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Some properties of a condensed polynuclear aromatic resin (COPNA) as a binder for carbon fibre composites

S. ŌTANI*, V. RASKOVIC, A. ŌYA
Faculty of Engineering, Gunma University, Kiryu, Gunma 376, Japan
A. KOJIMA
Gunma Technical College, Maebashi, Gunma 371, Japan

A new thermosetting resin consisting of condensed aromatic nuclei cross-linked with methylene bridges was prepared from a mixture of pyrene, phenanthrene and 1,4-benzene-dimethanol by heating above 393 K. This resin, named COPNA, adheres well to carbon fibres, and the carbon fibre/resin composite (CFRP) prepared by using this resin as a binder exhibits no remarkable changes in mechanical properties after heating at 523 K for 10 h and 573 K for 2 h. The CFRP specimens were converted into carbon fibre/carbon composite (CFRC) by further heating up to 1273 K without any trouble.

1. Introduction

A condensed polynuclear aromatic resin referred to as COPNA has been prepared [1] from condensed aromatic compounds (Aro) or their mixtures and 1,4-benzenedimethanol through the electrophilic substitution reaction

$$n\text{Aro} + n\text{HOCH}_2\text{phCH}_2\text{O} \xrightarrow{\text{H}^+} (\text{-Aro-CH}_2\text{phCH}_2\text{-}) + n\text{H}_2\text{O} \qquad (1)$$

where ph = phenol. This is a thermally stable thermosetting resin, of which the formation mechanism and some properties have been reported elsewhere [1]. The most characteristic features of COPNA resin are that it consists of condensed aromatic nuclei cross-linked with methylene bridges, and has outstandingly high thermal stability.

The present work was undertaken to evaluate preliminarily whether or not COPNA resin is suitable as a binder for carbon fibre/resin composite (CFRP) or the carbon fibre/carbon composite (CFRC).

2. Experimental details

2.1. Preparation of COPNA resin

COPNA resin is prepared from 1,4-benezenedimethanol and various condensed aromatic compounds, e.g. anthracene, pyrene, phenanthrene or their mixtures, the pitch materials. In the present work, a mixture of pyrene and phenanthrene (7/3 in molar ratio) was used as raw material (Table I). 1,4-benzenedimethanol was first added to this mixture by 1.25 times in molar ratio, followed by further addition of *para*-toluene sulphuric acid as an acid catalyst by 5 wt % to the resultant mixture. The mixture thus prepared was well pulverized. It began to soften at 367 K, to react through Reaction 1 at 397 K, and was cured completely after holding at 473 K for 1 h. As is well known, a fusible resin, a B-stage resin, is generally suitable as a binder for composite materials. When using the raw material compositions shown in Table I, such a B-stage COPNA resin was prepared by heating at 397 K for 65 min in a flow of argon (25 ml min^{-1}) with stirring.

2.2. Preparation of carbon fibre/COPNA resin composites

Three types of composite were prepared from COPNA resin and carbon fibre (CF): undirectional thin rod (UD rod) specimen, and two laminate plate specimens (CLP and PLP) using carbon fibre cloth or carbon fibre paper, respectively. Some properties of the carbon fibres used are summarized in Table II.

In the preparation of the PLP specimen, CF paper (50 × 50 mm) sprinkled with fine COPNA resin powder was superposed by another CF paper, followed by homogeneous sprinkling of fine COPNA resin powder. This process was repeated to result in a laminate with 35 pieces of CF paper, in which the weight ratio of CF paper to resin was 25/75. This laminate plate was hot-pressed to become 2 mm in thickness by using a spacer under the conditions shown in Fig. 1. Here the resin was somewhat leaked out from the moulding apparatus.

In the cases of the UD rod and CLP specimens, on the other hand, the softened resin at 363 K was carefully adhered to the CF tow (6000 filaments) and CF cloth to make the prepregs, followed by hot-pressing as stated above. The UD rod was pressed laterally under stretching according to the conditions shown in Fig. 1. The weight ratio of CF to resin of this specimen was 35/65. After hot-pressing, the specimens were cured at 473 K for 1 h in air. The sizes of the resultant

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*To whom all correspondence should be addressed.

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TABLE I Molar ratios of raw materials for B-stage COPNA resin*

Aromatics		Coupling reagent	Catalyst
Pyrene	Phenanthrene	(1,4-benzenedimethanol)	(*p*-toluene sulphuric acid)
7	3	12.5	5 wt %

*Preparation conditions: 65 min at 393 K in argon (25 ml min^{-1}).

UD rod and CLP specimen were 20 mm × 2 mm diameter and 50 mm × 50 mm × 2 mm, respectively.

2.3. Measurements of properties

2.3.1. Mechanical properties

Test pieces 10 mm × 50 mm × 2 mm were cut out from both the PLP and CLP specimens to serve for measurements of mechanical properties, using a Toyo Sokki universal tension tester UTM4L. From the stress–deflection curve under a cross-head speed of 4 mm min^{-1}, the three-point flexural strength for a span of 40 mm, and length/depth (l/d) of 20 was determined. Interlaminar shear strength (ILSS) was determined for 10 mm span and $l/d = 5$. A UD rod of 50 mm length was used for these mechanical property measurements under the same conditions.

2.3.2. Thermal stability

Test pieces with sizes stated above were maintained at a prefixed temperature between 523 and 673 K for 0.5 to 10 h in air, followed by measurements of mechanical properties at room temperature.

2.3.3. Chemical resistivity

By using test pieces with the same sizes as those described, weight change was measured after soaking in strong acids and bases as shown in Table III, for 1 to 65 h at room temperature.

2.4. Preparation of carbon fibre/carbon composites

Test pieces prepared as in Section 2.2 were heat-treated to 1273 K in an argon atmosphere to convert into CFRC composites. No impregnation was applied because the main purpose was just to examine the adhesion state between the CF and the matrix carbon. Measurements of the mechanical properties were carried out according to the methods used for the CFRP specimens.

3. Results

3.1. Properties of B-stage COPNA resin

COPNA resin at the B-stage was a yellowish hard solid at room temperature which softened at 348 K, became fluid around 373 K and cured rapidly above 393 K. Since this B-stage resin is in the course of Reaction 1, it contains some amount of oxygen. A typical element composition (wt %) was C: 88.4, H: 5.5 and O, S (difference): 6.1.

TABLE II Carbon fibre materials used for composites

Filament yarn	Carbolon Z-3 (6000 filaments) (Asahi-Nihon Carbon Co.)	σ: 300 kgf mm^{-2} (2.94 GPa) E: 23 000 kgf mm^{-2} (225 GPa)
Cloth	Torayca Cloth T200 (No. 6141) (Toray)	Weight: 210 g m^{-2} Thickness: 0.25 mm
Paper	Carbon Paper SH-35-Z (Asahi-Nihon Carbon Co.)	Weight: 33 g m^{-2} Thickness; 0.3 mm

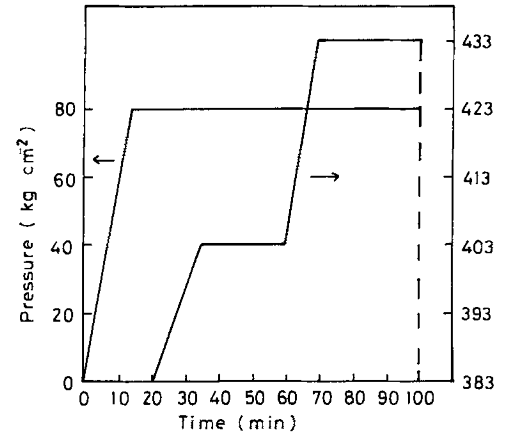

Figure 1 Pressing and heating programmes for moulding.

3.2. Properties of carbon fibre/COPNA resin composites

3.2.1. Mechanical properties

Table IV shows the mechanical and other properties. The porosity and weight ratio of the CF/resin were calculated from the weight and density of CF used, the weight and bulk density of the resultant specimen and the density of the COPNA resin (1190 kg m^{-3}). ILSS and other mechanical properties with standard deviations are the averages of 20 and 10 measurements, respectively. A point to note here is the large porosity of the PLP specimen. Since the flexural strength and the modulus of the pure COPNA rod are 80 MPa and 2.5 GPa [1] and the tensile strength of this CF is 300 kgf mm^{-2} (2942 MPa), the flexural strength, 130 MPa, of the UD rod containing 60 vol % of fibre is somewhat smaller than that calculated from the Rule of Mixtures. The two-dimensional composite CLP specimen exhibited a flexural strength half that of the UD rod and three times that of the PLP specimen. ILSS for the UD rod was almost equal to that of conventional CFRPs using epoxy resin as a matrix [2, 3]. Of course, the standard deviations for the present specimens are larger than that for the commercially available product prepared under well-controlled conditions.

TABLE III Chemical stabilities of carbon paper/COPNA resin composite (at room temperature)

Reagent	Concentration (%)	Time (h)	Weight change (%)
H_2SO_4	96	1	98.97
		65	106.19
HCl	37	1	98.77
		65	101.48
HNO_3	61	1	99.91
		65	107.44
KOH	30	1	98.32
		65	101.68
NaOH	30	1	98.16
		65	101.40
H_2O_2	30	1	101.87
		65	98.36

TABLE IV Properties of carbon fibre/COPNA resin composites*

Specimen	ϱ (kg m^{-3})	v (%)	V_f (%)	V_r (%)	V_p (%)	ILSS (MPa)	v (%)	σ (MPa)	v (%)	E (GPa)	v (%)	Remarks on CF
UD rod	1440	3.7	57.2	37.6	5.2	76.60	10.8	1354	5.1	78.48	3.0	UD filaments
CLP	1460	4.1	60.8	36.2	3.0	36.45	13.0	669	11.7	50.46	8.6	Cloth
PLP	1010	5.2	28.4	43.7	27.9	20.89	10.3	237	6.9	21.44	10.0	Paper

*v: standard deviation; V_f, V_r, V_p: volume of fibre, resin and pore; ILSS: interlaminar shear strength; σ: flexural strength; E: flexural modulus.

Fig. 2 shows SEM photographs of the fractured surface of the UD rod. The fibre adheres so well to the matrix resin that pull-out fibres were scarcely observed. Even when they were, the length of the fibre pulled out was usually less than 10 μm.

3.2.2. Changes in mechanical properties after heating in air

Figs. 3 to 6 show the changes of weight, flexural strength, flexural modulus and ILSS of PLP specimens after heating in air. As can be seen from Fig. 3, the weight increased by about 2% after heating at 573 K for 10 h but decreased by several per cent at 623 K, and fell remarkably at 673 K. The flexural strength shown in Fig. 4 decreased by 2 and 17% after heating for 10 h at 523 K and 573 K, respectively. Even after heating at 623 K for shorter than 2 h, the decrease in the flexural strength never exceeded 10%. No remarkably change was observed in the flexural modulus at temperatures lower than 573 K (Fig. 5). Such a trend was also observed in ILSS, as shown in Fig. 6. On the basis of these results, the maximum thermal resistance temperatures of this resin are concluded to be 523 K and 573 K for heating periods of 10 and 2 h, respectively.

3.2.3. Chemical resistivity

As can be seen from Table III, there were no weight changes except for small increases in the cases of H_2SO_4 and HNO_3 after 65 h soaking.

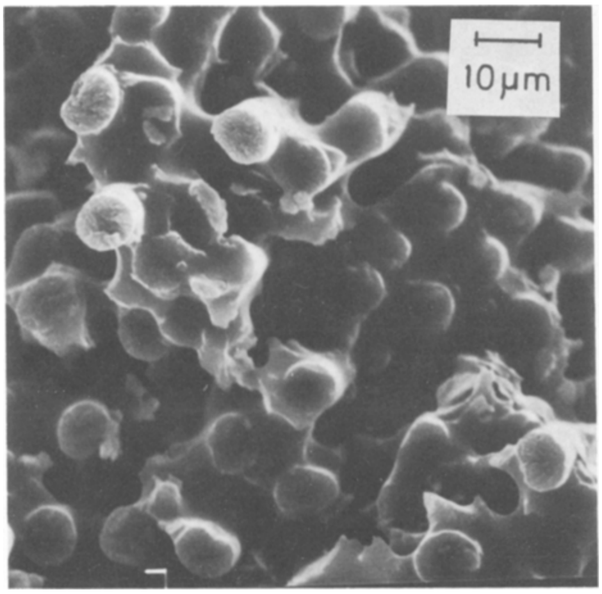

Figure 2 SEM photograph of the fractured surfaces of UD CFRP rod.

3.3. Properties of carbon fibre/carbon composites

3.3.1. Mechanical properties

Two heating programmes shown in Table V were used for the carbonization of carbon fibre/COPNA resin composites, but no influence of the programme was observed in the mechanical properties of the resultant CFRC composites for UD rod and PLP specimens. The diameter of the UD rod shrank from 2.0 to 1.8 mm after carbonization, which means that this CFRC composite contains 70 vol % (V_f) of CF. The thicknesses of the CLP and PLP specimens decreased by 10 and 15%, respectively, after carbonization.

The UD rod after carbonization, without impregnation, was characterized by a large density in addition to a high flexural modulus. Both CLP and PLP specimens exhibited almost equal values to those of conventional CFRC composites, using phenolic resin as the matrix and prepared according to methods similar to that used here. The flexural modulus of the carbonized UD rod was roughly equal to that calculated on the Rule of Mixtures.

3.3.2. SEM photographs

Some typical appearances of the fractured surfaces of CFRC specimens are shown in Fig. 7. In the carbonized UD rod shown in Fig. 7a, some voids, possibly resulting from insufficient impregnation of the resin, can be seen among the CF filaments, but the fibre seems to adhere to the matrix carbon quite well in view of there being no occurrence of fissures or cleavages between the two components. This good adhesion state can be also observed in Figs 7b and c, for example; the adhesion state in the CF bundle is analogous to that of the UD rod in Fig. 7a, and cleavage

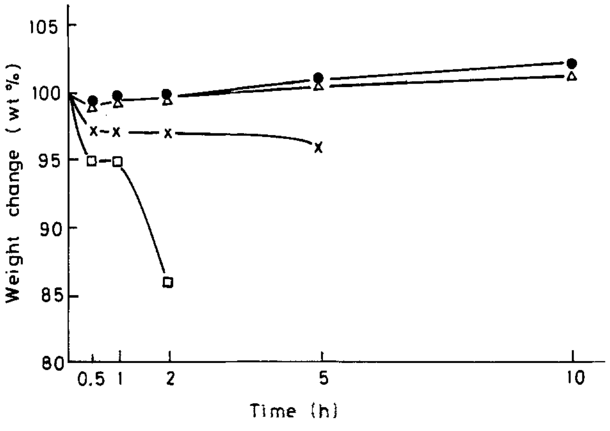

Figure 3 Weight changes of PLP specimens after maintaining at various temperatures in air. (●) 523 K, (△) 573 K, (x) 623 K, (□) 673 K.

TABLE V Properties of CFRC composites without densification treatment

	Heating rate*	ϱ (kg m^{-3})	v (%)	ILSS (MPa)	v (%)	σ (MPa)	v (%)	E (GPa)	v (%)	Yield (wt %)	V_f
UD	Slow	1360	2.6	15.54	3.8	254.5	6.7	178.20	6.5	72.3	57.2
rod	Fast	1360	1.5	16.85	4.4	246.7	6.1	159.60	4.4	71.9	57.2
CLP	Fast	1260	3.3	3.67	11.1	39.6	12.0	40.46	9.0	84.8	60.8
PLP	Slow	660	4.5	3.31	15.2	38.1	17.2	17.03	18.2	72.2	28.4
	Fast	660	4.7	3.50	11.5	40.0	16.5	17.24	13.1	72.8	28.4

*Fast: 293 to 573 K 300 K h^{-1}, 573 to 973 K 30 K h^{-1}, 1273 K 1 h. Slow: 293 to 573 K 300 K h^{-1}, 573 to 1273 K 10 K h^{-1}, 1273 K 1 h.

between the filament and the matrix carbon did not occur. The filaments in the PLP specimen orient so randomly with each other that a twisting shear stress is applied to the filaments, leading to cleavage between the filament and the matrix (arrowed). Such cleavage was, however, rarely observed.

4. Discussion

The matrix resin for CFRP should be evaluated from the following viewpoints in addition to thermal stability: (i) mechanical properties, (ii) adhesiveness with CF, (iii) mouldability, especially the possibility of preparing the prepreg, (iv) gas evolution during the moulding process and (v) the cost. COPNA resin is evaluated from such viewpoints below.

The degradation of mechanical properties by heating in air were examined in a holding period shorter than 10 h, which is not enough for such an evaluation. However, there was no noticeable degradation after heating at 523 K in air. Even after heating at 573 K for 5 h, furthermore, about 90% of the original values were maintained. These results suggest that COPNA resin is worth examining for its thermal stability over a longer period.

The specimens in this work were prepared without special care but exhibited considerably enhanced mechanical properties as shown in Table IV: in other words, CFRP using COPNA resin is on almost the same level as CFRP using an epoxy resin. The adhesive strength between the filament and resin can also be evaluated by the filament length pulled out from the matrix at a fractured surface. The following two phenomena suggest a favourable adhesion state between CF and COPNA resin, namely (i) the average CF length pulled out was of the order of 10 μm and (ii) no fissure or cleavage occurred between the CF and the matrix after carbonization, as can be seen from Fig. 7.

The B-stage COPNA resin fused completely at about 373 K and polycondensed quickly above 393 K. It is therefore possible to prepare the prepreg from CF and COPNA resin fused at 373 K. It is also possible to use the leaky mould method for a prepreg of CF cloth, or paper sprinkled with fine COPNA resin powder. When the preparation conditions shown in Fig. 1 are used, on the other hand, it takes 3 h for the specimen preparation, namely 2 h for the moulding and 1 h for the post-curing. The preparation time was not studied in detail in this work so that it may be shortened in future.

The next problem to be discussed here is how to suppress gas evolution during the moulding process. Since COPNA resin is formed according to Reaction 1 it is of course impossible to suppress gas evolution completely. As described in the previous paper [1], however, the reaction

$$n\mathrm{HOCH_2phCH_2OH} \xrightarrow{\mathrm{H^+}} \mathrm{HO(-CH_2phCH_2O-)_nH} + 2(n-1)\mathrm{H_2O} \quad (2)$$

also occurs simultaneously with the initial reaction process to result in a polyether. This polyether can supply cations in the presence of protons according to the reaction

$$\mathrm{HO(-CH_2phCH_2O-)_nH} \xrightarrow{\mathrm{H^+}} \mathrm{HO(-CH_2phCH_2O-)_{n-1}H} + {}^{+}\mathrm{CH_2phCH_2OH} \quad (3)$$

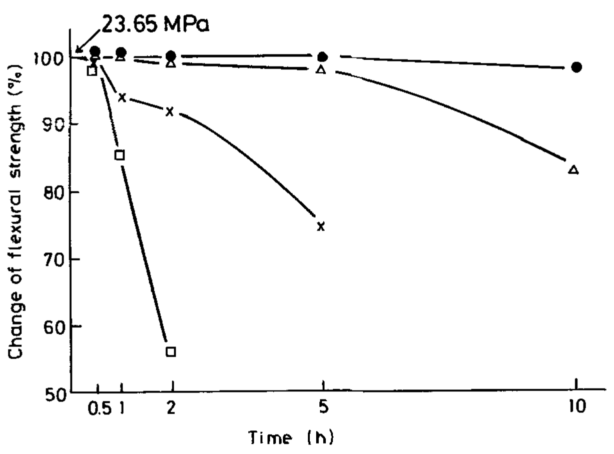

Figure 4 Changes of flexural strength of PLP specimens after maintaining at various temperatures in air. (●) 523 K, (△) 573 K, (x) 623 K, (□) 673 K.

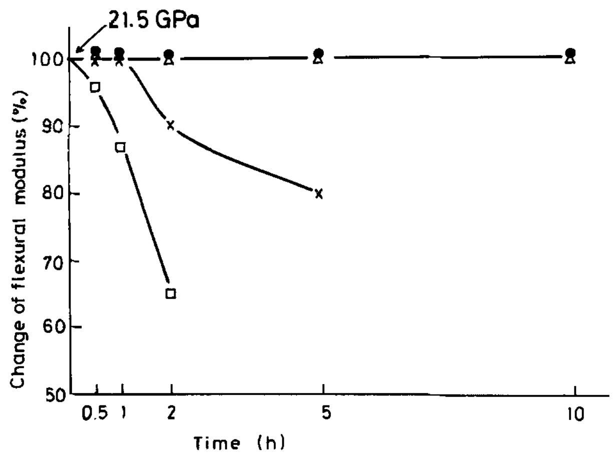

Figure 5 Changes of flexural modulus of PLP specimens after maintaining at various temperatures in air. (●) 523 K, (△) 573 K, (x) 623 K, (□) 673 K.

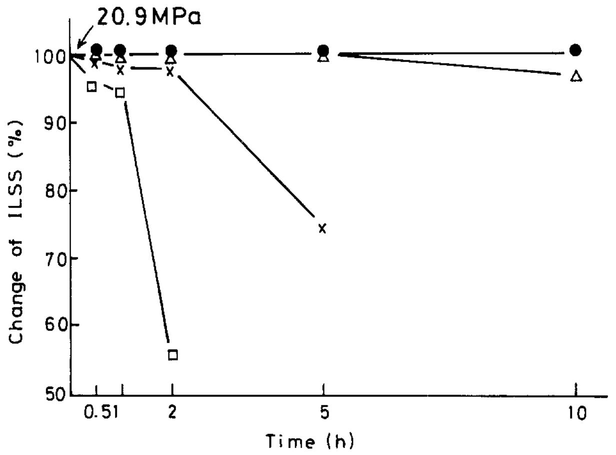

Figure 6 Changes of ILSS of PLP specimens after maintaining at various temperatures in air. (●) 523 K, (△) 573 K, (x) 623 K, (□) 673 K.

which is the reverse reaction of Reaction 2. The resultant cation is the same as that formed from 1,4-benzenedimethanol directly. During the first 40 min in the preparation of B-stage COPNA resin, bubbles were liberated violently by dehydration according to Reactions 1 and 2, but such gas liberation soon stopped to result in a viscous resin. The cross-linking reaction at the subsequent stage is thought to be proceeded by the cation supplied from the polyether according to Reaction 3. When B-stage resin reacted as highly as possible is used, therefore, the evolution of gas must be considerably suppressed.

All the chemicals used here are commercially available, but except for *para*-toluene sulphuric acid they are considerably expensive because they are not of extensive practical use. One way to solve this problem is to use other condensed aromatics such as naphthalene or coal-tar pitch instead of pure aromatic compounds [4]. Fortunately, methods of separating tricyclic or tetracyclic aromatic compounds from coal-tar pitch are now being investigated in the steel industry [5], and such compounds are also included in the heavy fractions of petroleum. Only the problem of 1,4-benzenedimethanol remains to be solved. Since the preparation procedure of the COPNA resin is quite easy, it may become less expensive.

As a result, it was concluded from the discussion above that COPNA resin is worth studying further as a binder for a heat-resistant composite material with carbon fibre or glass fibre, and for carbon fibre/carbon composites.

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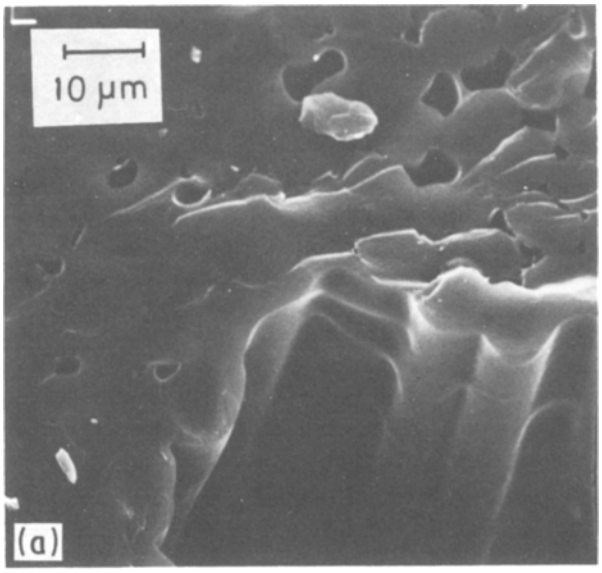
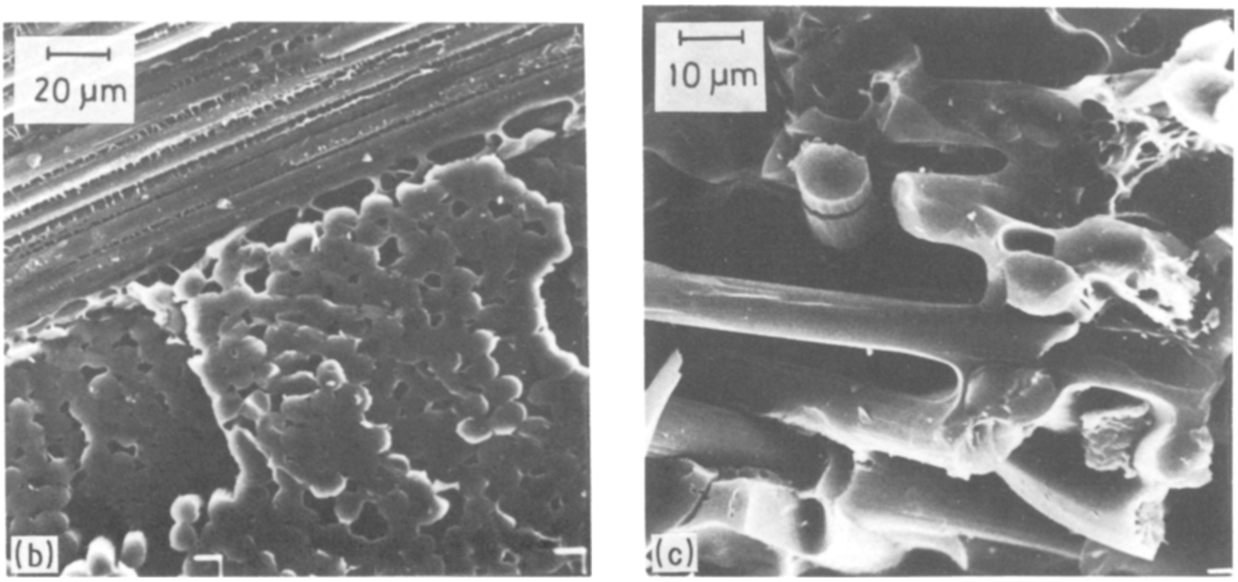


Figure 7 SEM photographs of the fractured surfaces of CFRC specimens: (a) UD, (b) CLP, (c) PLP.



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