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# Surface modification of superdrawn polyoxymethylene fibres

## Part I *Interfacial miscibility in the fibre/adhesive/rubber system*

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A new surface modification of superdrawn polyoxymethylene (POM) fibres, curing with resorcinol at mild temperatures, was developed to apply to rubber composites and the adhesion to the rubber matrix behaviour of modified fibres is discussed in terms of the interfacial miscibility between the fibre and adhesive surface layers. The modified fibre reached the maximum pull-out adhesion level in which a cohesive failure of the fibre occurs, resulting from the fact that the modified POM layer is spectroscopically close to the standard resorcinol–formaldehyde (RF) resin, thoroughly miscible and thermodynamically compatible with the resorcinol–formaldehyde–latex (RFL) adhesive.

## 1. Introduction

High-modulus and strength fibres have potential as reinforcing materials. The performance of fibre-reinforced composites depends on the interfacial affinity of adherends to adhesives. For example, a resorcinol–formaldehyde–latex (RFL) adhesive has been well known as the best adhesive agent for the adhesion of tyre cords such as nylon, aramid and poly(ethylene terephthalate) cords to a tyre–rubber matrix. The molecular chains of the cords consist of amide or ester linkages which are chemically active and wetted, so the RFL adhesive strongly adheres to the cords without surface pretreatment [1–4] or without an epoxy precoat [5, 6]. However, in the case of non-polar and chemically inactive fibres, surface pretreatment of the fibres is indispensable for high affinity to the matrix. Various pretreatments, chemical etching or oxidation using $O_2$–$O_3$ gas [7], fuming nitric acid [7, 8], a $K_2Cr_2O_7$–$H_2SO_4$ solution [9, 10], and electrical (plasma and corona) discharge [11–17] for polyethylene and polypropylene, and a sodium-naphthalene solution [18, 19] for poly(tetrafluoroethylene), have been developed.

In recent years, superdrawn polyoxymethylene (POM) fibres have been developed [20–23] and gradually applied to composite materials. The POM fibres consist of the repeating unit ($-CH_2-O-$), and thus are non-polar and chemically inactive as well as polyethylene fibres. An attempt has been made to make the surface of a POM resin or film active by chemical etching using a $K_2Cr_2O_7$–$H_2SO_4$ solution [8, 9], or Satinizing solution [24], etc., which can erode the amorphous phase contained in the POM. However, the improvements of the affinity of POM fibres to the matrix or adhesive agents caused by this chemical etching are far too small for application to reinforced composites, particularly to rubber composites, since a radical decomposition of POM molecular chains occurs due to the strong acidity and oxidation capacity of the etching agents without the generation of any functional groups in the fibre surface.

The present work is in two parts. The first presents a new surface modification of the superdrawn POM fibres and discusses the effect of the modification of the adhesion to a rubber matrix in terms of spectroscopic miscibility, the second part discusses the morphology and process of a single-fibre pull-out fracture in the fibre–rubber matrix system.

## 2. Experimental procedure

### 2.1. Preparation of superdrawn POM fibres

An undrawn POM tube with an outer diameter of 2.3 mm and inner diameter of 0.8 mm was first prepared by extrusion of an acetal homopolymer (Asahi Chemical Industry Company Ltd, "Tenac 3010"). The tube was continuously two-step drawn, up to a draw ratio of 20 in compressed silicone oil; and a drawn fibre with a diameter of 0.50 mm was obtained. The resulting fibre was completely washed with Freon-113 to remove any silicone oil adhering to the fibre. The tensile strength and Young's modulus along the fibre axis were 1.8 and 40 GPa, respectively. The details have been described in previous papers [22, 23].

### 2.2. Preparation of activating agents

Four different activating agents with the following compositions (by weight) were prepared to modify the fibre surface: (i) a 40% aqueous solution of resorcinol; (ii) a mixture of resorcinol (40 parts) and RF solution (60 parts); (iii) a mixture of resorcinol (40 parts), RFL solution (40 parts) and water (20 parts); and (iv) a mixture of resorcinol (40 parts), RF solution (20 parts),

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RFL solution (20 parts) and water (20 parts). The RF solution was prepared by stirring a mixture (by weight) of resorcinol (16.2 parts), 37% formalin (20.0 parts), sodium hydroxide (0.41 parts) and water (373.8 parts) at 23 °C for 6 h. The RFL solution was prepared in the same way as the adhesive agent whose preparation is described in the following section.

## 2.3. Preparation of the adhesive agent, RFL

The RFL solution was prepared by the usual method: a mixture (by weight) of resorcinol (16.2 parts), 37% formalin (20.0 parts), sodium hydroxide (0.41 parts) and water (373.8 parts), was stirred at 23 °C for 6 h. Then the following were added: a vinylpyridine terpolymer latex (Sumitomo-Naugatuck Inc., "Pyratex" 282.2 parts), a SBR latex (Nippon Zeon Company Ltd, J-9049 43.3 parts), a natural rubber latex (HMPB Company, "H&C" 11.8 parts) and water (233.3 parts). The mixture was stirred again at 23 °C for 24 h, and 28% ammonia was then added (18.0 parts).

## 2.4. Procedure of the surface modification

The principle of the surface modification is based on the chemical reaction between the POM molecule and resorcinol at mild temperatures. Fig. 1 shows a block diagram illustrating the continuous processing of surface-modified superdrawn POM fibres. The fibre, (A), is fed to a sand blaster, (3), through a feed belt, (2), from a creel, (1); it is sandblasted at the fibre surface, immersed in an activating agent, (4), cured in the first air oven, (5), dipped in the RFL solution, (6), cured in a second air oven, (7), taken up by a take-up belt, (8), and wound by a winder, (9). The experimental conditions were as follows: feed speed, 5 m min$^{-1}$; size of blasting sands, 120 mesh; blasting pressure, 4 kg cm$^{-2}$; dipping temperature in the activating agent, room temperature; curing temperature in the first oven, 130 °C; first curing time, 0.4 min; dipping temperature in the RFL solution, room temperature; curing temperature in the second oven, 160 °C; second curing time, 1.0 min; and take-up speed, 4.9 m min$^{-1}$. The tensile strength and Young's modulus of the modified fibre thus obtained were 1.5 and 36 GPa, respectively. For comparison, only RFL coating, sandblasting/RFL coating, and sandblasting/RF dipping/RFL coating were carried out using the same apparatus as above.

## 2.5. Adhesion test of the sample fibres to the rubber matrix

Adhesion of the fibres to the rubber matrix was assessed by a pull-out test. The sample fibres were moulded with a compounded crude rubber, used for automotive tyre carcasses, at 150 °C for 30 min under 35 kg cm$^{-2}$ to produce the pull-out testing specimens–ten composite bars, as shown in Fig. 2. This was followed by a T-pull-out test according to JIS L 1017 (1983) using an Instron tensile-testing machine. The conditions were as follows: sample gauge length, 100 mm; fibre length embedded in the rubber (adhesive length), 10 mm; crosshead speed, 100 mm min$^{-1}$; temperature, 23 ± 2 °C; relative humidity, 50 ± 5%. Measurement was carried out using twenty composite bars per sample and the results were averaged. The fluctuation in the observed pull-out load was within about ± 4%. The moulded rubber without embedding fibres had a 300% modulus of 16.0 MPa, a tensile strength of 21.5 MPa, and elongation at break of 410%. The pull-out stress of the fibre to the rubber matrix was calculated by

$$T = F/\pi DL \qquad (1)$$

where $T$ is the pull-out tensile stress, $F$ is the observed pull-out load, $D$ is the fibre diameter and $L$ is the adhesive length. The diameter $D$ was taken as the diameter of the intact fibre, since the diameter of the fibres hardly changed before and after the treatments.

## 2.6. Spectroscopic observation of the treated surface layer

The chemical structure of the fibre surface was investigated using a nuclear magnetic resonance (NMR) spectroscope (Japan Electron Optics Laboratory Company, FX-200) and Fourier-transform infrared (FT-IR) spectroscope (Japan Electron Optics Laboratory Company, JIR-100). An NMR sample was prepared as follows: the resorcinol-activated fibre was extracted with ethanol in a supersonic wave vessel, vacuum-dried, dissolved in methanol-d4, and tetramethylsilane added as an internal standard. The NMR measurement was operated at 200 MHz at room temperature. The fibre remaining after extraction was lightly planed on its surface by a cutterknife and the resulting fluffs were followed by a microfocus infrared (i.r.) microscopy measurement. For comparison, the intact POM fibre, resorcinol, and RF resin were used for i.r. measurement. The RF resin was prepared by vacuum drying of the gelling RF activating agent at 80 °C.

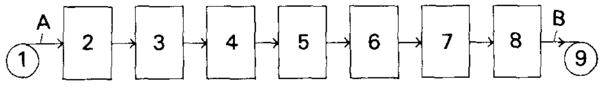

*Figure 1* Block diagram of the processing of surface-modified superdrawn POM fibres: (A) intact POM fibre, (B) treated POM fibre, (1) creel, (2) feed belt, (3) sand blaster, (4) activating bath, (5) the first oven for curing, (6) RFL-dipping bath, (7) the second curing oven, (8) take-up belt, and (9) winder.

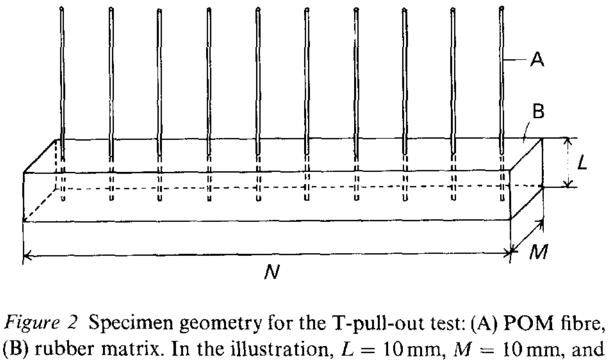

*Figure 2* Specimen geometry for the T-pull-out test: (A) POM fibre, (B) rubber matrix. In the illustration, $L$ = 10 mm, $M$ = 10 mm, and $N$ = 100 mm.

## 3. Results

### 3.1. Effect of fibre modification on adhesion

Table I shows a comparison of pull-out strength for samples prepared by different treatments. The adhesions of RFL-dipped fibres without activation treatments, intact fibre (sample A), only sandblasted fibre (sample B), sandblasted and RF-dipped fibre (sample C), were at low levels but the adhesion strength for the fibres treated with activating agents (samples D, E, F and G) were at a remarkably higher level. Some of the samples, F and G, could not be pulled out and fractured at the fibre emergent end of the sample block. These results indicate that surface roughening by sandblasting has a small effect on adhesion to rubber and that curing with resorcinol makes a substantial contribution to the improvement of interfacial wetting between the POM fibre and the RFL adhesive. The pull-out regions of samples A–C had the same appearances as before embedding in the rubber matrix and did not at all alter the adherence to rubber. On the other hand, the immersed regions of samples D–G were found to fracture at the fibre surface and they bonded to rubber in some places. This suggests chemical modification of the fibre surface, giving a high affinity to the RFL adhesive layer.

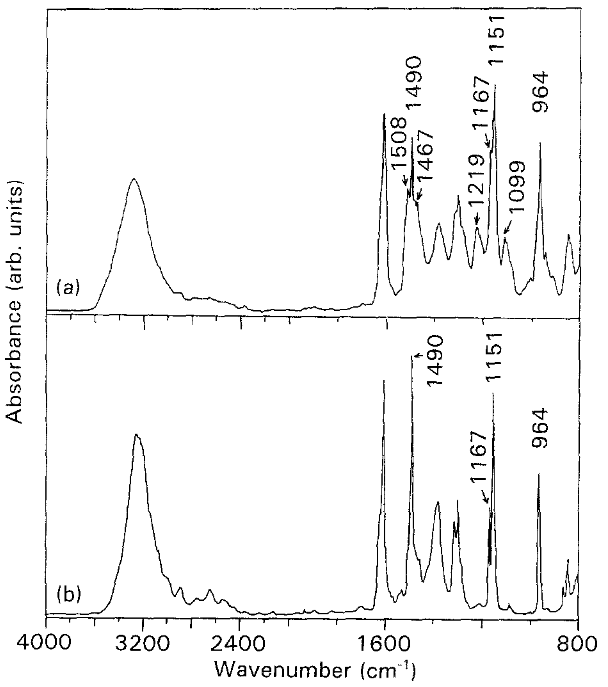

*Figure 3* I.r. spectra of the soluble materials contained in the modified layer: (a) the material extracted with ethanol from the superdrawn POM fibre activated with only resorcinol, and (b) resorcinol.

### 3.2. Spectra of the soluble material contained in the modified layer

Figure 3a and b shows i.r. spectra of the light-brown extraction of the sample activated with only resorcinol (treated up to process 5), and of resorcinol, respectively. The extraction is clearly a mixture of a reaction product and unreacted resorcinol. A comparison between Fig. 3a and b shows new peaks at 1508, 1467, 1219, 1099 cm$^{-1}$, a decrease of the 1490 cm$^{-1}$ peak, and an increase of the ratio of the intensities in the range 1167–1151 cm$^{-1}$. This spectroscopic change is similar to the change which has been observed in the reaction between resorcinol and formaldehyde under no catalyst or with an acid catalyst. The reaction products have been found to be mainly 4-, and 4,6-substituted derivatives of resorcinol, which exhibit new peaks at ca. 1505, 1440-1460, 1220, 1090 and 980 cm$^{-1}$; a disappearance of the 1490 cm$^{-1}$ peak; an increase of the peak ratio, 1170/1150 cm$^{-1}$; and a decrease of the 960 cm$^{-1}$ peak [25, 26]. It can be seen from the spectroscopic comparison that the product contained in the extraction is surely a resorcinol resin, possibly a 4-substituted derivative.

Fig. 4a and b show NMR spectra of the same extraction as used for i.r. measurement, and of resorcinol, respectively. For resorcinol, a triplet at 6.94–7.01 p.p.m. (parts per million) is assigned to the aromatic 5-proton and two peaks at 6.27–6.31 p.p.m. are assigned to the aromatic 2,4,6-protons from the standard spectrum (the Sadtler standard NMR spectra, No. 6672M, 1969). The characteristic peaks, a doublet at 6.81–6.86 p.p.m. two peaks at 6.25–6.28 p.p.m. and two peaks at 3.64 and 3.67 p.p.m. belong to the reaction product. The assignments of the peaks are as follows: a doublet at 6.8–6.9 p.p.m. to the aromatic 5-proton; two peaks at 6.25–6.28 p.p.m. to the aromatic 2,6-protons whose chemical shift overlaps those of the 2,4,6-protons of resorcinol; the peaks at 3.67 p.p.m. to the $CH_2$ group isolated between the aromatic rings, which is probably substituted with the 4-proton of resorcinol. The assignment of the isolated $CH_2$ group is based on the chemical shift of the methylene bridges of phenol-formaldehyde novolak. (The peak appears at 3.78 p.p.m. The Sadtler standard spectra: *Polymers*, Vol.1, No. D107M, 1969). The unassigned peaks at 3.64 p.p.m. may be phenolic protons, since those of the novolak resonate at 3.65 p.p.m. (*ibid.*). The peaks at 4.9 and 3.3 p.p.m. in Fig. 4a belong to the contaminations, $H_2O$ in the sample, and $CH_3OH$ in the NMR solvent, respectively. The peak at 5.1 p.p.m. in Fig. 4b is due to the exchange between the OH group and $H_2O$. The soluble product, which is dispersed in the modified surface layer, is probably

TABLE I Pull-out strength for the RFL dipped POM fibres via different surface pretreatments/rubber systems: sample A, no pretreatments; B, only sandblasted; C, sandblasted/RF dipped; D, treated with resorcinol; E, treated with the mixture of resorcinol and RF; F, treated with the mixture of resorcinol and RFL; and G, treated with the mixture of resorcinol, RF and RFL. The fibre diameter was 0.5 mm and the adhesive length was 10 mm

| Samples | Pull-out load (N) | Pull-out strength (MPa) | Appearance of pull-out regions |
|---|---|---|---|
| A | 3.9 | 0.3 | Clean surface |
| B | 46.5 | 3.0 | Clean surface |
| C | 50.0 | 3.2 | Clean surface |
| D | 196.0 | 12.5 | Cohesive failure |
| E | 219.5 | 14.0 | Cohesive failure |
| F | 226.4 | 14.4 | Some fibre fractures |
| G | 227.4 | 14.5 | Some fibre fractures |

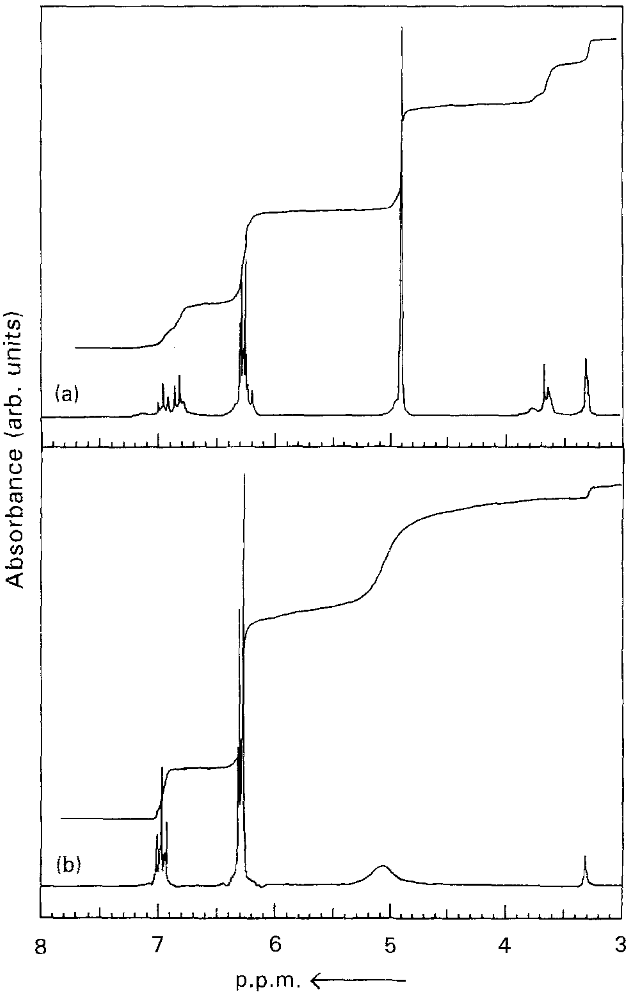

*Figure 4* NMR spectra of the soluble materials contained in the modified layer: (a) the material extracted with ethanol from the superdrawn POM fibre activated with only resorcinol, and (b) resorcinol.

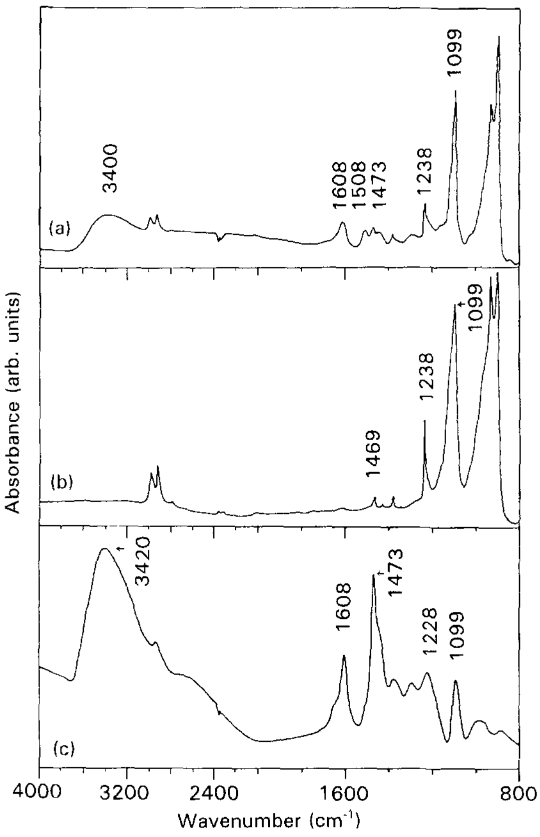

*Figure 5* I.r. spectra of the insoluble material produced on the fibre surface: (a) the fluffs obtained by planing the modified surface layer remaining after extraction, (b) the intact POM fibre, and (c) the resorcinol resin.

produced by the reaction between resorcinol and formaldehyde generated by an acid cleavage of the POM molecules.

## 3.3. Spectroscopic confirmation of the modified POM surface

The surface layer of the fibre remaining after extraction was light-brown and insoluble with the usual polar solvents such as DMF, DMSO, and chloroform. Fig. 5a shows an i.r. spectrum of the plane fluffs of the remaining fibre surface. For a comparison, the spectra of the intact POM fibre and the resorcinol resin are shown in Fig. 5b and c, respectively. The i.r. spectrum of the modified fibre surface is the superposition of the reaction product and POM fibre. The subtraction of the spectrum in Fig. 5b from Fig. 5a exhibits peaks at 3400, 1608, 1508, 1473 cm$^{-1}$ and a weak shoulder peak at 1228 cm$^{-1}$. Also, the subtraction of Fig. 5c from Fig. 5b shows absorption bands at 3420, 1608, 1473, 1228 cm$^{-1}$, which can be assigned to: the stretching vibration of phenolic OH, the in-plane vibration of a benzene skeleton the same and the C–O stretching, on the basis of the characterization of phenol [27], respectively. Therefore, the peaks at 3420, 1608, 1473 cm$^{-1}$ and the shoulder peak at 1228 cm$^{-1}$ for the modified fibre is due to a resorcinol resin. The unassigned peak at 1508 cm$^{-1}$ is probably due to the benzene skeleton [27]. These results confirm the existence of modified polyacetal which consists of the resorcinol functional groups bridged with methylene groups – a kind of resorcinol resin. The modified layer may be produced by a reaction between resorcinol and the POM molecules at the chain end or the decomposed POM.

## 3.4. Interfacial miscibility

The modified products consist of the components soluble in polar solvents and insoluble in these solvents. Since the modified products are essentially close to the RF part of the RFL adhesive, the exceptionally good adhesion of samples D–G results from the structural high affinity and miscibility between the modified POM and RFL coating layers. The RFL-dipped fibre, sample D, was brown at the surface. The fibre was transversely cut and the surface layer was observed in cross-section by an optical microscope. As a result, it was found that the brown colour of the surface continued throughout the depth of the modified layer. The miscibility of the modified POM and RFL layers probably occurs by diffusion of the RFL agent into the modified layer and the soluble modified component possibly makes the diffusion easier. The pull-out adhesion of the modified samples was in the order $D < E < F \fallingdotseq G$, although the difference in the pull-out load is very small among these samples. This suggests that the RF agent added to the resorcinol solution raises the interfacial miscibility to a still higher level and the addition of the RFL agent achieves the highest adhesion in the POM fibre/RFL system.

## 4. Discussion

The RFL adhesive agent is known to have the highest affinity to both nylon cords and a rubber matrix and is generally considered to have the following role in the cord–rubber composite system: the RF part adheres to nylon cords and the latex part causes adhesion of the RF resin to the rubber matrix by crosslinking bonds between the latex and rubber molecules.

Adhesion between adherands and adhesives is generally known to be related to the surface tension $\gamma$, and the thermodynamic solubility parameter, $\delta$, of both materials. $\gamma$ is the wetting parameter, which is the first key factor in the adhesive procedure. $\delta$ is the adhesion parameter between the adherand and adhesive in the composite. For the best wetting, the critical surface tension, $\gamma_c$, of the adherand must be larger than surface tension, $\gamma_{LV}$, of the adhesive according to Zisman's study [28]; and for the highest interfacial adhesion between the solid adherand surface and solid -adhesive-coating layer, the difference of each $\delta$ must be a minimum according to Iyengar's study [5].

The values of $\gamma_c$ for nylon 6, Kevlar and POM are $4.65 \times 10^{-2}\,\mathrm{N\,m^{-1}}$ [29], $4.90 \times 10^{-2}\,\mathrm{N\,m^{-1}}$ [30] and $38.5 \times 10^{-2}\,\mathrm{N\,m^{-1}}$ [29], respectively. The value of $\gamma_{LV}$ for resorcinol is $4.6 \times 10^{-2}\,\mathrm{N\,m^{-1}}$ [31]. The values of $\delta\,(\mathrm{cal\,cm^{-3}})^{1/2}$ for nylon 6, Kevlar and POM are 16.0 [5], 11.3 [32] and 10.2–11.0 [32], respectively; the value of $\delta$ of the RF part in the RFL adhesive is 15.9 [5]. Nylon 6 is, therefore, naturally very excellent in wetting and adhesion. Kevlar is comparatively excellent in wetting but unsuitable from an adhesive viewpoint. Adhesion of Kevlar to rubber has been improved by two-step adhesive systems (epoxy subcoat/RFL topcoat) based on the thermodynamic-compatibility concept [6]. POM is, however, almost lacking in both properties. The small pull-out strength for samples A–C is due to this reason. On the other hand, the $\gamma_c$ and $\delta$ values of the POM surface layer modified with the resorcinol–RFL agent is considered to be nearly equal to the value of RFL, since the modified surface layer can hardly be spectroscopically distinguished from the RFL. This is the reason the highest adhesive property of the surface-modified POM fibre causes the entire cohesive failure.

## 5. Conclusion

A new surface modification of superdrawn POM fibres was proposed for application to fibre-reinforced rubber composites, and the adhesion was discussed in terms of the interfacial miscibility between the modified fibres and RFL adhesive. The principle of the method is based on the chemical reaction between resorcinol and the POM molecules. The fibre surface reacts with resorcinol at a mild temperature into a resorcinol-modified POM layer which is spectroscopically assigned to a resorcinol resin. This modification remarkably enhanced the adhesion to rubber and caused a cohesive failure of the fibre surface. The high adhesion of the modified fibre to rubber is due to the chemical miscibility between the modified layer and the RFL coating layer or the thermodynamical compatibility of both layers.

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