7- 3.9. It is well known that there are one crack growth zone (near crack initiation point) at the beginning of the crack growth and one rapid crack growth zone (away from crack initiation point) when the instability criterion for crack growth is met with the continually increased loading [58]. The slow crack growth zone and the rapid crack growth zone micrographs are given in the same magnification for comparison. The direction of the crack growth is vertically downwards in all the micrographs.

SEM micrograph of the fracture surface of as-prepared neat polymer (3.7a) show brittle failure with smooth fracture surface. For the dried neat epoxy specimen (3.7b), almost identical brittle failure surface is observed, with only exception that, a network

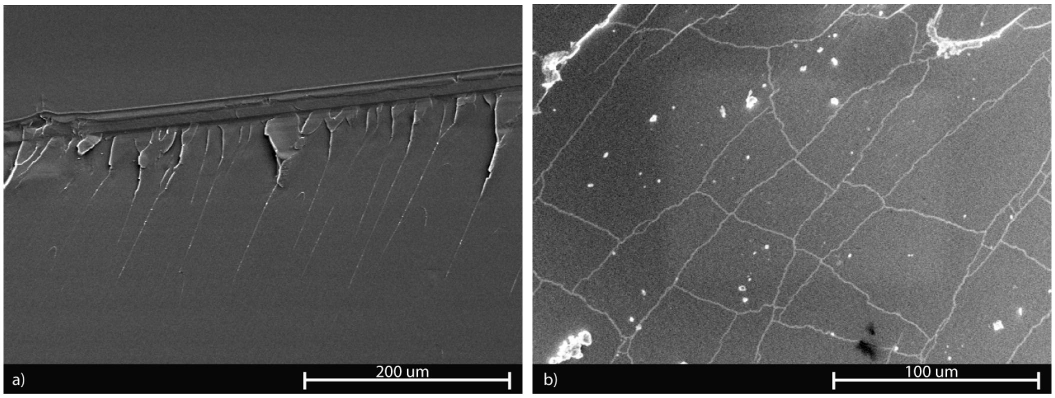


Figure 3.7: Scanning electron micrographs of Neat polymer; a) as-prepared and b) dried condition

of microcracks throughout the fracture surface is found. The difference between the fracture toughness of unaged and dried neat polymer can be attributed to the formation of these microcracks as a result of hygrothermal ageing and subsequent drying.

The SEM micrographs of clay incorporated epoxy systems showed significantly rougher surfaces compared to the neat polymer, which happens due to presence of hard substances like clay particles. Clay, if present in a system, resists and slows down the crack propagation. Crack pinning and crack bifurcation is observed in micrographs of both as-prepared nanocomposites. It is also evident from the images that, some clay particles were pulled out during the new surface formation. As a result of these mechanisms, higher amount of energy dissipation occurs for clay nanocomposites compared to the as-prepared specimens. Micrographs also show that as-prepared I.28E clay nanocomposite has a coarser surface compared to Somasif MAE clay nanocomposite, which might be the reason for I.28E nanocomposite having better fracture toughness.

In case of hygrothermally aged moisture absorbed specimens, both nanocomposites showed some form of shear yielding as the failure mechanism. As shear yielding requires less energy to form new surface, moisture absorbed specimens showed lower fracture toughness than as-prepared specimens. Although, shear yielding was found to be the principle mechanism of failure in these specimens, some form of crack bifurcation was also present in these failure surfaces.

Fracture surface micrographs of moisture desorbed dried I.28E nanocomposites showed more roughness than the moisture absorbed specimens, which indicate higher fracture toughness values for these specimens. It is interesting to observe that Somasif nanocomposites are not capable of providing good resistance to crack propagation after a sorption-desorption cycle.

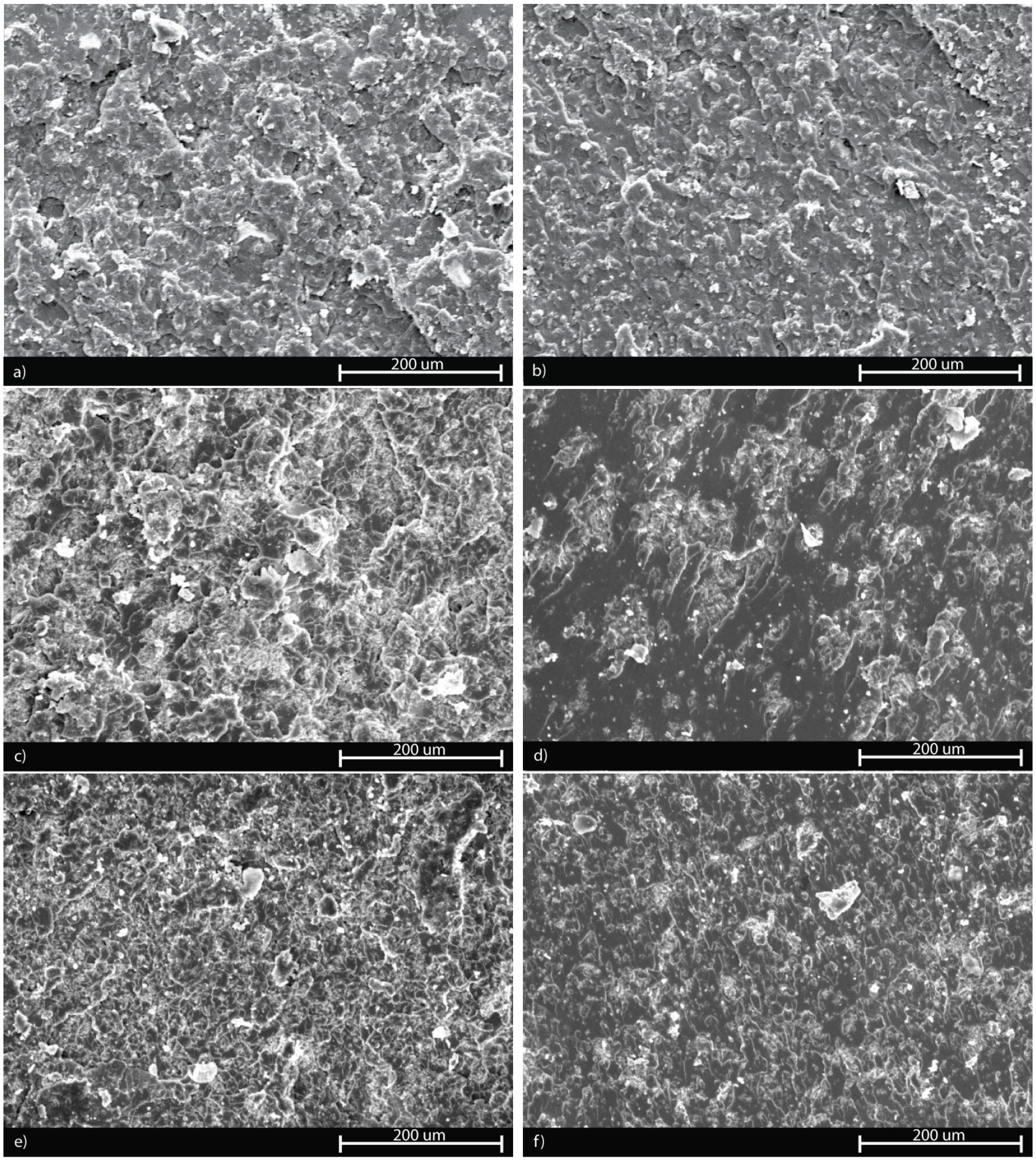


Figure 3.8: Scanning electron micrographs of 1.5wt% I.28E clay/epoxy nanocomposites; a) as-prepared: slow crack growth zone, b) as-prepared: fast crack growth zone, c) moist: slow crack growth zone, d) moist: fast crack growth zone, e) dried: slow crack growth zone, f) dried: fast crack growth zone

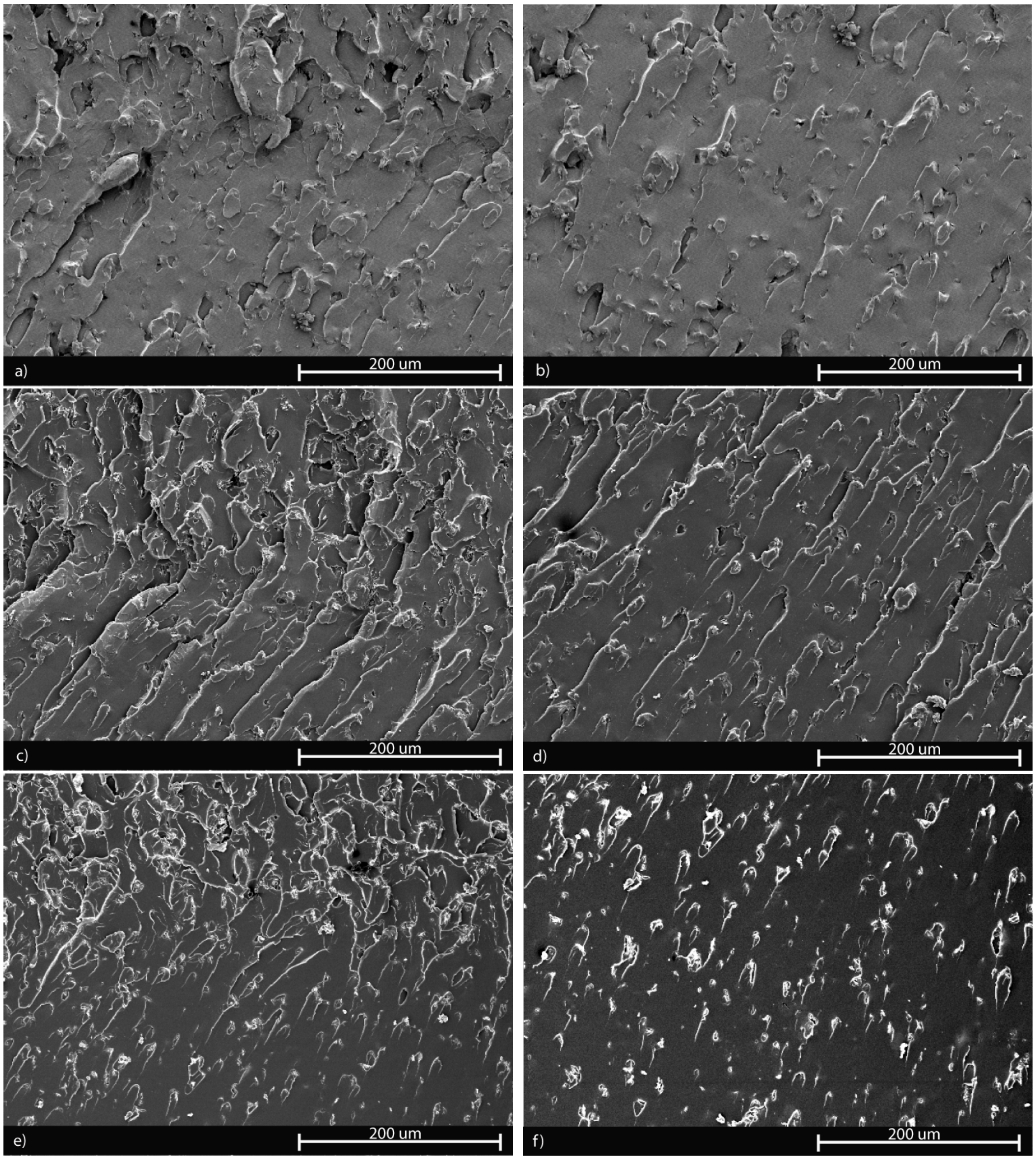


Figure 3.9: Scanning electron micrographs of 1.5wt% Somasif clay/epoxy nanocomposites; a) as-prepared: slow crack growth zone, b) as-prepared: fast crack growth zone, c) moist: slow crack growth zone, d) moist: fast crack growth zone, e) dried: slow crack growth zone, f) dried: fast crack growth zone

CHAPTER 4

CONCLUSIONS

Fracture toughness, flexural strength and modulus were determined for two different clay/epoxy nanocomposites following the ASTM standards. The effect of hygrothermal ageing on the mechanical properties of two different systems were investigated. After removing the free water by drying, the irreversible effect or the permanent damage due hygrothermal aging on the clay/epoxy nanocomposite systems were also studied. Irrespective of the clay reinforcement type, all three properties were degraded due to hygrothermal ageing. The permanent damage or degrdation was severe in case of fracure toughness, while flexural However, incorporation of clay in epoxy matrix has positive effects to some extent. It was observed from the collected data that, mechanical properties were less severely degraded for clay/epoxy nanocomposites compared to neat epoxy samples. I.28E clay nanocomposites were more damaged after hygrothermal aging compared to Somasif MAE clay nanocomposites. Having flurine ions on the tetrahedral sheets of Somasif MAE in place of hydroxyl ions present in I.28E might have reduced the hydrogen bonding on the matrix. As a result, for Somasif MAE nanocomposites both hygrothermally aged and dried specimens showed better properties compared to I.28E nanocomposites. For Somasif nanocomposites, no significant recovery of fracture toughness was observed from the moisture absorbed state.

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VITA

SALAH UDDIN AHMED HAMIM

Candidate for the Degree of

Master of Science

Thesis: VARIATION OF MECHANICAL PROPERTIES DUE TO HYGROTHERMAL AGEING AND PERMANENT CHANGES UPON REDRYING IN CLAY/EPOXY NANOCOMPOSITES

Major Field: Mechanical Engineering

Biographical:

Personal Data: Born in Dhaka, Bangladesh on December 5, 1985.

Education:
Received the B.S. degree from Bangladesh University of Engineering and Technology (BUET), Dhaka, Bangladesh, 2009, in Mechanical Engineering
Completed the requirements for the degree of Master of Science with a major in your major Oklahoma State University in July, 2011.

Experience:
Graduate Research Assistant in Mechanics of Advanced Materials Laboratory, Oklahoma State University
Graduate Teaching Assistant, Oklahoma State University

Name: Salah Uddin Ahmed Hamim Date of Degree: July, 2011

Institution: Oklahoma State University Location: Stillwater, Oklahoma

Title of Study: VARIATION OF MECHANICAL PROPERTIES DUE TO HYGROTHERMAL AGEING AND PERMANENT CHANGES UPON REDRYING IN CLAY/EPOXY NANOCOMPOSITES

Pages in Study: 38 Candidate for the Degree of Master of Science

Major Field: Mechanical Engineering

Epoxy polymers are an important class of material for use in various applications. Due to their hydrophilic nature, epoxy resins tend to absorb moisture. Absorption of moisture degrades the functional, structural and mechanical properties. For polymers, moisture absorption can lead to both reversible and irreversible changes. In this study, the combined effect of moisture and elevated temperature on the mechanical properties of Epon 862 and its nanocomposites were investigated. The extent of permanent damage on fracture toughness and flexural properties of epoxy, due to the aggressive degradation provided by hygrothermal ageing, was determined by drying the epoxy and their clay/epoxy nanocomposites after moisture absorption. From the investigation it was found out that, clay can help in reducing the negative effect of hygrothermal ageing. Significant permanent damage was observed for fracture toughness and modulus, while the extent of permanent damage was less significant for flexural strength. Failure mechanism of this nanocomposites were studied by using Scanning Electron Microscopy (SEM).

ADVISOR'S APPROVAL: ____________________