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EFFECT OF NANO-KAOLINITE WEIGHT FRACTION ON INTERFACIAL SHEAR STRENGTH OF FIBRE REINFORCED NANOCOMPOSITE

Many studies around the world focus on the use of organic and inorganic additions to polymer composites to enhance their mechanical properties. Investigations were conducted to study the mechanical properties of composites with nano-kaolinite weight fractions of 1, 3, 5, 7, and 12% incorporated into an epoxy matrix. Further investigations were carried out on the diffusion of the epoxy nano-kaolinite monomer into the interfibrillar space when polypropylene and Kevlar rope fibre were added. The Kevlar fibre/matrix and polypropylene fibre/matrix interfacial shear strength was evaluated by the single fibre drag-out method. The highest interfacial shear strength was observed at a 5 wt.% nano-kaolinite content. Energy-dispersive X-ray spectroscopy (EDX) and scanning electron microscopy (SEM), as well as characterisation by X-ray diffraction (XRD), were performed on all the epoxy/nano-kaolinite, Kevlar specimens.

Keywords: epoxy, nano-kaolinite, Kevlar fibre, polypropylene fibre, drag-out test, interfacial shear strength

INTRODUCTION

Because of their enhanced mechanical characteristics, polymer clay nanocomposites are used in the automotive as well as beverage packaging industries [1]. The most prevalent element of the kaolin family, kaolinite, is one of the most common clay minerals on the planet [2]. Kaolinite is a 1:1 coated dioctahedral aluminosilicate made up of silicate layers (Si_2O_5) bonded to gibbsite layers ($Al_2(OH)_4$). Individual layers are linked by hydrogen connections between the luminol classes of the octahedral sheet on each side and the siloxane macro-rings of the tetrahedral layers on the other, as well as heavy dipole interactions between non-centrosymmetric plates. The superposed dipoles having a lamellar structure provide a great deal of coherent electricity [3, 4]. Epoxy resins are some of the most commonly used thermosetting polymers in manufacturing. Nevertheless, since brittleness is an intrinsic issue for these extremely crosslinked resins, toughening has piqued interest. Clay is a possible candidate in the production of high-performance epoxy because of its low cost, high strength, and broad specific region [5]. Polymer composites can be classified into three groups depending on the degree of dispersion of the nanosized layer structure: exfoliated nanocomposites, intercalated nanocomposites, and microcomposites that can be further subdivided into organised and disordered exfoliation. Intercalation occurs as clay layers extend to facilitate polymer insertion, while exfoliation occurs when clay layers split to create single nanolayers in the matrix. Partial exfoliation is a morphology that occurs halfway between intercalation and exfoliation [6]. The morphological variations described above greatly influence the mechanical and physical characteristics of polymer nanocomposites. The recent advances in the exfoliation and synthesis of polymer nanocomposites are demonstrated in this work using epoxy/clay nanocomposites [7]. The interfacial shear strength (IFSS) is the main variable that affects the adhesion between the matrix and fibre. It has a significant function in fibre reinforced composite materials, directly influencing the load transfer efficacy between the composite matrix and fibres [8]. The drag-out configuration test was applied to examine the interfacial shear adhesion at the fibre-matrix interface [9].

This work aims to study the enhancements of composites based on an epoxy nano-kaolinite matrix reinforced with Kevlar fibre and epoxy nano-kaolinite matrix with polypropylene fibre, whose results can be applied in automotive brake friction materials.

MATERIALS AND METHODS

The composite material used in this study had five main constituents – binder, curing agent, activator, embedded system, and reinforcement:
1. The epoxy resin matrix, 3,4-epoxycyclohexylmethyl and 3,4-epoxycyclo-hexane carboxylate (ERL 4221, Tetrachem, China), consisting of 100 parts by weight of hexanediol diglycidyl ether resin was used, purchased from the Dow Chemical Company.

2. The curing agent – (34 parts) methyl-hexahydro phthalic anhydride (MHHPA, $\geq$ 98%, Bangcheng CO. LTD, China).
3. The activator was 2-ethyl-4-methylimidazole (EMI, 99%, Bangcheng CO. LTD, China).
4. The nanoclay particles used in this investigation were nano-kaolinite $Al_2Si_2O_5(OH)_4$, 80 nm. The nano-kaolinite was added to the epoxy in the ratios of 0, 1, 3, 5, 7 and 12% of the total weight.
5. Reinforcement: The first was Kevlar 49 fibre (p-phenylene terephthalamide) from DuPont™Kevlar. The second was a polypropylene fibre with a 200 μm radius from Shenzhen Chinary Co. China. U-shaped embedded lengths of 3, 4, and 5 mm were made for each single type of Kevlar and polypropylene fibre.

The epoxy resin was mixed with nano-kaolinite powder of different weight fractions as shown in Table 1. These components were mixed for 50 minutes using an ultrasound mixer, then one part epoxy hardener was added to the mixture and mixing was continued for 10 minutes. Afterwards the mixture was poured gradually into polysiloxane moulds. The matrix materials must be carefully poured into the mould to avoid the formation of bubbles. All the samples were cured in the in the mould at the temperature of $30^{o}C$ for five days and then were carefully removed from the mould. In this manner 36 composite were produced.

RESULTS AND DISCUSSION

The drag-out force for the samples and the interfacial shear strength τ_{IFSS} was estimated using Equation (1) [9]:

$$\tau_{IFSS} = \frac{P_D}{\xi l_e} \qquad (1)$$

where P_D is the component pull out force, ξ is the fibre perimeter and l_e [mm] is the embedded length.

A Mark-10 ESM301 motorised force test stand (Wagner Instruments) was employed to determine the interfacial shear force for all the specimens as shown in Table 2.

TABLE 1. **Compositions of produced samples**

Matrix materials – weight fraction	Fibre material and embedded length [mm]					
	Sample 1	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**	**Sample 6**
Epoxy (100%) Nano-kaolinite (0%)	Kevlar $3l_e$	Kevlar $4l_e$	Kevlar $5l_e$	Polypropylene $3l_e$	Polypropylene $4l_e$	Polypropylene $5l_e$
Epoxy (99%) Nano-kaolinite (1%)	Kevlar $3l_e$	Kevlar $4l_e$	Kevlar $5l_e$	Polypropylene $3l_e$	Polypropylene $4l_e$	Polypropylene $5l_e$
Epoxy (97%) Nano-kaolinite (3%)	Kevlar $3l_e$	Kevlar $4l_e$	Kevlar $5l_e$	Polypropylene $3l_e$	Polypropylene $4l_e$	Polypropylene $5l_e$
Epoxy (95%) Nano-kaolinite (5%)	Kevlar $3l_e$	Kevlar $4l_e$	Kevlar $5l_e$	Polypropylene $3l_e$	Polypropylene $4l_e$	Polypropylene $5l_e$
Epoxy (93%) Nano-kaolinite (7%)	Kevlar $3l_e$	Kevlar $4l_e$	Kevlar $5l_e$	Polypropylene $3l_e$	Polypropylene $4l_e$	Polypropylene $5l_e$
Epoxy (88%) Nano-kaolinite (12%)	Kevlar $3l_e$	Kevlar $4l_e$	Kevlar $5l_e$	Polypropylene $3l_e$	Polypropylene $4l_e$	Polypropylene $5l_e$

TABLE 2. **Interfacial shear force of all samples**

Specimen (l_e mm)	Peak force – displacement	0 wt.% nano-kaolinite	1 wt.% nano-kaolinite	3 wt.% nano-kaolinite	5 wt.% nano-kaolinite	7 wt.% nano-kaolinite	12 wt.% nano-kaolinite
Kevlar-fibre $3l_e$	Peak force [N]	0.5515	6.58	14.85	13.855	8.2	5.92
	Head distance [mm]	3.876	3.75	3.176	3.92	4.74	3.434
Kevlar fibre $4l_e$	Peak force [N]	0.732	6.305	21.845	11.085	10.23	9.2
	Head distance [mm]	1.602	3.6	4.764	3.78	3.909	4.704
Kevlar fibre $5l_e$	Peak force [N]	1.79	6.76	18.575	16.025	12.035	9.65
	Head distance [mm]	2.072	2.976	2.52	3.966	3.748	5.358
Polypropylene fibre $3l_e$	Peak force [N]	0.1195	1.295	3.355	2.19	1.29	1.045
	Head distance [mm]	2.44	2.58	5.858	12.96388	9.528	6.9188
Polypropylene fibre $4l_e$	Peak force [N]	0.373	1.045	3.63	3.54	2.56	1.52
	Head distance [mm]	10.434	14.8	10.862	11.31	9.018	9.06
Polypropylene fibre $5l_e$	Peak force [N]	0.5975	1.125	3.835	2.82	2.145	2.14
	Head distance [mm]	12.002	7.775	12.77596	15.98	9.56	10.004

From the data presented in Table 2 and Figure 1, the maximum interfacial shear stress was calculated using Equation (1), which reflects the adhesion strength or bond strength between the fibre and the matrix [10]. Figure 1 shows the maximum interfacial shear stress at the peak of shear force for each specimen, which reveals that the highest adhesion strength was exhibited by the epoxy with 5 wt.% nano-kaolinite reinforced with Kevlar and polypropylene fibres with the embedded length of 5 mm.
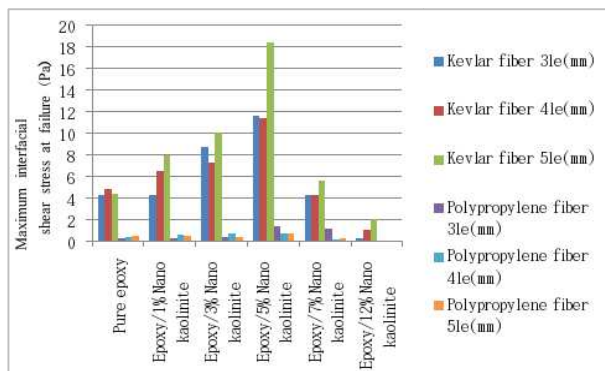

Fig. 1. Maximum interfacial shear stress from drag-out test

The relation between the interfacial shear strength and the weight fraction of nano-kaolinite is affected by:
1. The degree of exfoliation the nanoclay particles in the polymer matrix.
2. The extension of the fibre/polymer interfacial bond.
3. The reduction in the cohesive energy strength within the interface between the fibre and the matrix.

Theoretically, the interfacial shear strength rises as the embedded length of the fibres increases because of the fibre surface area. Nonetheless, defects or imperfect bonding between the fibres and the matrix influence the adhesion strength [11]. The dispersion of nanoparticles affects the adhesion strength, which can take the form of phase-separated, intercalated nanocomposites, or exfoliated nanocomposites as presented Figure 2 [12].
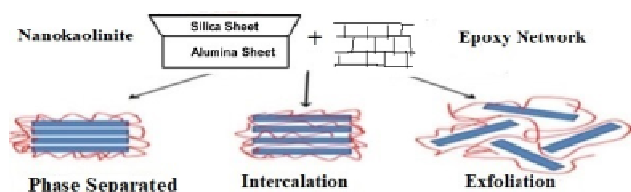

Fig. 2. Nano-kaolinite/epoxy structures

The excellent adhesive properties of the epoxy polymer matrix are due to the attracting forces between the epoxy resin and the surface area of the fibres; these forces are polar forces or direct bonds. Typical epoxy resins have pendant hydroxyl (-OH) groups along their chain that can form bonds or strong polar attractions to oxide or hydroxyl surfaces.

Energy dispersive X-ray spectroscopy (EDX) coupled with scanning electron microscopy (SEM) were used to show the distribution of elements and to determine the chemical composition. EDX is also one of the better-known methods employed in failure analysis [13]. The EDX analysis results revealed Ca, K, Cl, Si, Al, Mg, Na, O, N and C elements (as seen in Table 3) in different amounts. Elements C, N and O originated from the epoxy, while elements Ca, K, Cl, Si, Al, Mg and Na were from the nano-kaolinite. The increase in the atomic percentage of carbon atoms in the 5 wt.% nano-kaolinite sample over the other samples is owing to the presence of long chains of epoxy in the sample or an exfoliated nanocomposite structure.

TABLE 3. **EDX elemental analysis results of epoxy/nano-kaolinite matrix**

Element	Pure epoxy	Epoxy/1 wt.% nano-kaolinite	Epoxy/3 wt.% nano-kaolinite	Epoxy/5 wt.% nano-kaolinite	Epoxy/7 wt.% nano-kaolinite	Epoxy/12 wt.% nano-kaolinite
C	61.07	71.84	69.14	74.52	66.01	63.86
N	12.63	5.62	3.35	4.48	3.94	3.98
O	26.30	15.04	15.84	12.89	16.08	14.57
Na	-	1.16	0.76	0.73	0.85	0.92
Mg	-	0.98	0.87	0.80	1.03	1.65
Al	-	1.30	2.54	2.02	3.32	4.26
Si	-	2.86	5.86	3.77	7.47	9.40
Cl	-	0.70	0.70	0.41	0.68	0.74
K	-	0.26	0.24	0.23	0.27	0.32
Ca	-	0.24	0.70	0.15	0.35	0.30
Total	100%	100%	100%	100%	100%	100.%

Scanning electron microscopy (SEM) was used to produce micrographs of all the specimens to analyse the distribution of elements and to determine the structure of the matrix. Silicate aggregates can be determined by detecting the distributions of aluminium and silicon in the SEM micrographs (Fig. 3).

X-ray diffraction (XRD) spectra of the epoxy/nano-kaolinite were characterised as shown in Figure 4. The appearance of maxima between 18° and 19° show highly amorphous behaviour due to the epoxy/nano-kaolinite, which originates from the layered structure [14]. The intensity will certainly depend on the orientation of the constituents. Some peaks are high in intensity, as shown in Table 4 because the polymer nano-kaolinite is based on layered silicate materials. The relative intensity for epoxy/5 wt.% nano-kaolinite is 57.14%, which is attributed to the contribution of the nano-kaolinite layer arrangement in the epoxy resin.

The epoxy/nano-kaolinite material contains a large variety of systems and is frequently regarded as amorphous. The height of the peaks (Table 4) depends on the epoxy and nano-kaolinite layer arrangement, whether it is phase-separated, intercalated or exfoliated (Fig. 4).
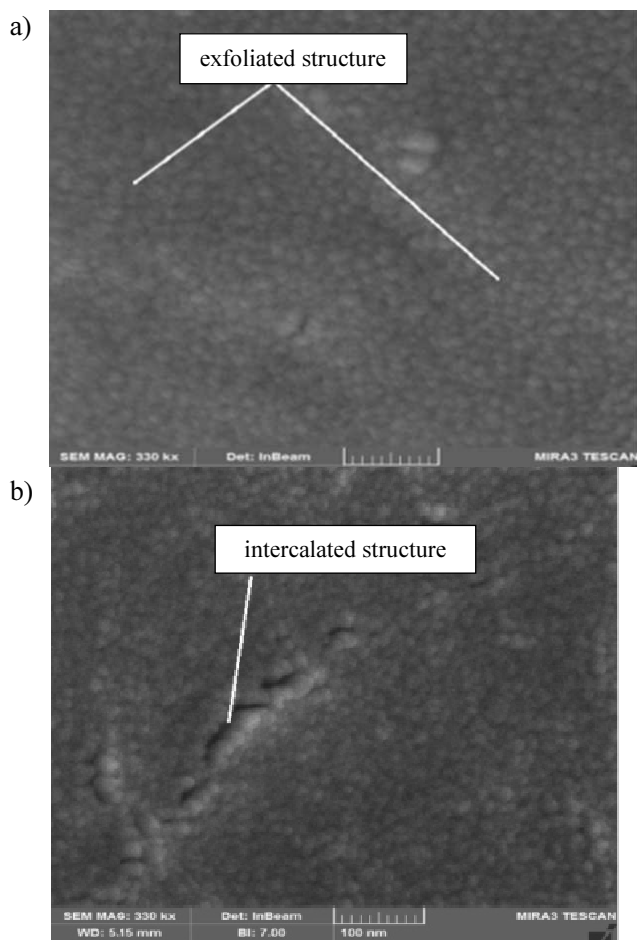
Fig. 3. SEM micrographs of epoxy/nano-kaolinite composites: a) 5 wt.% nano-kaolinite, b) 7 wt.% nano-kaolinite

TABLE 4. **XRD results**

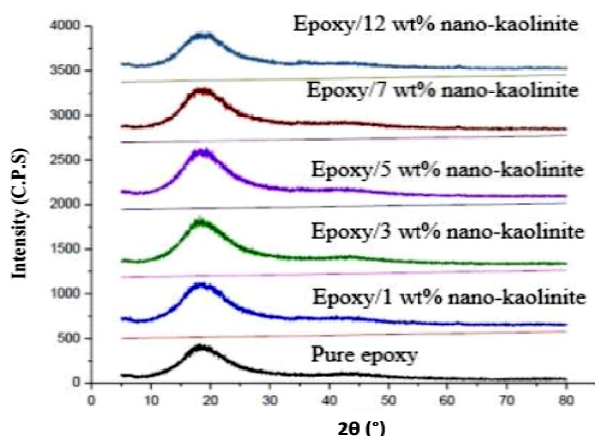| Sample	2θ [°]	Intensity (c.p.s)
Pure epoxy	18.28	444
Epoxy/1 wt.% nano-kaolinite	18.86	520
Epoxy/3 wt.% nano-kaolinite	18.22	590
Epoxy/5 wt.% nano-kaolinite	19.34	592
Epoxy/7 wt.% nano-kaolinite	19.18	512
Epoxy/12 wt.% nano-kaolinite	18.54	458

Fig. 4. XRD spectra for all specimens

The properties of the epoxy/nano-kaolinite matrix samples depend on the weight fraction of nano-kaolinite, affecting how the nano-kaolinite is dispersed inside the polymer matrix, which leads to an intercalated or exfoliated structure, and in turn, the interfacial shear strength is affected.

CONCLUSIONS

A reduction in the interfacial shear bond strength was caused by poor dispersion of nano-kaolinite in the epoxy matrix, which was strongly affected by the weight fraction. The highest interfacial shear strength was obtained by the material with the 5% nano-kaolinite weight fraction. EDX was used to describe and understand the dynamics of the composite matrices and the XRD method was used to identify the intercalated layered silicate structure.

The main elements C, N and O originated from the epoxy and elements Ca, K, Cl, Si, Al, Mg and Na from nano-kaolinite were quantified using EDX coupled with SEM. The investigation showed that the increase in the atomic percentage of carbon atoms for the 5 wt.% nano-kaolinite sample exhibited an exfoliated nanocomposite structure as shown by the SEM micrographs. The XRD spectrum characterisation of all the epoxy/nano-kaolinite samples revealed highly amorphous behaviour between 18° and 19° because of the epoxy/nano-kaolinite layered structure. Moreover, the XRD spectra exhibited high intensity for the epoxy/5 wt.% nano-kaolinite due to the layer arrangement.

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