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Hybrid C/Pet/epoxy composites

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Hybrid carbon/PET/epoxy composites were prepared by a wet layup technique and characterized by standard methods of fracture and impact tests. The influence of PET fibre surface treatment with polyfunctional amine on the composite properties has been studied in order to determine the role of the fibre/matrix interface. The state of the fibre/matrix interface has been examined by several techniques, such as SEM, differential scanning calorimetry (DSC) and contact angle measurements. A significant hybrid effect of the PET/aminated fibres on the curing reaction and T_g of the epoxy matrix in the composites was established. It is probably due to the reaction between the amine groups of the fibre surface and the epoxy component of the resin, as determined by DSC.

1. Introduction

It is well known that the carbon-fibre based composite materials are rather susceptible to impact damage. Many reports have been presented concerning impact improvement of carbon-fibre/polymer matrix composites, initially through hybridizing with other fibres, especially organic ones [1–3].

Thus, fibre composites with a wide range of mechanical properties can be fabricated through the hybridization of two or more different fibres in a matrix material. The properties of the hybrid composites might not follow the role-of-mixtures prediction and, as a result, a positive or negative hybrid effect can be defined [4]. In order to improve and control the specific properties of a hybrid composite, the effects of the type and amount of hybridization and the fibre/fibre, fibre/matrix, as well as interply interactions, which dictate the "hybrid effect", have been studied.

Investigations of epoxy-based C/PE, C/Kevlar, C/PET and C/nylon hybrid composites have shown that, as a result of the complex nature of the fibre/fibre and fibre/matrix interface, these composites exhibit different types and levels of hybrid effects [5, 6].

The influence of different parameters, such as the stiffness and the strength of the constituent fibres, processing parameters (volume fraction and stacking sequence of the fibres, etc.) on the hybrid effect has been long recognized. In general, high-ductility fibres (among them polyethyleneterephthalate, PET) are found to improve the impact performance of brittle C/epoxy composites [1, 2].

In this work, an attempt has been made to create a hybrid C/PET/epoxy composite. The effect of hybridization on impact toughness and the basic mechanical properties of the composites were investigated, as well as the influence of the PET fibre surface treatment with polyfunctional amine on the hybrid properties.

2. Experimental procedure

2.1. Composite sample preparation

Several two-layer composites were prepared: C/PET/epoxy, C/PET$_{\mathrm{amin}}$/epoxy, C/C/epoxy. The specimens were prepared by a wet layup technique, using the bifunctional epoxy resin as a matrix (50%), phthalic anhydride (50%) as a curing agent, and dimethylaniline (2%) as an accelerator. Carbon roving (used as-received) and PET fibres, supplied by "Hemtex" Macedonia, were used as reinforcements in hybrid composites.

Fibre layers were preimpregnated in the epoxy resin mixture, stacked up in the mould and then pressed, precured at 80 °C for 1 h and cured at 120 °C for 2 h in the oven. Samples were then allowed to cool to room temperature before removal from the oven and each sample was then machined into specimens to be used for characterization.

2.2. Amination of PET fibres

In order to modify the surface, PET fibres were treated with polyfunctional amine, thriethylenetetramine (TETTA) as described elsewhere [7]. Mechanical properties of PET fibres were determined on an Instron Tensile Machine, density measurements were made using a mixture of two liquids with different composition, until the sample remained suspended in the mixed liquids, and amine groups were determined by acid dye staining with Nylosan blue 26 FL at 100 °C, 30 min [8].

2.3. Contact angle measurements

The contact angle measurements were performed on a single fibre with epoxy resin at 20 °C on an optical polarizing microscope.

2.4. Scanning electron microscopy (SEM) analysis

The changes on the surface of the fibres and the state of the interface in the composites were observed using a Philips 501 scanning electron microscope (vacuum Au/Pd alloy deposition of the samples in a Polaron Sputtering apparatus was performed previously).

2.5. Thermal analysis

Thermal characterization of the fibres and composites was performed by differential scanning calorimetry (DSC) carried out with a Mettler TA-3000 apparatus equipped with a control and programming unit (microprocesor TC-11) and a calorimetric cell, under a nitrogen atmosphere, in the range 30–270 °C. The crystallinity content of PET was calculated from the relation $X_c = \Delta H^*/\Delta H$, where ΔH^* is the apparent enthalpy of melting per gram of 100% crystallized PET, equal to 115 J g^{-1} and ΔH is the heat of melting of the test sample. In order to determine the glass transition temperature, a second run was performed after a rapid cooling of the sample (heating rate 5 °C min^{-1}).

TG analyses were performed using a Mettler M3 (TG50) connected with TA processor Mettler TG 10A, under nitrogen, in a temperature range of 40–500 °C and a heating rate of 20 °C min^{-1}.

2.6. Impact tests

Charpy impact tests were performed with a pendulum (Ceast Autographic Pendulum MK2) instrument. The specimens were notched at their mid-length as follows: first a blunt notch was made with a shaped machine tool and then a sharp notch, 0.2 mm deep, was produced using a razor blade fixed on a micrometric apparatus. The Charpy tests were carried out at room temperature.

The hardness of the composite specimens (10 mm × 15 mm × 3 mm) was studied using a hardness tester (O.M.A.G.-Breveti 150 MPL-2) with applied load of 961 N mm^{-2}.

The impact toughness of the composites was determined with a Frank apparatus applying a force of 1 J. Composite specimens with the same dimensions as for the hardness determination were used.

3. Results and discussion

3.1. Characterization of PET fibres

To achieve adequate interfacial adhesion on PET fibres to be used as reinforcing elements in composites, appropriate treatment must be followed [8]. The introduction of new functional groups by means of chemical modification reactions is one possible way for altering the physical and chemical nature of the fibre. In our work, amine groups in the PET fibres were introduced by reaction with TETTA. Reaction of TETTA with an ester group of PET leads to chain scission at the reaction site and to amide formation [8, 9] (see Fig. 1).

The amination reaction was carried out at 55 °C for 20 min. Short heat setting of PET fibres (annealing) at 170 °C had been previously performed to confine the amination treatment to the surface [7]. The presence of amine groups is expected to increase wettability and also provide potential sites for the covalent chemical bonding with polymer matrix in the composite [8, 9]. Amine groups introduced by TETTA treatment were revealed by acid-dye staining and multiple internal reflection infrared spectroscopy; the results are presented in Fig. 2 and Table I. The data clearly indicate the presence of amine groups on the fibre surface. In fact, after amination of the heat-set fibres no significant changes in the mechanical properties were found (Table I).

Scanning electron micrographs of untreated and treated fibres are shown in Fig. 3. Untreated fibres show a characteristic smooth surface, while significant etching effects are present on PET-aminated fibres (small circular-shaped pits could probably serve as nucleation centres for crack formation), probably due to the aggressive action of monofunctional amines present in TETTA [10].

The roughness of the PET fibre surface is expected to influence the physical bonding of the fibres with the epoxy matrix in the hybrid composite as well.

It is well known that fibre wetting by liquid resin is a key factor influencing the interphase state and also the bulk composite properties. The results of contact angle measurements are shown in Table II. The

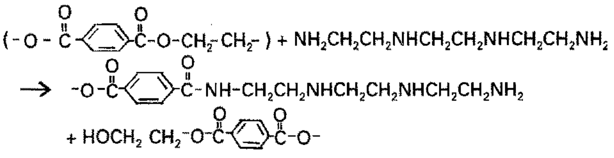

Figure 1 Reaction mechanism of TETTA with PET fibres.

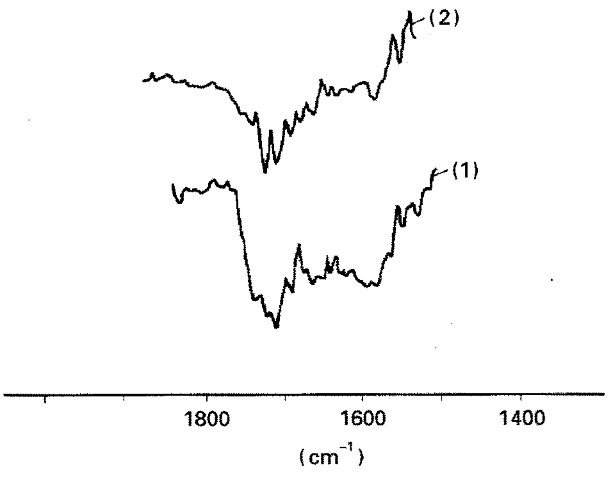

Figure 2 IR–MIR spectra of PET untreated (1) and treated (2) fibres.

TABLE I Basic properties of the PET fibres treated with TETTA

Fibre	T^a (dtex)	F^b (cN/tex)	I^c (%)	ρ^d (g cm^{-3})	x_c^e	[NH_2] (mg/g fibre)
Control	3.37	42.7	50.7	1.380	0.42	–
PET-amin (55 °C, 20 min)	3.59	39.9	48.7	1.381	0.43	0.036

[a] T Linear density.
[b] F Tenacity break.
[c] I Extension break.
[d] ρ Density.
[e] X_c Crystallinity index, determined by X-ray diffraction.

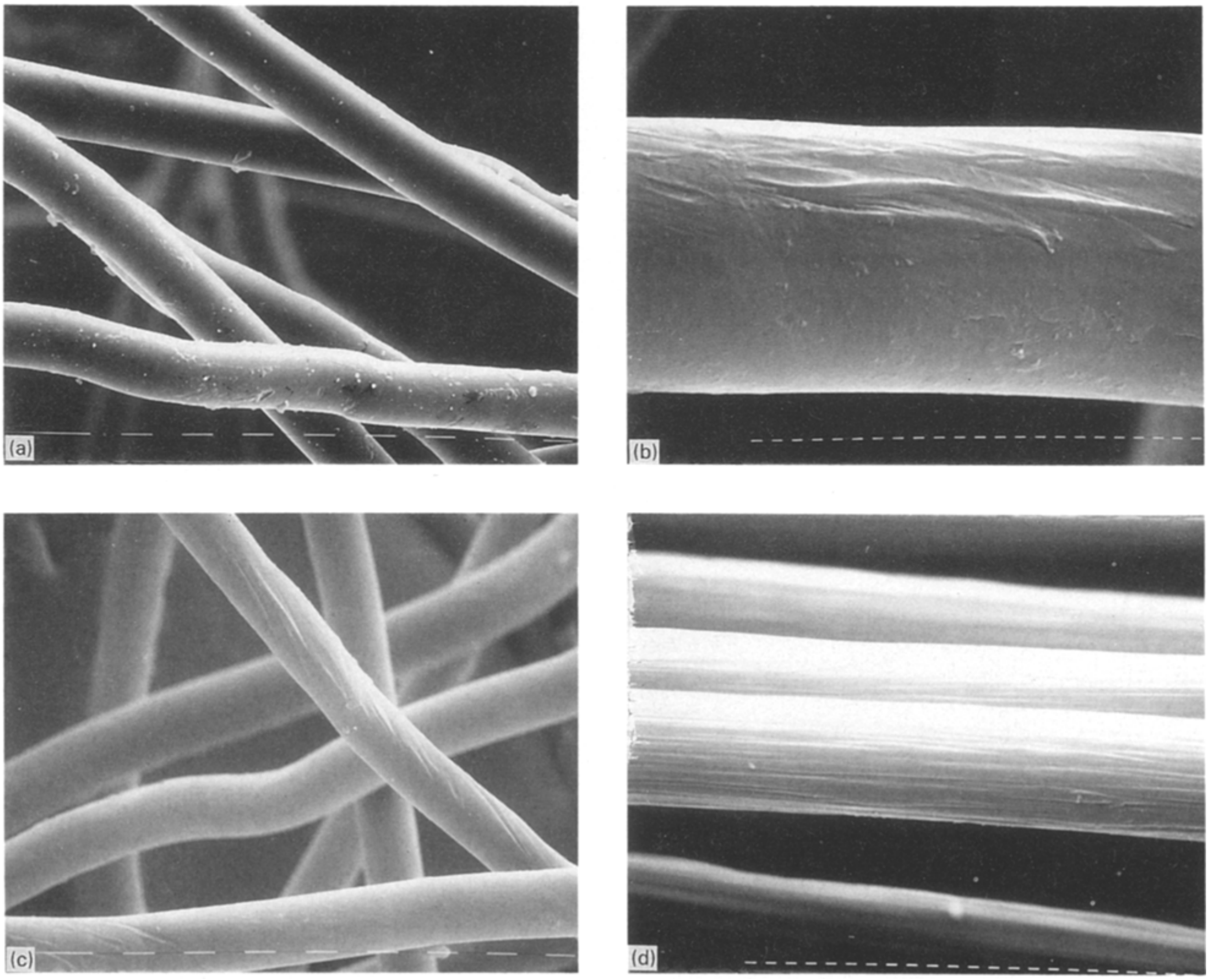

Figure 3 Scanning electron micrograph of the PET fibres: untreated, × 640; (b, c) treated (b) × 2500, (c) × 640, (d) carbon fibre (× 2500).

TABLE II Contact angles of PET and carbon fibres wetted with epoxy resin

Fibre	θ (deg)
PET/control	37.0
PET/aminated	30.0
Carbon	51.9

increasing in wettability of aminated PET fibres could be caused by the presence of the polar NH_2-groups on the fibre surface and partly related to the roughening effect.

Thermal analysis data of PET fibres are presented in Figs 4 and 5 and Table III. The depression of the glass transition temperature, T_g, is very obvious for PET-aminated fibres. There is no significant difference in other parameters. x_c also decreases from the first to the third run for all fibres, probably due to the melting of the small crystals. As confirmed by TG analysis, thermal stability of PET fibres remains unchanged after the amination.

3.2. Composites characterization

Scanning electron micrographs of hybrid C/PET/epoxy fractured specimen composites containing untreated and aminated PET fibres are shown in Fig. 6. A smooth, clean fibre surface (without resin) and empty holes left in the epoxy matrix after fracture (Fig. 6a) are observed in the composites containing untreated PET fibres, as a result of poor fibre/matrix adhesion. Polymer adhering to the fibre surface and broken fibres in the holes after fracture are noticed in composites containing PET aminated fibres (Fig. 6b), indicating the higher degree of polymer matrix/fibre adhesion.

The increase in T_g found in hybrid composites with PET-aminated fibres is probably a result of a stronger interaction between the fibres and epoxy matrix [11]. Because amine and amide groups from the fibre surface can interact with epoxy end groups of the resin, forming covalent bonds, they can act as coupling agents between the fibre and the matrix, or have a catalytic effect on the curing reaction, especially in the vicinity of the fibre surface. In fact, a higher degree of cross-linking of the epoxy resin in the composites containing PET-aminated fibres is established on the basis of DSC data (see Fig. 7: there is no thermal heat residue).

The composite specimens were exposed to hygrothermal treatment (6 h at 80 °C in distilled water) and subsequently analysed by DSC, in order to examine the adhesive bonding in the composites, which can be weakened or destroyed by environmental factors [12]. The results are represented in Table IV. The degree of swelling of the composites is within the range of the swelling of neat epoxy resin. Obviously, the absorbed water plasticizes the resin thus lowering its T_g (from 161 °C to 138.6 °C) and weakening the interfacial interactions. This effect is seen only for C/PET$_{amin}$ composite; all the others show no difference.

The mechanical properties of the composites obtained from the fracture tests are shown in Table V. The fracture parameters, the critical strain energy

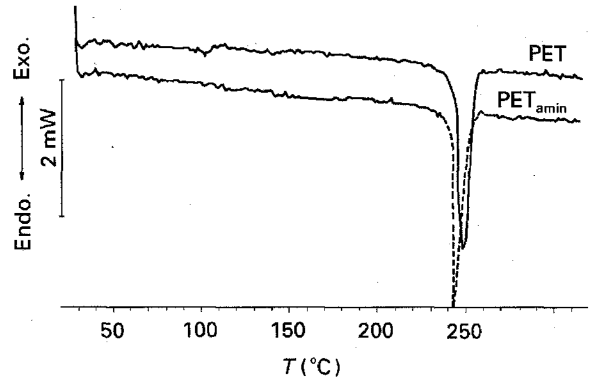

Figure 4 DSC thermograms of PET untreated and treated fibres (Run I).

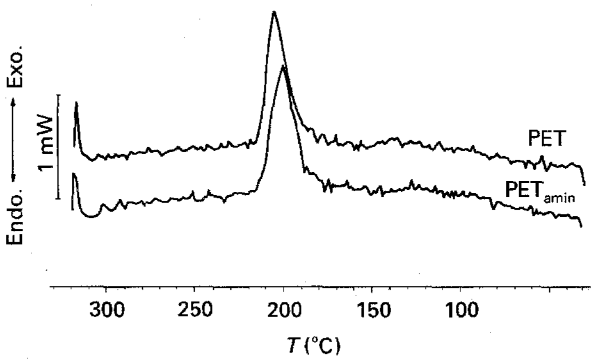

Figure 5 DSC thermograms of PET untreated and treated fibres (Run II).

TABLE III DSC data for PET fibres

Run	Parameter	PET$_{control}$	PET$_{amin}$
I	ΔH_m (J g^{-1})	50.6	52.4
	T_m (°C)	248.3	248.3
	X_c (%)	44.0	45.5
II	ΔH_c (J g^{-1})	44.1	39.2
	T_c (°C)	207.0	201.5
	X_c (%)	38.3	34.5
III	ΔH_m (J g^{-1})	38.1	37.4
	T_m (°C)	251.4	251.5
	X_c (%)	33.1	32.5
	T_g (°C)	80.0 (90)^a	62.0 (82)^a
	T_d (°C)	411.4	410.8

^{a} Determined by the acid-dye method.

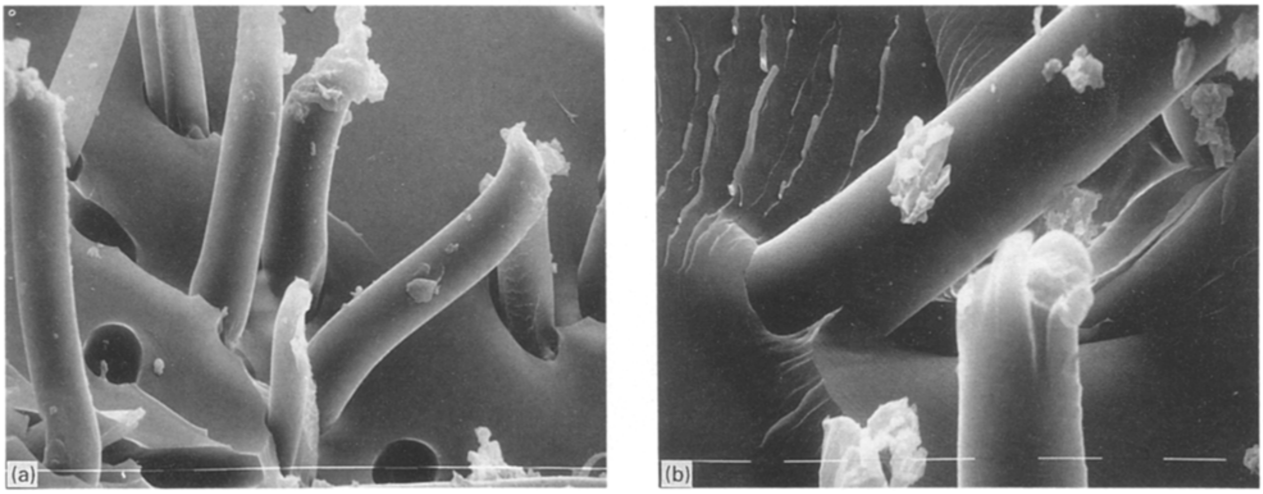

Figure 6 Scanning electron micrographs of hybrid C/PET/epoxy composites: (a) composites with PET fibres without surface treatment, × 1250; (b) composites with aminated PET fibres, × 640.

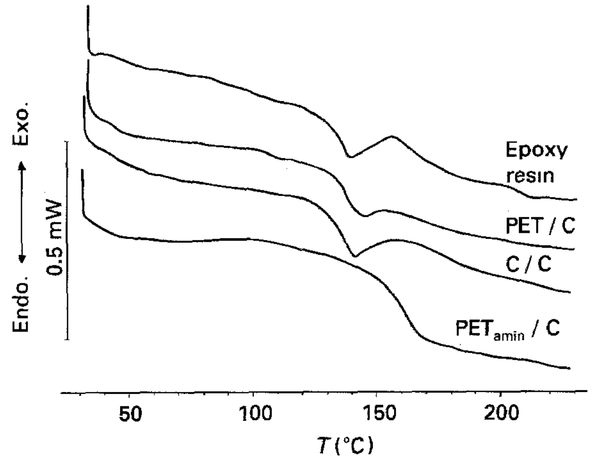

Figure 7 DSC thermograms for the composites.

TABLE IV Thermal data and degree of swelling for the composites before and after hygrothermal treatment

Composites	T_g (°C)		Swelling (%)
	Before	After	
Epoxy	130	132	1.04
C/C/epoxy	135	136.2	0.05
PET/C/epoxy	133	136.0	1.28
PET$_{amin}$/C/epoxy	161	138.6	1.50

TABLE V Critical strain energy release rate, G_c, and critical strain intensity factor, K_c, calculated from the fracture test data of two-layer composites

Composite	F_{max} (N)	G_c (kJ m^{-2})	K_c (MN m$^{-3/2}$)
Epoxy	26.5	0.15	0.009
C/C/epoxy	109.2	6.12	0.180
C/PET/epoxy	66.3	2.99	0.099
C/PET$_{amin}$/epoxy	92.0	4.15	0.140

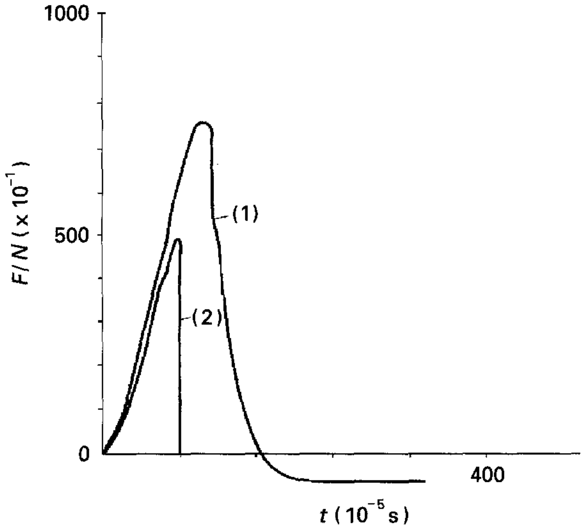

Figure 8 Typical load–time response curve determined by fracture tests for hybrid composites, containing (1) aminated and (2) untreated PET fibres.

TABLE VI Experimental results for the hardness and impact toughness of two-layer C/PET/epoxy composites

Composite	Hardness (N mm^{-2})		Impact toughness, σ (kJ m^{-2})	
	C[a]	PET[b]	C[a]	PET[b]
C/PET/epoxy	259	245	13.6	4.3
C/PET$_{amin}$/epoxy	278	228	12.9	6.7

[a] Carbon fibre facesheet.
[b] PET fibre facesheet.

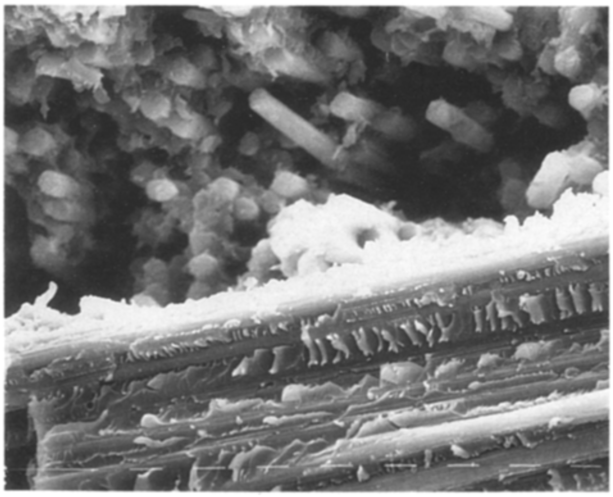

Figure 9 Typical mode of fracture of the C/PET/epoxy composite, (×640).

release rate, G_c, and the critical stress intensity factor, K_c, were calculated according to the linear elastic fracture mechanics (LEFM) theory [13]. As the C/PET fibre ratio in all the examined composites was equal, the differences in G_c and K_c must be caused by the different interphase zone, created when aminated PET fibres are used in the composites instead of untreated fibres. In the PET-aminated fibres, a significant hybrid effect is obviously reached: as can be seen, both G_c and K_c increased (96% and 93%, respectively).

The fracture mode in C/PET$_{amin}$/epoxy composites is quite different compared to the C/PET/epoxy system (Fig. 8), which could be attributed to higher interfacial bonding of the PET$_{amin}$ fibre/matrix system.

Experimental data for the hardness and impact toughness of the composites are presented in Table VI. The effect of the aminated surface of PET fibres is also confirmed by hardness and impact toughness measurements, especially by the impact toughness of the hybrid C/PET$_{amin}$ composite when the PET layer is facing the impactor. The higher value for the impact toughness of the C/PET$_{amin}$ composite is probably a result of the higher impact energy absorption of aminated PET fibres. This result indicates that PET fibres can be used effectively to improve the impact resistance of C/epoxy composites.

SEM fractographs show that there is no any significant difference in the fracture between the composites with untreated and treated PET fibres. The typical mode of fracture of the composites is shown in Fig. 9.

4. Conclusions

A comprehensive experimental study was conducted to establish the surface structure–property relationship between fibre and matrix in hybrid C/PET/epoxy composites. Hybrid C/PET/epoxy composites were prepared using aminated PET in order to improve the fibre/matrix adhesion in the composites.

Surface modification of PET fibres by reaction of aminolysis is confirmed by the decrease in the contact angles with the epoxy matrix, and the etching effects of the surface, as found using SEM.

Hybrid C/PET/epoxy composites were characterized by SEM, DSC, fracture and impact toughness measurements. Adhesion in the hybrid composites was increased as a result of NH_2 groups on the surface of the PET fibres. They showed a positive hybrid effect which increased the T_g of the composites and eliminated the thermal residues in the composites.

Improvement of the adhesion was also confirmed by fracture and impact toughness measurements. In the case of PET-aminated fibres, a significant hybrid effect is produced: both fracture parameters, G_c and K_c, increased, as also was the impact toughness when the PET layer is facing the impactor.

These results suggests that PET fibres can be used to improve the impact resistance of C/epoxy composites.

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