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THE EFFECT OF REPROCESSING ON THE EMI SHIELDING EFFECTIVENESS OF CONDUCTIVE FIBRE REINFORCED ABS COMPOSITES

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Abstract—In this investigation, the acrylonitrile–butadiene–styrene copolymer (ABS) was used as the matrix. Ni-coated conductive carbon fibre (NCF) and conductive carbon fibre (CF) were used as the conductive fillers. For processing, a Twin-Screw Extruder (TSE) and the Brabender Plasti-Corder were used here for compounding composites. The fibre length of composites which were compounded by the twin screw extruder were below the critical length, 200 μm. Thus, the tensile strength and modulus were not increased by adding fibres. At the same time, the conductive fibre cannot form a conductive network. In this case, the shielding effectiveness (SE) value of composites was 0 decibel (dB). But, when the composites were compounded by the Brabender, the fibre length was above critical length, 200 μm, even after three processings. The maximum SE value of conductive composites was 47 dB. The SE values of composites decreased with increasing the number of processing cycles. The viscosity of composites decreased with increasing the number of processing cycles. In addition to the polymer chain being scissored, the short fibre length was another reason. SEM shows that the interfacial adhesion between NCF and ABS was not so good. The interfacial adhesion between ABS and CF was better than that of between ABS and NCF. © 1997 Elsevier Science Ltd

INTRODUCTION

Conductive plastic products are used to provide electrostatic discharge (ESD) and electromagnetic interference-radiofrequency interference (EMI/RFI) shielding [1]. There are primarily three methods to make conductive composites, including metallic plated and electroless deposited coatings on the inside of the housing [2]. These techniques have the drawback of being time consuming, labour intensive and costly. The second method is to mix thermoplastics with conductive flake and (or) fibre [3]. The products that were produced by the second method have good mechanical properties (tensile strength, modulus). In this investigation, the second method was used. The third method to produce conductive plastics is to synthesize the intrinsically conductive polymers (ICP). For example, polyacetylene and polyrrole [3], the conjugated organic polymer, could attain high levels of electronic conductivity.

In this investigation, the acrylonitrile–butadiene–styrene copolymer (ABS) was used for the matrix. It is because that ABS provides processability, economy and more reliable notch impact resistance. The Ni-coated conductive carbon fibres and the conductive carbon fibres were used as the conductive fillers in this study.

For processing, the Twin-Screw Extruder (TSE) and Brabender Plasti-Corder were used here for compounding composites. As for the reprocessing effect on the polymeric conductive composites, the researches are usually discussed in terms of the properties of injection molding parts of recycles. Here, the authors used the compressing molding products for reprocessing to study the variations of all properties.

The good products should be balanced in respect to the electronic properties and the mechanical properties. The authors tested the Electromagnetic Shielding effectiveness (SE value) in the electronic properties. As for the mechanical properties, tensile strength, Young's modulus and notched Izod impact strength were measured. The rheology and melt flow index (MFI) of composites were also studied here to discover the processability of composites.

EXPERIMENTAL

Materials

Acrylonitrile–butadiene–styrene (ABS) used in this work was the commercial product of POLYLAC 777-A, heat-resistant grade, made by Taiwan CHI MEI Co. Ltd. The carbon fibres used were a Ni-coated conductive carbon fibre (NCF) of MC-HTA-C3-US (made by Japan Rayon Co. Ltd) and a conductive carbon fibre (CF) of HTA-C3-US (made by Japan Rayon Co. Ltd).

Compounding

(1) By using the Brabender Plasti-Corder. The ABS was preheated at 100°C for 3 hr before blending. Three processing cycles were carried out in a Brabender Plasti-Corder, PLE 330, at 240°C. The screw speed during blending was respectively 30 rpm.

(2) By using Twin-Screw Extruder (TSE). The machine

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was needed to preheat for 2 hr. When the temperature was on the setting values, ABS was used to clean the extruder for 10–15 min. The fillers (NCF,CF) were loaded to the machine by controlling the four-step temperature at 240–240–240–240°C and the rolling speed about 100 rpm. The model of TSE was W&P ZSK30.

The relative detail compounding data were described in Table 1.

Compression molding

After compounding, a batch of composites could be sent into the frame, delivered into a pair of plates and pressed by compression molding at temperature of 240°C, and at pressure 150 kg/cm^2. When the blends were completely melted, the ultimate pressure was kept for 4 min and then cooled by water at the rate of $\sim$30°C/min until the temperature fell below 100°C.

Mechanical properties

The tensile strength was measured according to the ASTM D638 test method using an Instron Universal Testing Machine Model 1130. The cross head was 500 kg, the speed was at 5 cm/min, and the chart speed was 100 cm/min. The elastic modulus was determined from the slope of the initial part of the stress–strain curve within the linear trend. Notched Izod impact strength was measured according to the ASTM D256 test method using Izod type and the impact energy was 30 kg cm. The thickness of testing sample was 3 mm.

Coaxial transmission line test method

The coaxial transmission line method modelled on an ASTM ES7-83 test method was used to test the shielding effectiveness (SE) of conductive composites. The detailed construction of the insertion loss measuring system was described by Chiang and Chiang [4].

Melt flow index (MFI)

The melt flow index was measured according to the ASTM D1238 test method using a Melt Flow Index tester model Kayeness 7050. Two basic methods have been developed for running flow rates under ASTM D1238, Method A and B. Method A is simply the collection of extrudate over time, while Method B is the measurement of time for the flow of a fixed volume of polymer. The authors used Method A in this study.

Rheology

The rheological properties of conductive ABS composites were measured on an extrusion capillary rheometer, Model Rheograph 2001 (GOTTFERT, Germany), using a capillary dye of $L/D = 10/1$ at temperature of 240°C.

SEM micrographs

For examining phase morphology, compression-molded Izod bars were immersed in liquid N_2 and fractured. The fractured surfaces were coated with gold and viewed end-on by a ISI ABT-55 scanning electron microscope.

Table 1. Detailed data of compounding conditions

Matrix	Filler	Temperature (°C)	Speed (rpm)	Time (min)
ABS[a]	NCF	240	30	8–10
ABS[a]	CF	240	30	8–10
ABS[b]	NCF	230	20	Continue
ABS[b]	CF	230	20	Continue

[a]Brabender compounding.
[b]Twin-screw extruder compounding.

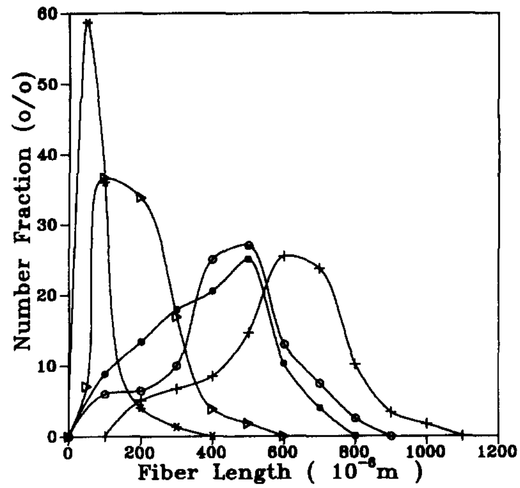

Fig. 1. Number fraction vs fibre length distribution of ABS/NCF (90/10) for different numbers of processing cycles: (+) 1st Brabender; (○) 2nd Brabender; (●) 3rd Brabender; (△) 1st twin-screw extruder; (⋊⋉) 2nd twin-screw extruder.

RESULTS AND DISCUSSION

Fibre length distribution

From a previous paper [5], it is known that the fibre length of conductive composites is important in determining the EMI shielding effectiveness and the mechanical properties. To understand the change of fibre length after the compounding of different machines and the compounding of reprocessing, it could help us to know the change of properties of composites. This investigation used the number average length ($\bar{l}_n = \Sigma n_i l_i / \Sigma n_i$) in the counting of $\sim$100 fibres to give a representative value. Figures 1–3 show that the NCF fibre lengths of ABS/NCF compounded by TSE were shorter than those of fibres compounded by the Brabender; the fibre

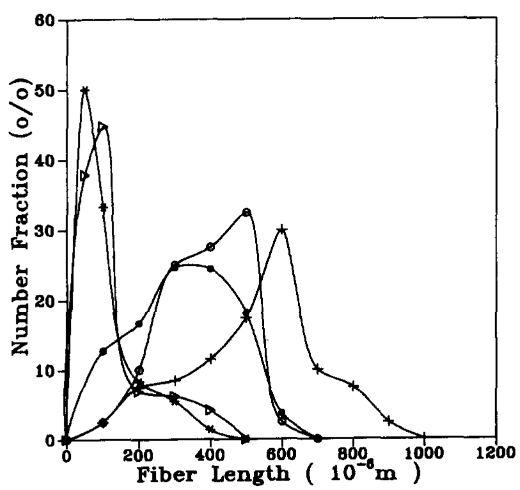

Fig. 2. Number fraction vs fibre length distribution of ABS/NCF (80/20) for different numbers of processing cycles: (+) 1st Brabender; (○) 2nd Brabender; (●) 3rd Brabender; (△) 1st twin-screw extruder; (⋊⋉) 2nd twin-screw extruder.

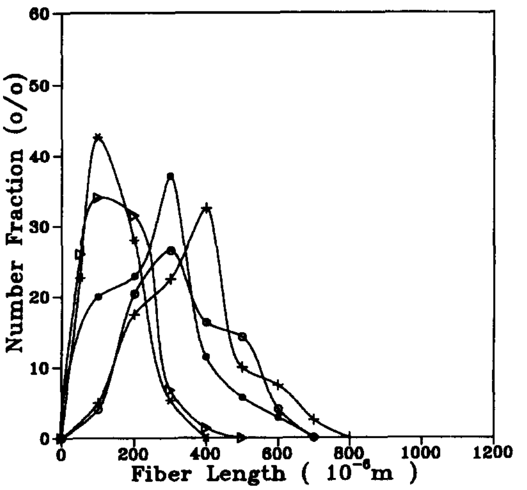

Fig. 3. Number fraction vs fibre length distribution of ABS.NCF (70/30) for different numbers of processing cycles: (+) 1st Brabender; (○) 2nd Brabender; (●) 3rd Brabender; (△) 1st twin-screw extruder; (✕) 2nd twin-screw extruder.

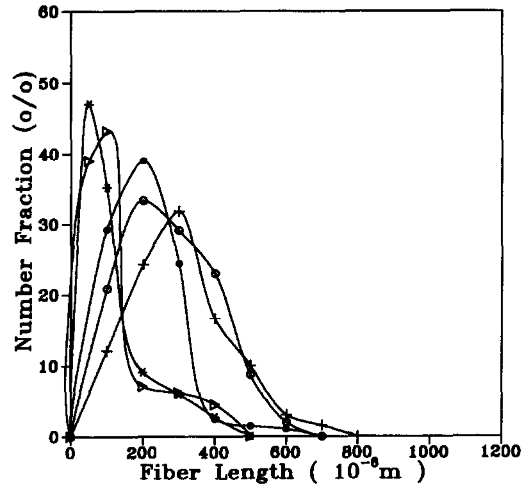

Fig. 5. Number fraction vs fibre length distribution of ABS/CF (80/20) for different numbers of processing cycles: (+) 1st Brabender; (○) 2nd Brabender; (●) 3rd Brabender; (△) 1st twin-screw extruder; (✕) 2nd twin-screw extruder.

length distribution curve shifted to left. Therefore, the latter showed better EMI shielding effectiveness and better mechanical properties.

Figures 1–3 show that the curve of the NCF fibre length distribution shifted to the left when the added amount of fibres increased and when the number of compounding cycles increased. However, in Figs 4–6, the curve of CF fibre length distribution shift to the left is not so clear when the added amount of fibres increased and when the number of compounding cycles increased. It is due to the torque value increasing with compounding at adding of fibre. On the other hand, the CF was more brittle than that of NCF. After the first compounding, the CF was broken more seriously than that of NCF. Czarnecki and White [6], favour the long fibres rather than the continued reduction of short fibres. Therefore, the fibre length distribution curves which after TSE second compounding were near the fibre length distribution curves after TSE first compounding.

As a result, the fibre length was below 200 μm using TSE to compound and the fibre length was above 200 μm using Brabender to compound even after three compoundings.

EMI shielding effectiveness (SE values)

Figure 7 shows that the EMI shielding effectiveness (SE value) of ABS/NCF was ~47 dB as the NCF was 30 parts per hundred of resin (phr) content on the first number of cycles. This SE value

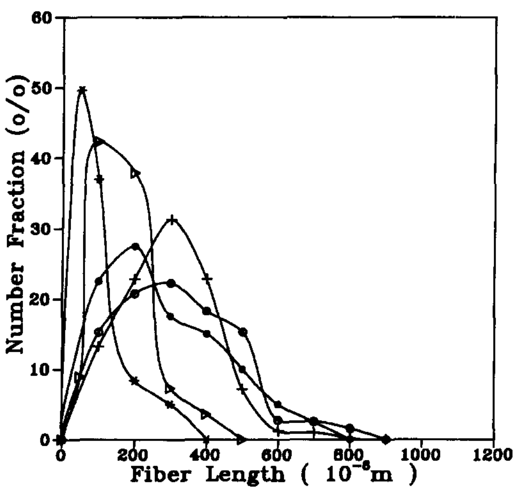

Fig. 4. Number fraction vs fibre length distribution of ABS/CF (90/10) for different numbers of processing cycles: (+) 1st Brabender; OO) 2nd Brabender; (●) 3rd Brabender; (△) 1st twin-screw extruder; (✕) 2nd twin-screw extruder.

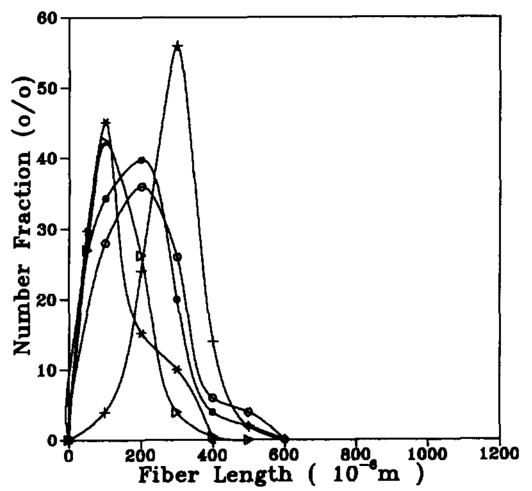

Fig. 6. Number fraction vs fibre length distribution of ABS/CF (70/30) for different numbers of processing cycles: (+) 1st Brabender; (○) 2nd Brabender; (●) 3rd Brabender; (△) 1st twin-screw extruder; (✕) 2nd twin-screw extruder.

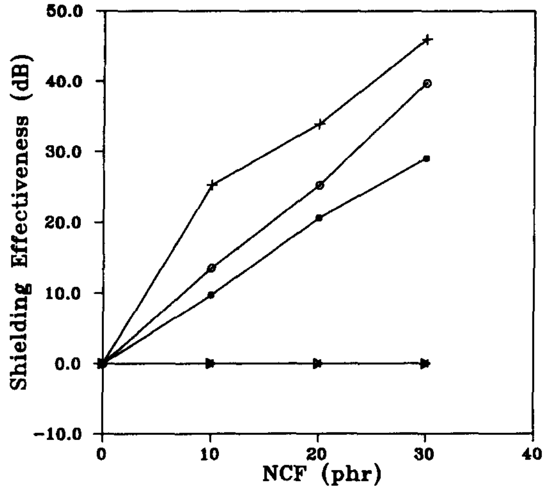

Fig. 7. Shielding effectiveness at 1000 MHz vs NCF content for different numbers of processing cycles: (+) 1st Brabender; (○) 2nd Brabender; (●) 3rd Brabender; (△) 1st twin-screw extruder; (✕) 2nd twin-screw extruder.

was very near the results of PC/ABS/NCF [4] and ABS/ENCF [7, 8] conductive composites. When the added fibre was CF, the SE value of ABS/CF was about 31 dB on the first number of cycles (Fig. 8). It is because the conductivity of NCF was better than that of CF. Surely, when the composites were reprocessed, the lengths of fibre were broken more and more. Therefore, the SE values were decreased with increasing the number of processing cycles. The SE value was 50 dB as using Al instead of conductive composites.

In this investigation, the TSE and Brabender were used to compound the conductive ABS composites. The kneading elements of TSE were designed to make different polymers homogeneous. At this time, the

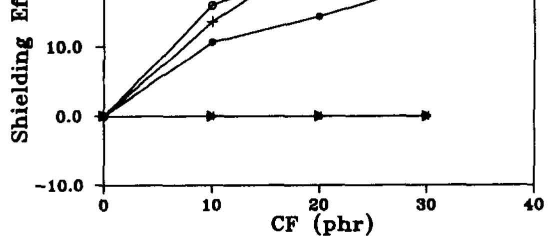

Fig. 8. Shielding effectiveness at 1000 MHz vs CF content for different numbers of processing cycles: (+) 1st Brabender; (○) 2nd Brabender; (●) 3rd Brabender; (△) 1st twin-screw extruder; (✕) 2nd twin-screw extruder.

Table 2. Tensile strength (MPa) of composites

phrcycles	1st (B[a])	2nd (B[a])	3rd (B[a])	1st (T[b])	2nd (T[b])
Fibre 0	25.1	–	–	–	–
NCF 10	69.4	65.5	63.5	21.9	21.5
NCF 20	73.1	68.1	82.7	21.1	20.4
NCF 30	78.8	92.8	95.1	19.2	19.8
CF 10	72.6	70.9	76.0	27.3	25.4
CF 20	82.4	85.2	103.8	26.1	21.7
CF 30	96.3	87.2	107.5	22.5	20.4

[a]Using Brabender compounding.
[b]Using twin-screw extruder compounding.

fibre will be seriously broken (the fibre length below 200 μm) and the conductive network path cannot be formed. For this reason, the SE value of composites compounded by the TSE were the same as that of the original ABS. However, the composite possessed long fibre distribution (fibre length above 200 μm) as using the Brabender to compound. Therefore, the SE value of conductive ABS composites compounded by Brabender was higher than those compounded by TSE. From a previous paper [6], it is also found that the L/D value (length/diameter) of conductive fibre plays an important role in determining the SE value.

Mechanical properties

From Table 2, the tensile strength of composites evidently increased with increasing the amount of fibres by using Brabender to compound. It was suggested that the length of most fibres were over the critical length (200 μm). However, the tensile strength of ABS/NCF or ABS/CF composites did not increase with increasing the amount of fibres using TSE compounding. Bowyer and Baderm [9] have verified the use of the equation below for relating the strength of the composite to its composition of its components

$$\sigma_c = CX + CY + Z,$$

where C is an orientation factor, X, Y, and Z are the contributions to the reinforcement made by the sub-critical fibres ($l < l_c$), super-critical fibres ($l > l_c$) and the polymer, respectively. Therefore, the length of fibres is one of the factors in determining the strength of composites. Comparing Figs 1–6 with Table 2, the composites possessed the strength above 60 kg/cm^2 for fibre length above 200 μm, however, the composites lost their strength below 30 kg/cm^2 for fibre length below 200 μm. Therefore, the authors suggested that the critical fibre length (l_c) was $\sim$200 μm.

Even though the CF fibre length was shorter than that of NCF, Table 2 shows that the tensile strength of ABS/CF composites was better than that of ABS/NCF composites. From SEM observation, the CF fibres were seldom pulled out and their lengths were shorter than those of NCF. This reveals that the interface adhesion between ABS and fibre was another variable in determining the mechanical properties of composites. In this investigation, the tensile strengths of ABS/NCF or ABS/CF were higher than those of PC/ABS/NCF [4]. In PC/ABS/NCF [4] and PP/NCF [10] composites, the tensile strength decreased with increasing NCF content. Di Liello *et al.* [10] reported that it is caused by the brittle behaviour of the composites and not by the

Table 3. Young's modulus (GPa) of composites

phr/cycles	1st (B[a])	2nd (B[a])	3rd (B[a])	1st (T[b])	2nd (T[b])
Fibre 0	0.54	–	–	–	–
NCF 10	2.28	2.12	2.35	0.57	0.56
NCF 20	2.92	2.48	2.36	0.59	0.57
NCF 30	3.03	3.02	3.30	0.61	0.57
CF 10	2.45	2.35	2.45	0.58	0.56
CF 20	3.13	2.36	2.87	0.67	0.59
CF 30	3.14	3.56	3.24	0.54	0.47

[a]Using Brabender compounding.
[b]Using twin-screw extruder compounding.

Table 5. Melt flow index (g/10 min) of composites

phr/cycles	1st (B[a])	2nd (B[a])	3rd (B[a])	1st (T[b])	2nd (T[b])
Fibre 0	3.32	–	–	–	–
NCF 10	1.04	1.42	2.03	1.41	1.53
NCF 20	0.85	1.11	1.45	1.15	1.46
NCF 30	0.18	0.49	1.03	–	–
CF 10	0.88	1.58	1.96	0.75	1.05
CF 20	0.62	1.29	1.76	0.78	1.33
CF 30	0.41	0.95	1.42	–	–

[a]Using Brabender compounding.
[b]Using twin-screw extruder compounding.

interfacial weakness between the fibres and matrix. According to the impact strength properties of ABS/NCF or ABS/CF composites, the ABS/NCF and ABS/CF composites show brittle behaviour. However, the tensile strength increased with increasing NCF or CF content. This result was different from that of Di Liello *et al.* [10] reported.

From Table 2, the tensile strength of composites did not increase with increasing the amount of fibres by using TSE to compound. It was due to the fact that the fibres were too short to transfer the shear stress. As to the reprocessing effect on the mechanical properties, Czarnecki and White [6], favour the breakdown of long fibres rather than the continued reduction of short fibres. Using TSE to blend, the result shows that the tensile strength varies little on different numbers of reprocessing. Different to the TSE compounding composites, Table 2 showed the reinforced effect by using Brabender to blend.

Table 3 shows the Young's modulus vs fibre content for ABS/CF and ABS/NCF composites on different number of cycles. It shows that the composites using Brabender to compound had higher modulus values than those using TSE to compound. It was because the fibre length of composites compounded by the Brabender were longer than that of those compounded by TSE.

The impact strength was shown in Table 4. Table 4 shows that the impact strengths of the composites were lower than that of ABS. It is known that the ABS material was a kind of ductile material, however, the carbon fibre was a brittle material. As the brittle material was added to ductile material, it would cause the impact strength of ductile materials to decrease.

Processability

Table 5 shows that the MFI of composites increased with increasing the number of cycles of ABS/fibre composites. It was due to the polymer chain and fibres being broken during reprocessing. The MFI of composites compounded by TSE were higher than that of those compounded by the Brabender. It is because the fibres were broken by twin-screw more seriously; the shorter fibre length made viscosity decrease, therefore, the MFI was increased.

Figure 9 shows that the viscosity decreased with increasing the number of cycles. It was consistent with the MFI. At shear rate below 10^3 S^{-1}, the viscosity (η) of 1st, 2nd and 3rd processing composites were higher than that of pure ABS and the composites compounded by TSE. This may be due to the fibres being solid during the test temperature, therefore, adding fibres results in the increasing of viscosity. The long length of fibres is harmful for the fluidity, thus, the viscosity of 1st processing composites is higher than that of 2nd and 3rd processing composites. However, the viscosity of composites are similar at the shear rate above 10^3 S^{-1}. Comparing Fig. 9 with Fig. 2, shows that the viscosity of composites is near the pure ABS as the fibre length below 200 μm.

From Fig. 10 we can see the rheological behaviour of composites. Figure 10 shows that the flow-behaviour index (FBI), n, was 1.4, 0.8 and 0.6 at the low (shear rate between 10 and 10^2 S^{-1}), middle (shear rate between 10^2 and 10^3 S^{-1}) and high (shear rate between 10^3 and 10^4 S^{-1}) shear rate. This pointed out that the composites were the pesudo-plastic fluid. When the flow was in the middle shear

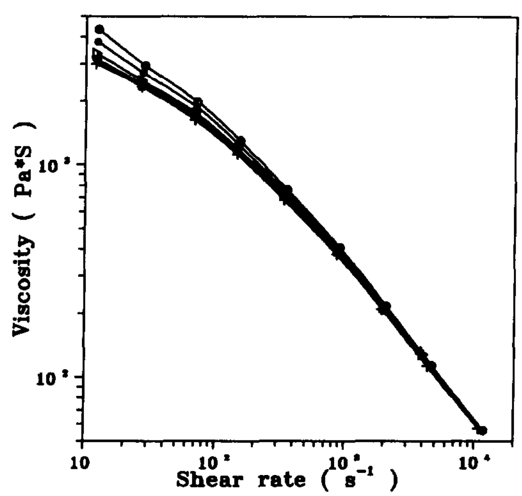

Fig. 9. Viscosity of ABS/NCF (80/20) vs shear rate for different numbers of processing cycles: (+) pure ABS; (○) 1st Brabender; (●) 2nd Brabender; (△) 3rd Brabender; (X) 1st twin-screw extruder; (■) 2nd twin-screw extruder.

Table 4. Notched Izod impact strength (Kg cm/cm) of composites

phr/cycles	1st (B[a])	2nd (B[a])	3rd (B[a])	1st (T[b])	2nd (T[b])
Fibre 0	9.70	–	–	–	–
NCF 10	3.92	3.31	3.52	4.07	2.80
NCF 20	4.64	3.42	3.91	3.68	3.32
NCF 30	4.98	3.95	4.15	3.70	3.78
CF 10	3.92	3.31	3.52	4.07	2.86
CF 20	4.64	3.42	3.91	3.68	3.32
CF 30	4.98	3.95	4.15	3.70	3.78

[a]Using Brabender compounding.
[b]Using twin-screw extruder compounding.

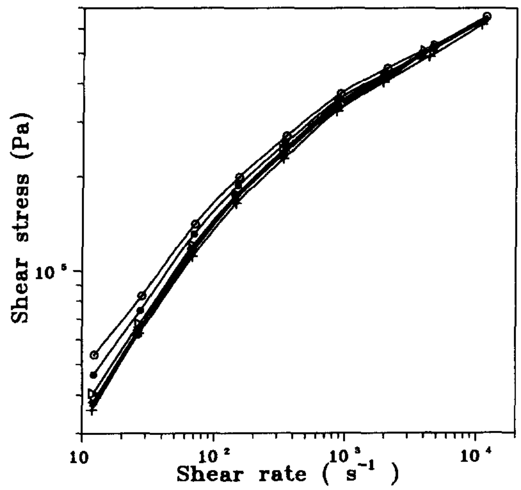

Fig. 10. Shear stress of ABS/NCF (80/20) vs shear rate for different numbers of processing cycles: (+) pure ABS; (○) 1st Brabender; (●) 2nd Brabender; (△) 3rd Brabender; (Ж) 1st twin-screw extruder; (■) 2nd twin-screw extruder.

rate region, the fluid approached the Newtonian fluid.

Morphology

In this study, the authors also used scanning electron micrographs to investigate the fracture mechanism. In Figs 11 and 12, the fibres were pulled out and just had a small amount of ABS adhering to NCF, therefore, the fracture was taken between the ABS and NCF and the interfacial adhesion was not so good. However, in PC/ABS/NCF [4], SEM shows that the NCF is pulled out and has no polymer adhering to NCF; therefore, the fracture takes place at the interface. Moreover, the edge of the void is very clear, reflecting a very weak adhesion interaction between the PC/ABS and NCF. This result is very similar to that of the POM/CF [11] composite. Nevertheless, the interface of the ABS/CF composite seldom showed the phenomenon of pulling out of fibres. For this reason, the tensile strength of ABS/CF was higher than that of ABS/NCF or PC/ABS/NCF composites.

It is known that the pulling-out and debonding effects are helpful to the Izod impact strength. However, the break elongation of fibres and the stress concentration at the regions of fibres ends, areas of poor adhesion and regions where they contact one another are harmful to the Izod impact strength. In our study, the composites turned brittle. This latter factor was the most important.

CONCLUSIONS

ABS/NCF (ABS/CF) composites show good properties in the EMI shielding effect, modulus and tensile strength. The length of fibres and the interface adhesion of composites were important in determining the properties of composites. The properties of the composites were also strongly influenced by machine design, processing number of cycles and mixing methods. The composites are rigid and brittle; therefore, it is important to improve the impact strength of composites in any future

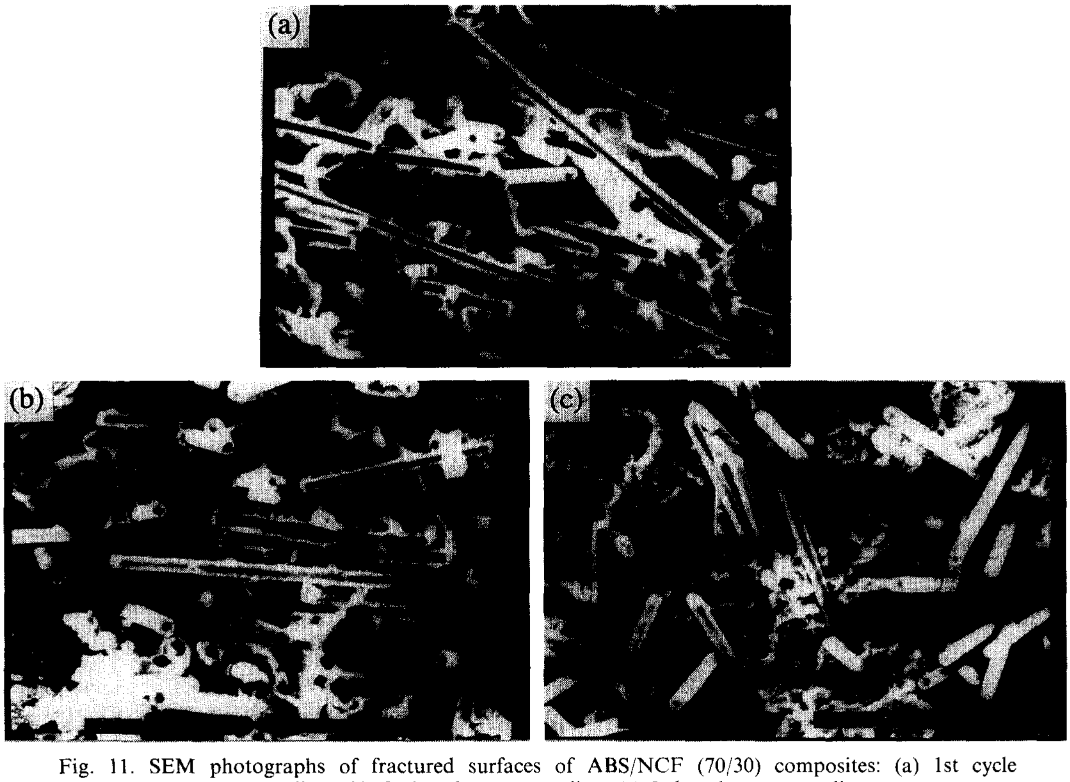

Fig. 11. SEM photographs of fractured surfaces of ABS/NCF (70/30) composites: (a) 1st cycle compounding; (b); 2nd cycle compounding; (c) 3rd cycle compounding.

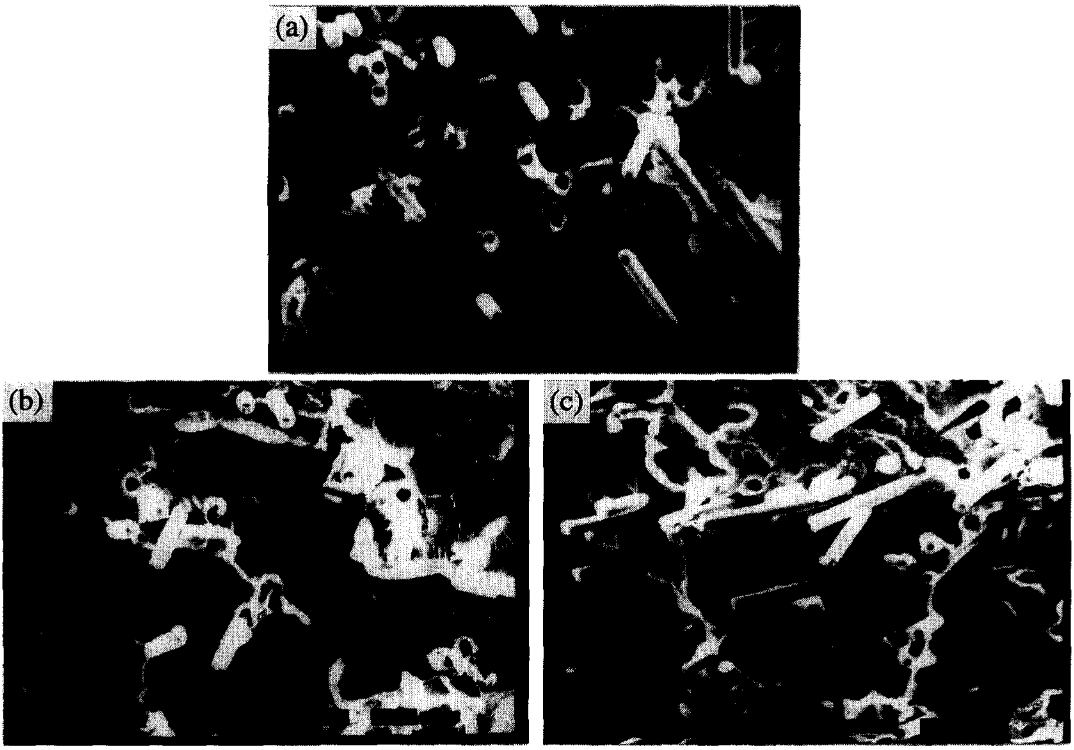

Fig. 12. SEM photographs of fractured surfaces of ABS/CF (70/30) composites: (a) 1st cycle compounding; (b) 2nd cycle compounding; (c) 3rd cycle compounding.

investigation. In this investigation, the EMI SE value of ABS/NCF was 47 dB as the NCF was 30 phr content on the first number of cycles of Brabender compounding. The EMI SE values of above composite possessed ~27 dB, although after three Brabender compoundings. Therefore, adding NCF to ABS could offer a good EMI SE of composites.

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