ENGINEERING THERMOPLASTIC/KENAF FIBRE COMPOSITES: THE CURING EFFECT OF EPOXY USING DDS

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ABSTRACT

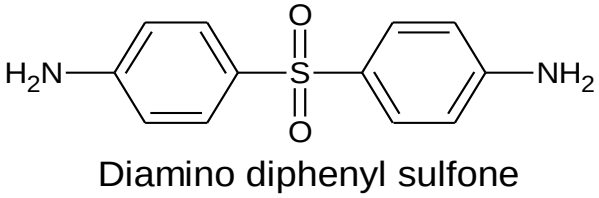
The aim of this work is to investigate the curing effect of epoxy in epoxy coated kenaf fibres (EKF) compounded with engineering thermoplastics [Poly (acrylonitrile-butadiene-styrene) (ABS), polycarbonate (PC) and recycled poly (ethylene terephthalate) (rPET)]. The composites were prepared by first treated the kenaf fibres with 6% NaOH, followed by precoating with 40% epoxy resin, dried at low temperature in an oven before compounding and dynamically cured with diamino diphenyl sulfone (DDS) *at twin screw extruder using temperatures profile of 175 – 230°C, 195 – 240°C and 120 – 170°C for ABS, PC and rPET composites respectively using 70rpm each. The pelletized composites were compression moulded thereafter. The cured composites displayed superiorities in density, flexural modulus and impact strength over the non-cured composites while results of MFI, tensile and flexural strength as well as hardness properties are thermoplastic dependence.*

Keywords: ABS, PC, rPET, Curing and Mechanical Properties.

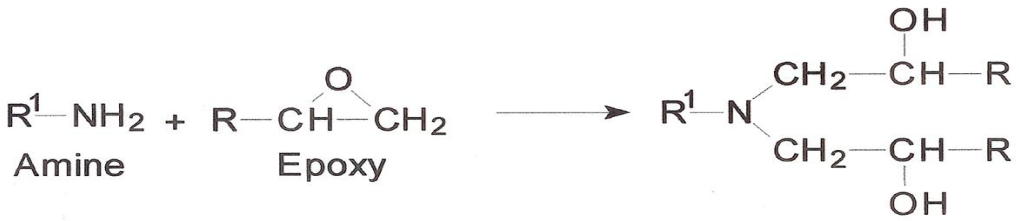
INTRODUCTION

The interest in natural fibre-reinforced polymer composite materials is rapidly growing both in terms of their industrial applications and fundamental research (Kozlowski & Wladyka-Przybylak, 2004 & 2007; Bledzki & Gassan, 1997 & Thomas, 2002). They are renewable, cheap, completely or partially recyclable, and biodegradable. The hydrophilic nature of natural fibres is incompatible with hydrophobic polymer matrix and has a tendency to form aggregates. These hydrophilic fibres exhibit poor resistant to moisture, which lead to high water absorption, subsequently resulting in poor tensile properties of the natural fibre reinforced composites. Moreover, fibre surfaces have waxes and other non-cellulosic substances such as hemi-cellulose, lignin and pectin, which create poor adhesion between matrix and fibres (Lee *et al.*, 2009).

Recently, kenaf is used as a raw material to be alternative to wood in pulp and paper industries (Ashori and Raverty, 2007) and fibre reinforced plastics (FRP) to replace synthetic fibres such as glass is receiving attention (Abdullah et al., 2011), and also used as non-woven mats in the automotive industries, textiles and fibreboard (Ibraheem *et al.*, 2011). Due to the versatility of epoxy resins towards a wide variety of chemical reactions, epoxy resins can be cured using a range of materials with different types of curing conditions. The choice of curing agents (also called 'hardeners') depends on the curing conditions applicable and the final application of the resin. Epoxies can be cured with amines, thiols, and alcohols. Amines are widely used as hardeners for epoxy resins. During the curing reaction, two epoxy rings react with a primary amine. Chemical modification of matrix resin networks with engineering thermoplastics; phenolic hydroxyl terminated poly (aryl ether sulfone)-epoxy system was studied by Hedrick and co-workers (Hedrick *et al.*, 1985) where they used diamino diphenyl sulfone (DDS) as shown in scheme 1a and 1b.



Scheme 1a: Chemical structure of DDS (Source: www.ismither.net)



Scheme 1b: Curing of Epoxy with Amine like DDS (Source:www.ismither.net)

Saliu *et al.* (2014) determined the optimum curative concentration of epoxy-coated kenaf fibre / ABS thermoplastic composites using diamino diphenyl sulfone (DDS) curing agent on epoxy and their results showed that 4% DDS gave the best of all mechanical properties. Song and Sung (1993) worked on the fluorescence studies of diamino diphenyl sulfone curing agent for epoxy cure characterization where the emission and excitation were studied during the curing process with a bifunctional epoxide or a tetrafunctional epoxide and concluded that as the cure reaction proceeds, both emission and excitation spectra exhibit red shifts of about 25 nm for DDS due to the conversion of the primary amino DDS (pp-DDS) to the tertiaryamino DDS (tt-DDS). The excitation spectra provide

much sharper peaks than the emission spectra, with an overall spectral shift of about 25 nm. In this study, kenaf fibre was incorporated into engineering thermoplastics without being degraded by their high processing temperatures of these thermoplastics due to the curing effect of epoxy on the fibre.

Materials and Methods

Materials

Recycled Poly (ethylene terephthalate) (rPET), Polycarbonate (PC), Poly (acrylonitrile butadiene styrene) (ABS) pellets, 3mm kenaf fibres (KF) were produced in Kenaf Fibre Industries Sdn. Bhd. (KFI) Malaysia, Sodium Hydroxide, Acetic Acid, Epoxy, curing agent (4,4-diamino diphenyl sulfone, DDS), Hydrofluoric Acid and Chloroform. All materials were supplied by the Science and Engineering Research Centre (SERC) of Engineering Campus, Universiti Sains Malaysia, Nibong Tebal, Malaysia.

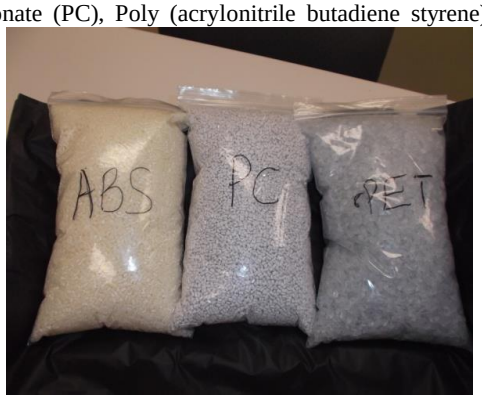


Plate 1: Engineering Thermoplastics (ABS, PC & rPET)

Plate 2: Epoxy coated Kenaf fibre (EKF)

METHODS

Surface Treatment and Coating

Kenaf fibres (Plate 2) of 3mm sizes used were firstly dried in the oven at about 37°C for 2days prior to being immersed in 6% NaOH solution for 3hrs, washed and neutralized with 100% acetic acid, finally washed thoroughly with distilled water until neutral pH was attained. Thereafter, the fibres were oven dried at 80ºC for 16hrs. 40 wt.% epoxy resin of very low viscosity thinned with chloroform was used to coat the NaOH treated fibres, first oven dried between 30 – 40ºC for 16hrs and then at 80ºC for additional 8hrs to dry finally.

Thermoplastic preparation

The engineering thermoplastic (ABS, PC and rPET) in Plate 1 was dried in a vacuum oven at 90ºC for 3hrs.

Twin Screw Extrusion

The mixing of curative with epoxy coated kenaf fibres (EKF) was carried out prior to mixing with each engineering thermoplastics in a bowl container before pouring into the hopper feeder of the twin screw extruder for compounding. The mixed materials (30/70) were extruded in a twin screw extruder with temperatures profile of 175 – 230°C, 195 – 240°C and 120 – 170°C for ABK, PCK and rPK respectively using 70rpm each. The extruded composites were then quenched in cold water before pelletizing (Plates 3 and 4). One EKF loading (30%) cured and non-cured was used for all the thermoplastics. Thereafter, the pelletized composites were compression moulded into test samples for characterization.


Plate 3: Extrudate quenched in cold water


Plate 4: Pelletized composites from extruder

Density and Melt Flow Index (MFI)

Density measurements were carried out with Precisa TX 220A densimeter at room temperature. Measurement of MFI was performed with die length of 8mm and die diameter of 2.096mm, according to ASTM D1238-04c method. The testing temperature was set at 260ºC for the composites with preheat time of 240s and 3.8kg load. Twenty seconds timing between each cut was used.

Tensile Test

The specimens of 140 x 25 x 1mm were prepared for tensile test by cutting with a band saw and test was conducted

using the Universal Testing Machine, Instron 3366 at 23 $\pm$ 2ºC and 50 $\pm$ 5% relative humidity in accordance to ASTM D882 - 97 with a gauge length of 100mm and cross-head speed of 1mm/min. Five measurements were carried out on each sample.

Flexural Test

Three-point bending flexural testing was performed on composites using the same Instron 3366 at 23 ± 2ºC and 50 ± 5% relative humidity in accordance to ASTM D790, with a support span length of 50mm and cross-speed of 5mm/min. Five measurements were carried out on each sample.

Impact Test

Izod impact test of un-notched composites samples were performed by using Pendulum Impact Machine (Zwick Roell Group, Germany) according to ASTM D256 with pendulum energy of 7.5J. The impact strength (kJ/m^2) was calculated by dividing the recorded absorbed impact energy by the cross-sectional area of the samples. Five measurements were carried out on each sample.

Hardness Test

The hardness of the composites was determined according to ASTM D2240 D. The hardness of compression moulded flat shaped samples with dimensions (width-22mm and thickness-1mm) was determined with the use of the TECLOCK GS-702G TYPE D (Japan) Automatic Digital Hardness Tester. Five measurements were carried out on each sample.

Scanning Electron Microscopy (SEM)

Fractured from the un-notched Izod impact test samples of composites were observed under a field-emission scanning microscope (FESEM) (Zeiss LEO Supra 35VP, Germany). Prior to observation, the samples were sputter-coated with a thin layer of gold to avoid electrical charging during examination.

RESULTS AND DISCUSSION

Physical Characteristics

Length of kenaf fibre	3 mm
Diameter	60 – 70 µm
Colour	Golden brown

Density and Melt Flow Index (MFI) of Composites

Densities can be easily measured at some standard temperature by means of a calibrated density-gradient column while MFI is inversely related to an average molecular weight as higher average molecular weight gives lower MFI. The test polymer may be used in any convenient form; powder, granules or moulded pieces. The pelletized composites were used in this research test. MFI analysis is frequently used as one of the first tests when conducting failure analysis (Tay *et al*., 2012).

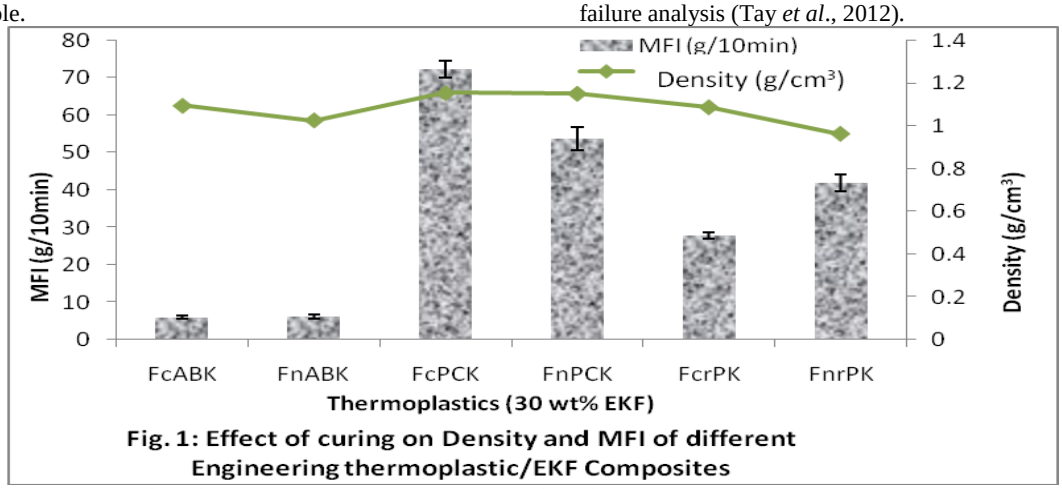


Fig. 1: Effect of curing on Density and MFI of different Engineering thermoplastic/EKF Composites

FcABK = Cured fibre of ABS/EKF composite, FnABK = Non-cured fibre of ABS/EKF, FcPCK & FnPCK = Cured & non-cured PC/EKF, respectively, FcrPK & FnrPK = Cured & non-cured rPET/EKF, respectively.

The results of densities and MFI for different thermoplastic, ABK, PCK and rPK are depicted in Fig. 1. It shows that the MFI of cured fibre composites are less than that of the non-cured with a significant difference between them for rPK while the ABK reduced insignificantly. The low flow of cured composites than the non-cured can be assigned to the cross-linkages by curative on the epoxy kenaf fibres preventing the easy flow of the composites and increase in molecular weight of the composites due to addition of curative. This corresponds with the findings of Dhal and Mishra (2013). The flow of PCK is the opposite of others when the cured composite superseded that of non-cured. This might be attributed to the disintegration of the polymer chains of PC by the curative used on epoxy. It is important to note that the cured composites are denser than the non-cured. This might also be in connection with increase in molecular weight of the composites due to addition of curative.

Tensile

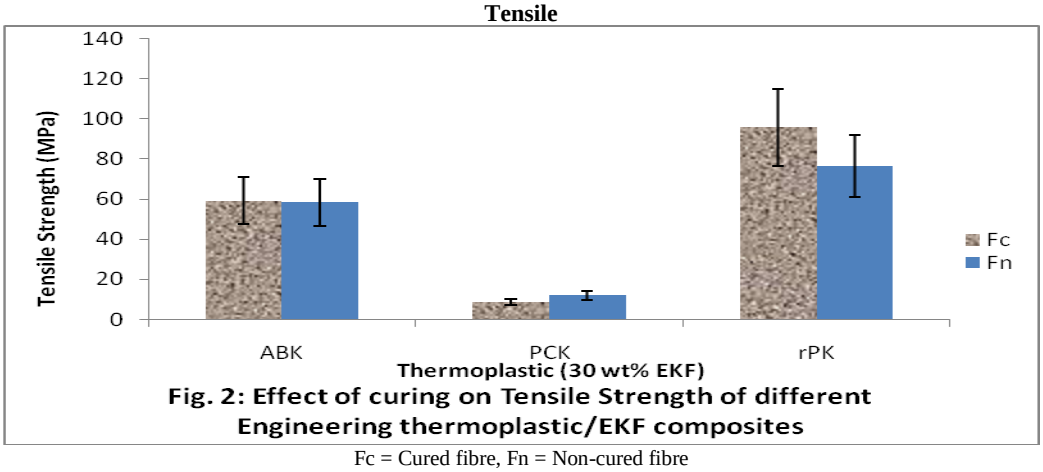


Fig. 2: Effect of curing on Tensile Strength of different Engineering thermoplastic/EKF composites

Fc = Cured fibre, Fn = Non-cured fibre

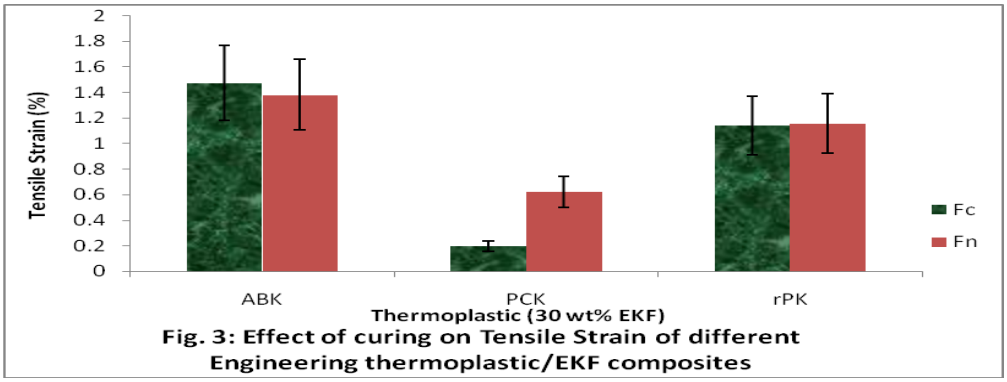


Fig. 3: Effect of curing on Tensile Strain of different Engineering thermoplastic/EKF composites

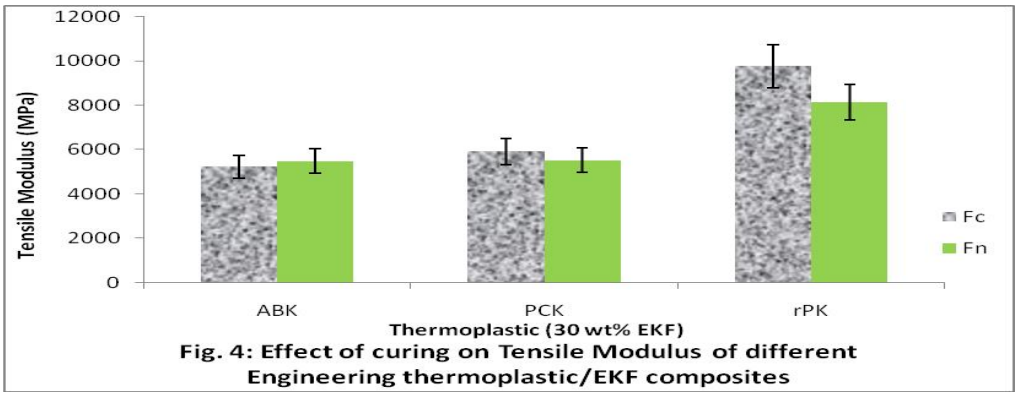


Fig. 4: Effect of curing on Tensile Modulus of different Engineering thermoplastic/EKF composites

Figs. 2 – 4 represent the effect of curing of ABS, PC, rPET/EKF composites on tensile properties. The tensile strength of cured ABK and rPET are higher with 2 and 25% respectively than that of the non-cured. This might be due to proper cross-linking of epoxy on the fibre by the curative, DDS (see Fig. 8) while that of PCK is the reverse of ABK and rPK, which might be attributed to the breaking of polymer chains by the curative. Results as presented in Fig. 2. The tensile strain (Fig. 3), value of non-cured of PCK is outrageously more than that of the cured composites (68% over), reason as earlier mentioned but little disparity between that of rPK as the non-cured has more strain value than the cured while that of ABK's cured is 7% more in strain than that of the non-cured, opposite that of PCK and rPK. The tensile modulus of non-cured ABK is 5% higher than that of the cured, reason might be cured fibres have impact on the composite than the matrix. The cured of that of PCK and rPK are higher than the non-cured by 7 and 20% respectively (as presented in Fig. 4), this can be due to the matrices effects. That of PCK may also be as a result of disintegration of the cured composites during compounding. The tensile strength and modulus of cured rPK is significantly higher (25 and 20% each) than that of the non-cured while the strain of the non-cured is unnoticeable higher value (2%) ahead of the cured composites.

Flexural

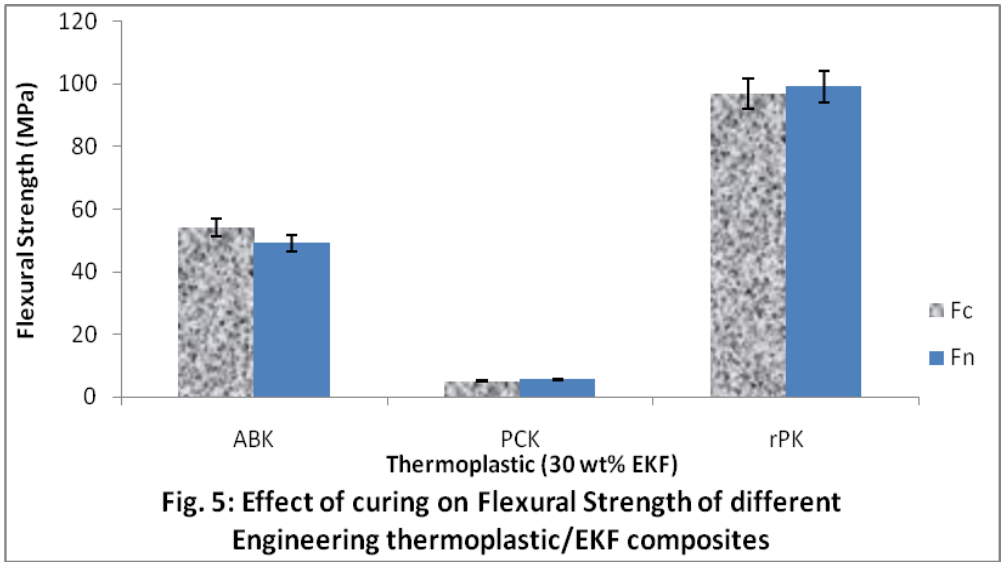


Fig. 5: Effect of curing on Flexural Strength of different Engineering thermoplastic/EKF composites

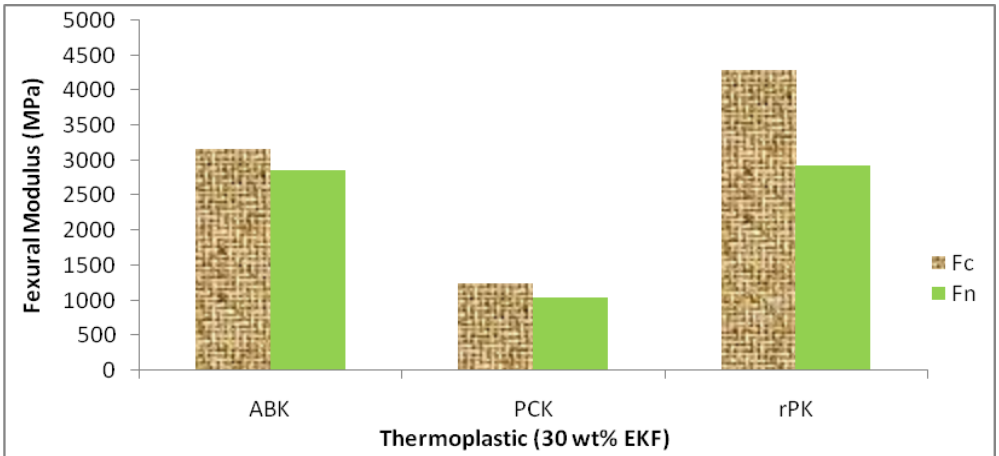


Fig. 6: Effect of curing on Flexural Modulus of different Engineering thermoplastic/EKF composites

The effects of epoxy curing for different thermoplastic composites on flexural strength in Fig. 5 and that of flexural modulus represented in Fig. 6. Rowell *et al*. (1999) explained that it is usually the lignin that is responsible for the combination of individual fibre together to make fibre bundles while Moh'd Ishak *et al*. (1997) explained further that the fibre-fibre adhesion in fibre bundles reduces the contact area between the fibres and the matrix which can cause poor stress transfer from the matrix phase to the dispersed fibres. These fibre bundles can affect the flexural properties of composites. From Fig. 5, the cured fibre of ABK composites has higher values of 10% in strength than the non-cured fibres. This could be due to the interfacial bonding that is stronger in cured fibre than the non-cured. Both the PCK and rPK composites exhibit similar behaviour where the strength of cured fibres is lower by 10 and 3% respectively than that of the non-cured. However, the flexural moduli of cured composites of all the thermoplastics are higher than those of the non-cured (10, 19, 46% for ABK, PCK, rPK respectively) as depicted in Fig. 6. This may be attributed to molecular interactions within the composites during compounding (Moh'd Ishak *et al*. 1997).

Impact and Hardness values

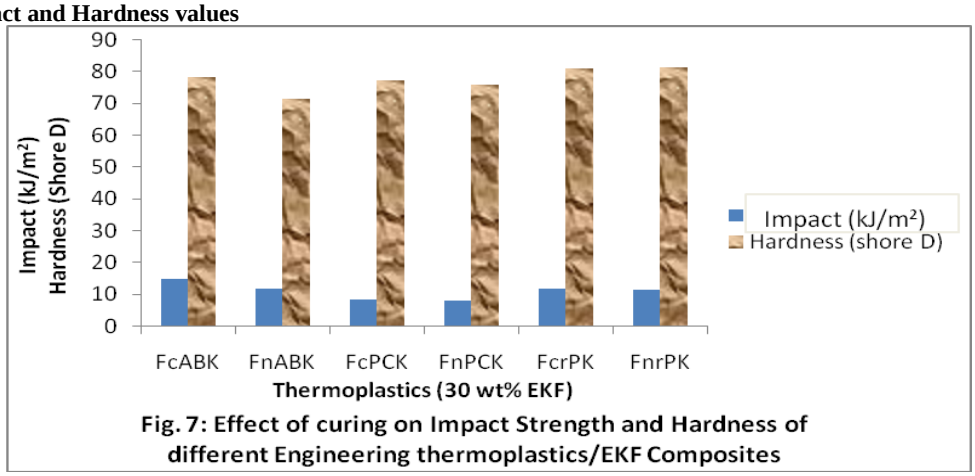


Fig. 7: Effect of curing on Impact Strength and Hardness of different Engineering thermoplastics/EKF Composites

When a composite is subjected to an impact, rapid crack propagation is initiated through the material. When this type of crack propagation encounters filler particles in the filled composites, the filler particles can absorb the energy and stop the propagation, if filler matrix interaction is strong (Ramakrishna & Rai, 2006). Fig. 7 shows the effect of different thermoplastic, reveals that impact strength of all the thermoplastic cured fibres composites (Fc) are greater than the non-cured fibres (Fn) and this might be as a result that the cured composites can absorbed more energy than the non-cured (Tay *et al*., 2012). The hardness values of ABK and PCK cured fibres are greater than non-cured. This can be attributed to a well cross-linked interface by the curative on epoxy fibres composites. That of rPK is vice-visa meaning that the non-cured fibre composite is harder than the cured. The nature of the matrix, rPET which is a recycled thermoplastic cannot be ruled out. Moreover, it is observed from this same Fig. 7 that ABK has the highest impact strength while rPK shows the best hardness property among others.

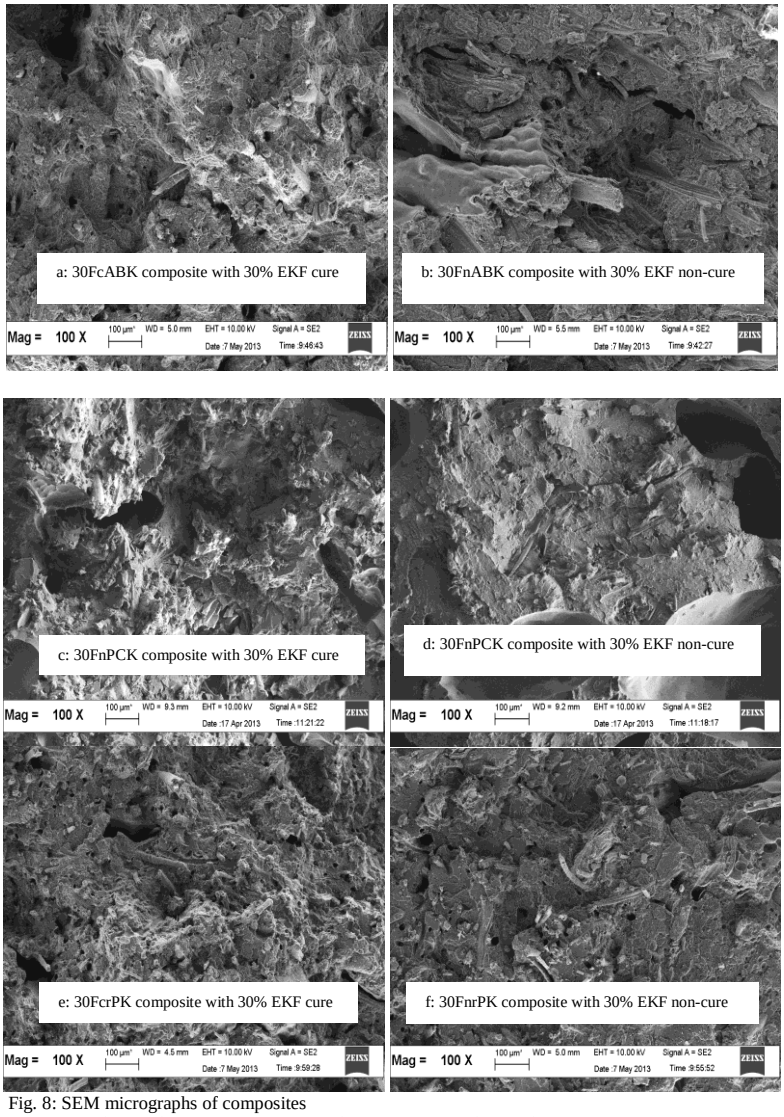


Fig. 8: SEM micrographs of composites
[(a) Cured fibres of ABK, (b) Non-cured of ABK, (c) Cured fibres of PCK, (d) Non-cured PCK, (e) Cured fibres of rPK and (f) Non-cured of rPK].

The effect of curing on different thermoplastics composites are shown in Figs. 8a and 8b for ABS, 8c and 8d for PC and 8e and 8f for rPET as cured and non-cured composites respectively. It was clearly observed that the cured fibres were well embedded in the matrix and well wetted than the non-cured. Pull out is more seen in the non-cured than the cured. It is also important to mention that the PC melts off during compounding with epoxy coated fibres which must have affected its strength as it was earlier mentioned. Therefore, the fibre cured composites was well bonded and there was no pull out of fibres while the non-cured composite fibres remained scattered as seen in the micrographs (Figs. 8c and 8d). For the rPk composites, pull out occurred in both cured and the non-cured but, it was more common with the non-cured as depicted in Figs. 8e and 8f. Generally, the composites from cured fibres were observed to have less pull out fibres than the non-cured.

CONCLUSION

The effect of curing on the physical and mechanical properties of epoxy coated kenaf fibre in engineering thermoplastics was studied and found that the densities of cured fibre are higher than that of the non-cured. The melt flow of ABS/EKF (ABK) and rPET/EKF (rPK) are retarded with curative while the PC/EKF (PCK) flow was induced by curative. Cured fibre composites displayed better properties in impact strength and tensile modulus than that of the non-cured. Tensile strength of cured composites of ABK and that of rPK was higher than the non-cured while non-cured of PCK is higher than the cured. The tensile modulus of cured PCK and rPK is more than that of the non-cured while the reverse is the case with ABK. Meanwhile, cured of ABK and PCK are harder than the non-cured but that of rPK is the opposite. The SEM micrographs have shown that pull out of fibres are prominent with the non-cured composites than the cured.

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