JOURNAL OF MATERIALS SCIENCE 22 (1987) 3477–3484

Wettability of glass fibres with different sizings and their adhesion to unsaturated polyester matrices

C. SELLITTI*, S. VARGIU‡, E. MARTUSCELLI*, D. FABBRO‡
*Consiglio Nazionale Delle Ricerche – ITPR Via Toiano, Arcofelice Naples, Italy
‡SAVID S.p.A., Via S. Pellico, 12, Como, Italy

The wetting characteristics of unsaturated polyester resins on glass fibres with different sizings have been studied by contact angle determination periods. The styrene content of the matrix and the nature of the coatings result to be determinant in the wettability of glass fibres by the polyester matrices. Highest styrene content and styrene-soluble-coatings determine better wetting characteristics. Mechanical properties of the cured specimens and scanning electron microscopy on the fracture surfaces were also performed. Interesting correlations between the nature of the sizing agent and cohesive energy density with mechanical properties and fibre/matrix adhesion were found.

1. Introduction

The continually increasing interest in composites is closely connected with their high resistance/weight ratio and their mechanical and ultimate properties. Different factors contribute to the improvement of a composite material's properties; undoubtedly of fundamental importance are the wettability of the fibre by the resin, and the adhesion of the fibre to the matrix, leading to the transfer, by shearing stress, of the load from one fibre to another, through the matrix. The manufacturing process for a composite material requires the impregnation of different types of fibres, in the form of continuous filaments or mat, with polymeric resins. The more uniform and continuous the impregnation process, the better will be the properties of the laminate, in fact, a poor impregnation of the fibres will cause the formation of voids, which, together with poor adhesion, will impair the properties of the material [1, 2].

In the present work we have studied the influence of the chemical structure of the polyester matrix, of the styrene level, and of the sizing type, on the wettability of the fibre by the matrix before the curing reaction. We have also investigated the fibre/matrix adhesion in composite materials after the curing reaction. For this purpose we have studied as matrices four different unsaturated polyester resins at four styrene levels, and two glass fibres with different types of binder.

2. Experimental procedure

2.1. Materials

In the SAVID research laboratories we have synthesized four polyester matrices at different degrees of unsaturation, using the well-known polyesterification procedure. All the components of the resins (both glycols and anhydrides) are simultaneously charged into the kettle. At the first stage the formation of semiesters takes place by gradually increasing the temperature from 100 to 150° C in about 2 h, and subsequently the polymerization is completed at a temperature of 210° C until the acid number is approximately equal to 60. At a reduced pressure of about 20 mm Hg the final properties of acid number and viscosity, shown in Table I, are reached.

The molecular structures of the different matrices are shown in Fig. 1, from which it can be seen that resins 402/35 and 318/19 are maleic anhydride esters with different glycol types. Resins 549/160 and 363/27 are copolymers of phthalic and maleic anhydrides with dipropylene and diethylene glycols, respectively. With a Waters Gel Permeation Chromatograph we have evaluated the molecular weights of the resins, using for calibration polystyrene standards with the molecular weights given in Table I. Using the calculation programme of the instrument, we have found the values of $\bar{M}_n$, $\bar{M}_w$, $\bar{M}_z$ and $\bar{M}_w/\bar{M}_z$ shown in Table II.

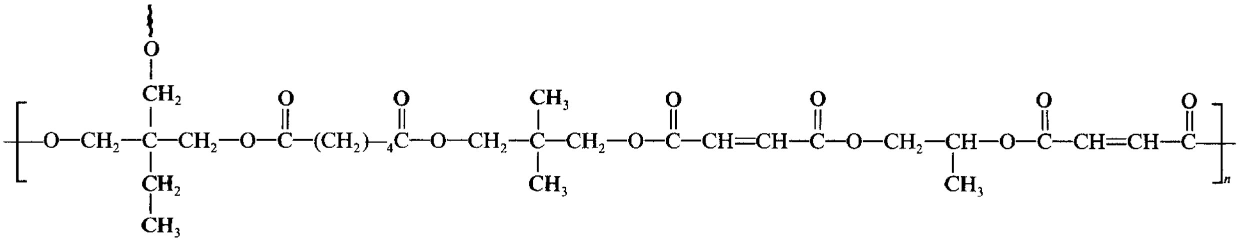
On the basis of the molar contributions of cohesive energy and the molar volumes of the single components, we have calculated [3] for each resin the values of cohesive energy density (*CED*) shown in Table II. From these data the solubility parameters can be calculated from the equation $\sigma = (CED)^{1/2}$. The surface tension values given in Table II have been calculated from the empirical equation $\gamma = 0.75\ CED^{2/3}$.

TABLE 1

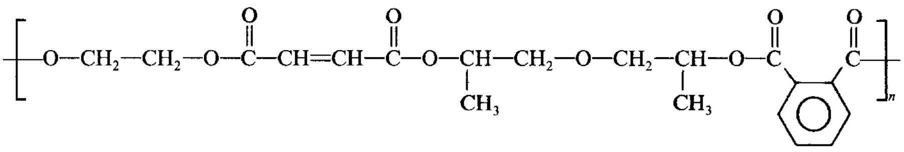
Molecular weight	Retention time
110×10^3	9.68
34.5×10^3	10.61
17.5×10^3	11.41
8.5×10^3	12.37
4×10^3	12.91
1.8×10^3	13.64

0022–2461/87 $03.00 + .12

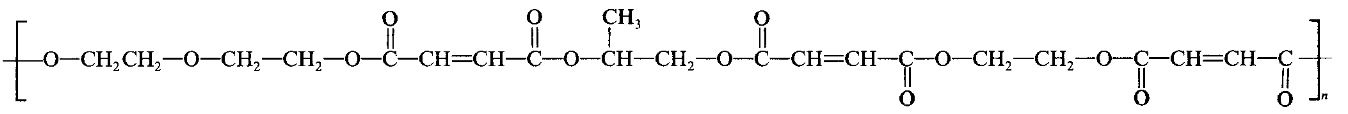
402/35 Copolymer of maleic anhydride and adipic acid with propylene glycol, 2-ethyl-2-(hydroxymethyl)-1,3-propandiol and 2,2-dimethyl-1,3 propandiol



549/160 Copolymer of maleic and phthalic anhydrides with ethylene glycol and dipropylene glycol



318/19 Copolymer of maleic anhydride with ethylene glycol, propylene glycol, and diethylene glycol



$$\left[\mathrm{-O-CH_2CH_2-O-CH_2-CH_2-O-\overset{O}{\overset{\|}{C}}-CH=CH-\overset{O}{\overset{\|}{C}}-O-\overset{CH_3}{\overset{|}{C}H}-CH_2-O-\overset{O}{\overset{\|}{C}}-CH=CH-\underset{O}{\underset{\|}{C}}-O-CH_2-CH_2-O-\underset{O}{\underset{\|}{C}}-CH=CH-\underset{O}{\underset{\|}{C}}-} \right]_n$$

363/27 Copolymer of maleic and phthalic anhydrides with ethylene glycol and diethylene glycol

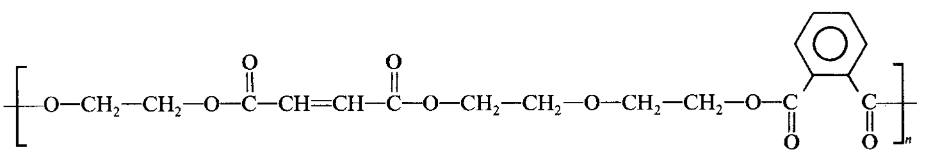


Figure 1 Molecular structures of the resins.

2.2. Wettability

The evaluation of the wettability of a monofilament by a liquid resin is usually made by the measurement of the contact angle θ between the fibre and the resin. It is well known that wettability improves as the θ angle tends to zero; for $\theta = 0$ optimal wettability values are reached (Fig. 2). Many methods are known for the measurement of the contact angle for plane substrates, and the values obtained are reproduceable [4]. On the other hand, for cylindrical substrates, the contact angle is difficult to measure, owing to the sharp variation in slope in the vicinity of the point of contact between the surface of the liquid and the fibre: this implies a wide spreading of the experimental values

TABLE II Properties of the resins

Properties	Resin type			
	318/19	363/27	402/35	549/160
Acid number (mg KOH g^{-1}) (for the solid resin)	35	37	38	36.9
Solid content (%)	65.8	59.6	68	70.4
Brookfield viscosity at 25° C (mPa sec)	1560	800	1140	2720
Cohesive energy density (*CED*)				
Calculated values (J cm^{-3})	478	485	491	480
Surface tension γ				
Calculated values (mJ m^{-2})	45.8	46.3	46.7	46.0
Degree of unsaturation (mol kg^{-1})	6.1	4.5	5.4	4.3
$\bar{M}_n$	2.2×10^3	2.5×10^3	2.5×10^3	2.4×10^3
$\bar{M}_w$	14.6×10^3	9.8×10^3	10.2×10^3	16.1×10^3
$\bar{M}_z$	153×10^3	44×10^3	33×10^3	170×10^3
$\bar{M}_w/\bar{M}_n$	6.7	3.9	4	6.7

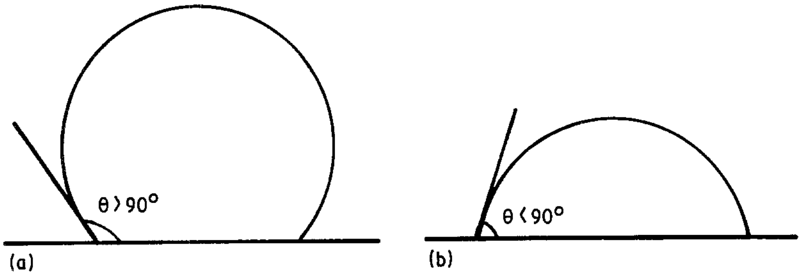


Figure 2 Wettability profiles of a drop: (a) poor wetting power, (b) good wetting power.

[5]. Moreover, the real contact angle θ may possibly be confused with the α angle, which is easier to measure, and which gives a higher slope variation, taking place immediately after the θ angle [6] (Fig. 3a). The influence on the wettability of the formulation of the resin, of its styrene content and of the type of sizing, was investigated through measurements of contact angles by optical microscopy with the tangent method. By this method we observed the profile of single drops of resin on the fibre under testing, and we measured both θ and α contact angles of the resin to the fibre. In order to improve the method we operated as follows:

(i) The fibre, extracted from a strand, was placed on a metal stand in order to avoid resin/fibre/microscopy-glass interactions (Fig. 4).

(ii) To minimize gravitational effects and obtain perfectly symmetrical drops, microdrops were made with a capillary; in this way we were able to obtain many drops of comparable size.

(iii) Drops within a limited size range were measured.

Experimental conditions were as follows: a single filament was placed on a metal stand and observed by means of an optical microscope in order to establish the uniformity of the size. Then, with the capillary, a drop of resin was poured on to the filament, repeating this operation until the desired size of drop had been obtained. After 10 min the drops were in a stationary state, optical photomicrographs of all the drops were then made. From each photogram, suitably enlarged, the contact angles were measured.

At the same time, in order to show possible correlations between the θ angle and other parameters, the length and the major diameter of the drop, and two other data were measured: the α angle, and the axial and equatorial lengths, found by measuring the distance between the intersection points of the prolongation of the α angles, respectively, parallel and perpendicular to the fibre (Fig. 3b).

2.3. Solubility of the sizing for the glass fibres

It is well known that glass fibres are sized with mixtures of various products, including: filmformers, lubricants, antistatic agents, plasticizers and coupling agents (silanes). Glass fibres are produced with sizings at different solubility levels in styrene or in unsaturated polyester resins dissolved in styrene. Other studies have tried to correlate the solubility of the sizing and the mechanical properties of SMC-type materials.

We carried out tests of solubility in styrene at 25° C with the two types of glass fibres covered by this study, and measured weight loss against time of the fibres immersed in styrene. Results are given in Fig. 5. From now on, in the figures and the text, 951 glass, whose sizing has a low solubility in styrene, is called "insoluble glass", whereas P233, which has a very soluble sizing, is called "soluble glass".

2.4. Mechanical properties

SMC laminates were made from the resins under test and the two different types of glass. In these laminates we tried to maintain the glass content around 51 to 53% by weight. The thickening of the matrices was followed against time by measuring the viscosity with Brookfield RVF and HBR rotational viscometers. When values of approximately 30 kPa sec were reached, the laminates were moulded at 150° C with a pressure of $12\,\mathrm{MN\,m^{-2}}$ for 3 min. From these laminates test pieces were made for mechanical characterization. The results of these evaluations are given in Table III.

A differential scanning calorimetry (DSC)

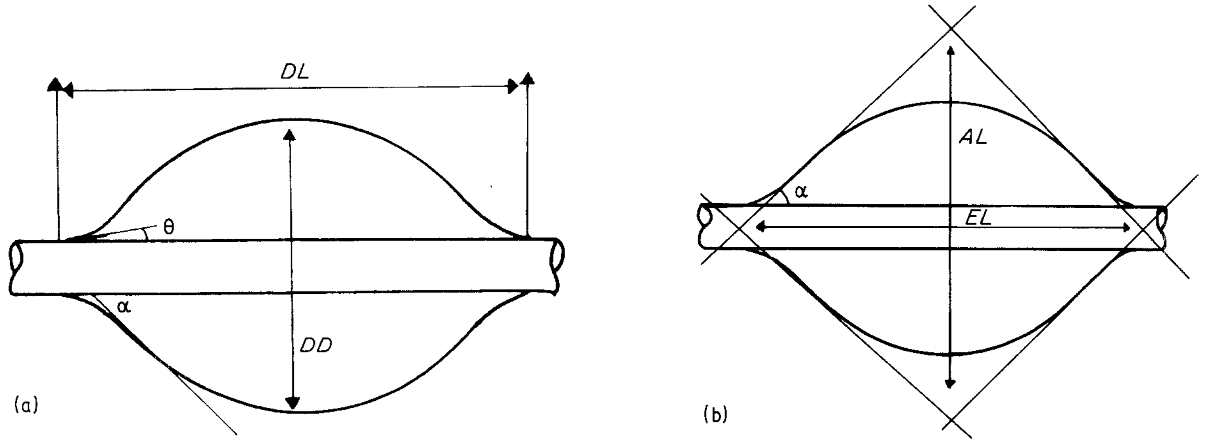


Figure 3 (a) Cross-section of a drop and parameters: contact angle θ; angle α; *DL*, drop length; *DD*, drop diameter. (b) Cross-section of a drop parameters: *EL*, equatorial length; *AL*, axial length; angle α.

TABLE III Properties of SMC made with the resins of Table I

Properties	Resin type							
	318/19		363/27		402/35		549/160	
Tensile strength ($MN\,m^{-2}$)	142 ± 9	91 ± 16	168 ± 9	139.5 ± 10	137 ± 10	91.3 ± 21	174 ± 12	133 ± 7
Flexural strength ($MN\,m^{-2}$)	288 ± 13	208 ± 57	311 ± 17	246 ± 16	279 ± 13	254 ± 33	283 ± 15	260 ± 19
Izod impact ($J\,m^{-1}$)	1589 ± 147	1442 ± 382	1471 ± 147	1658 ± 363	1481 ± 294	1579 ± 255	1619 ± 98	1618 ± 265
Specific gravity ($kg\,dm^{-3}$)	1.68	1.64	1.68	1.65	1.65	1.62	1.64	1.65
Glass fibre:								
Amount (%)	53	52	53	52	52	51	52	51
Type	A	B	A	B	A	B	A	B
Brookfield viscosity at 25° C (kPa sec)	30	30	33	33	32	32	30	30

Formulation: Resin 96.16%, MgO 2.88%, Catalyst (terbutylperbenzoate) 0.96%.
Moulding conditions: $T = 150°\,C$ $P = 12\,MN\,m^{-2}$ $t = 3\,min$.
Glass fibre types: Glass (A): soluble sizing (P233), Glass (B): insoluble sizing (951)

investigation confirmed that the residual polymerization heat (ΔH_{res}) of the specimens was practically zero.

2.5. Scanning electron microscopy

The fracture surfaces of the specimens, broken by tensile and flexural tests, were examined using scanning electron microscopy (SEM) to evaluate the influence of the resin and sizing structure on the fibre/matrix adhesion. The surfaces were previously metallized with a sputtering polaron with a layer of gold-palladium alloy and then observed with a Philips SEM 501 scanning electron microscope.

3. Results and discussion

3.1. Wettability

Table IV shows the values of the contact angles θ, the α angles, the drop length/drop diameter ratios (*DL*/*DD*) and the equatorial length/axial length ratios (*EL*/*AL*). Figs 6a to d show, for each of the four resins studied, the trend of θ as a function of styrene level for each type of glass fibre. We must point out that, for relatively low styrene concentrations (30%), owing to the high viscosity of the solutions, it has not always been possible to obtain reliable values for the contact angles, which in these cases have not been shown in Table IV.

The examination of the patterns of Figs 6a to d shows the following:

(a) The contact angle θ, formed at the glass/resin interface, decreases as the styrene content increases. This applies to all the resins studied and to both types of glass.

(b) The angle θ, for all the resins at different dilutions, is, for the soluble glass, always lower than the corresponding angle with the insoluble glass.

TABLE IV Values of: contact angle θ, α angle, drop length/drop diameter ratio (*DL*/*DD*) and equatorial length axial length ratio (*EL*/*AL*) as a function of styrene level, glass and resin type

Styrene (%)	Insoluble glass				Soluble glass			
	θ angle	α angle	*DL*/*DD* ratio	*EL*/*AL* ratio	θ angle	α angle	*DL*/*DD* ratio	*EL*/*AL* ratio
Resin 402/35								
60	21 ± 2.2	40 ± 1.5	1.67 ± 0.05	1.20 ± 0.05	18 ± 1.1	38 ± 1.5	1.76 ± 0.03	1.30 ± 0.05
50	22 ± 2.8	37 ± 1.9	1.73 ± 0.04	1.33 ± 0.07	18 ± 1.1	41 ± 2.0	1.63 ± 0.02	1.15 ± 0.05
40	26 ± 1.3	39 ± 0.9	1.60 ± 0.02	1.24 ± 0.03	21 ± 2.8	39 ± 2.7	1.69 ± 0.05	1.25 ± 0.07
30					25 ± 2.0	41 ± 1.8	1.60 ± 0.03	1.15 ± 0.05
Resin 549/160								
60	21 ± 1.4	38 ± 3.8	1.75 ± 0.08	1.27 ± 0.05	20 ± 2.2	39 ± 2.1	1.09 ± 0.04	1.24 ± 0.05
50	22 ± 3.1	43 ± 1.6	1.58 ± 0.04	1.07 ± 0.06	21 ± 3.3	41 ± 1.8	1.62 ± 0.04	1.16 ± 0.07
40	23 ± 1.7	38 ± 2.4	1.67 ± 0.05	1.39 ± 0.10	22 ± 1.5	40 ± 1.5	1.63 ± 0.04	1.20 ± 0.02
30	28 ± 1.4	43 ± 2.3	1.55 ± 0.02	1.10 ± 0.06	27 ± 0.4	46 ± 1.6	1.48 ± 0.04	0.96 ± 0.06
Resin 318/19								
60	20 ± 2.5	38 ± 1.6	1.74 ± 0.04	1.29 ± 0.07	17 ± 1.8	32 ± 2.2	1.88 ± 0.05	1.61 ± 0.11
50	22 ± 2.2	41 ± 1.5	1.66 ± 0.04	1.19 ± 0.05	20 ± 1.7	38 ± 1.8	1.71 ± 0.03	1.31 ± 0.07
40	23 ± 2.1	37 ± 2.0	1.73 ± 0.05	1.33 ± 0.07	22 ± 1.7	38 ± 2.9	1.68 ± 0.05	1.27 ± 0.11
30					25 ± 0.8	37 ± 1.7	1.73 ± 0.08	1.32 ± 0.06
Resin 363/27								
60	19 ± 2.6	40 ± 2.7	1.72 ± 0.04	1.20 ± 0.10	18 ± 2.2	36 ± 1.7	1.80 ± 0.04	1.41 ± 0.01
50	22 ± 4.1	35 ± 2.7	1.75 ± 0.05	1.26 ± 0.11	19 ± 1.7	40 ± 2.0	1.68 ± 0.04	1.20 ± 0.06
40	26 ± 2.0	43 ± 2.3	1.55 ± 0.04	1.08 ± 0.06	19 ± 1.5	38 ± 1.4	1.75 ± 0.04	1.30 ± 0.05
30					21 ± 1.6	37 ± 1.7	1.70 ± 0.03	1.36 ± 0.06

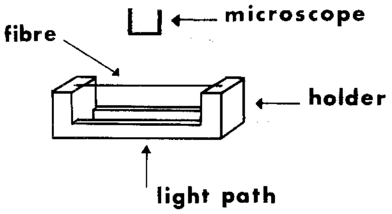


Figure 4 Schematic set-up for the experimental evaluation of drop parameters.

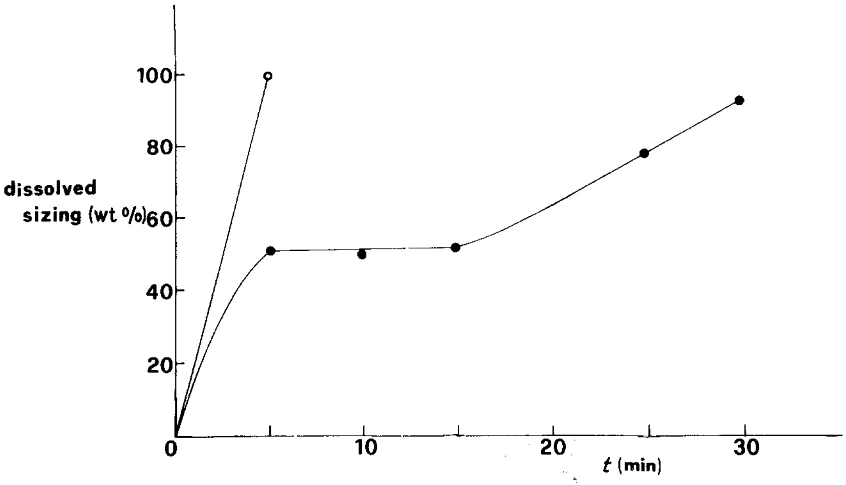


Figure 5 Solubility in styrene of different sizing. (○) soluble glass P233, (●) insoluble glass 951.

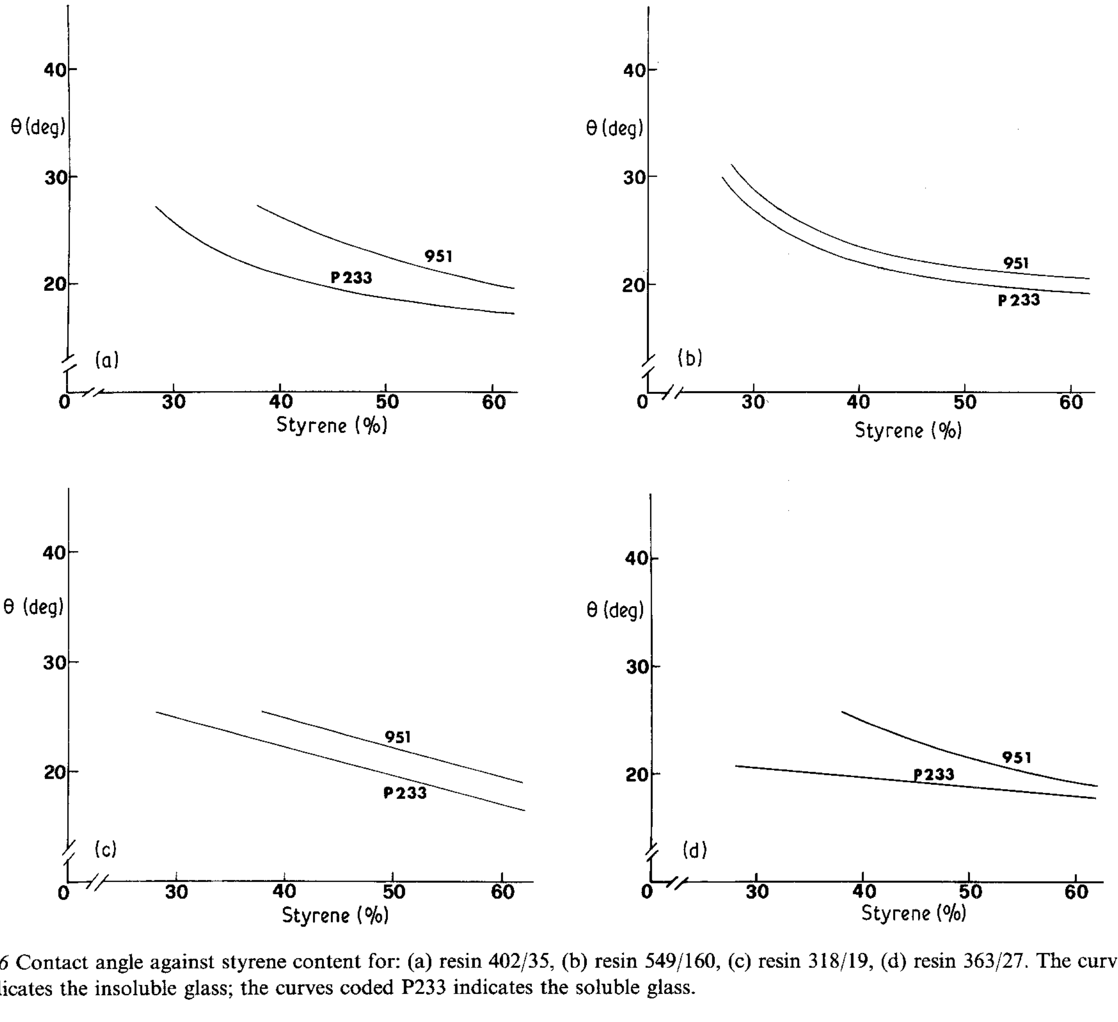


Figure 6 Contact angle against styrene content for: (a) resin 402/35, (b) resin 549/160, (c) resin 318/19, (d) resin 363/27. The curves coded 951 indicates the insoluble glass; the curves coded P233 indicates the soluble glass.

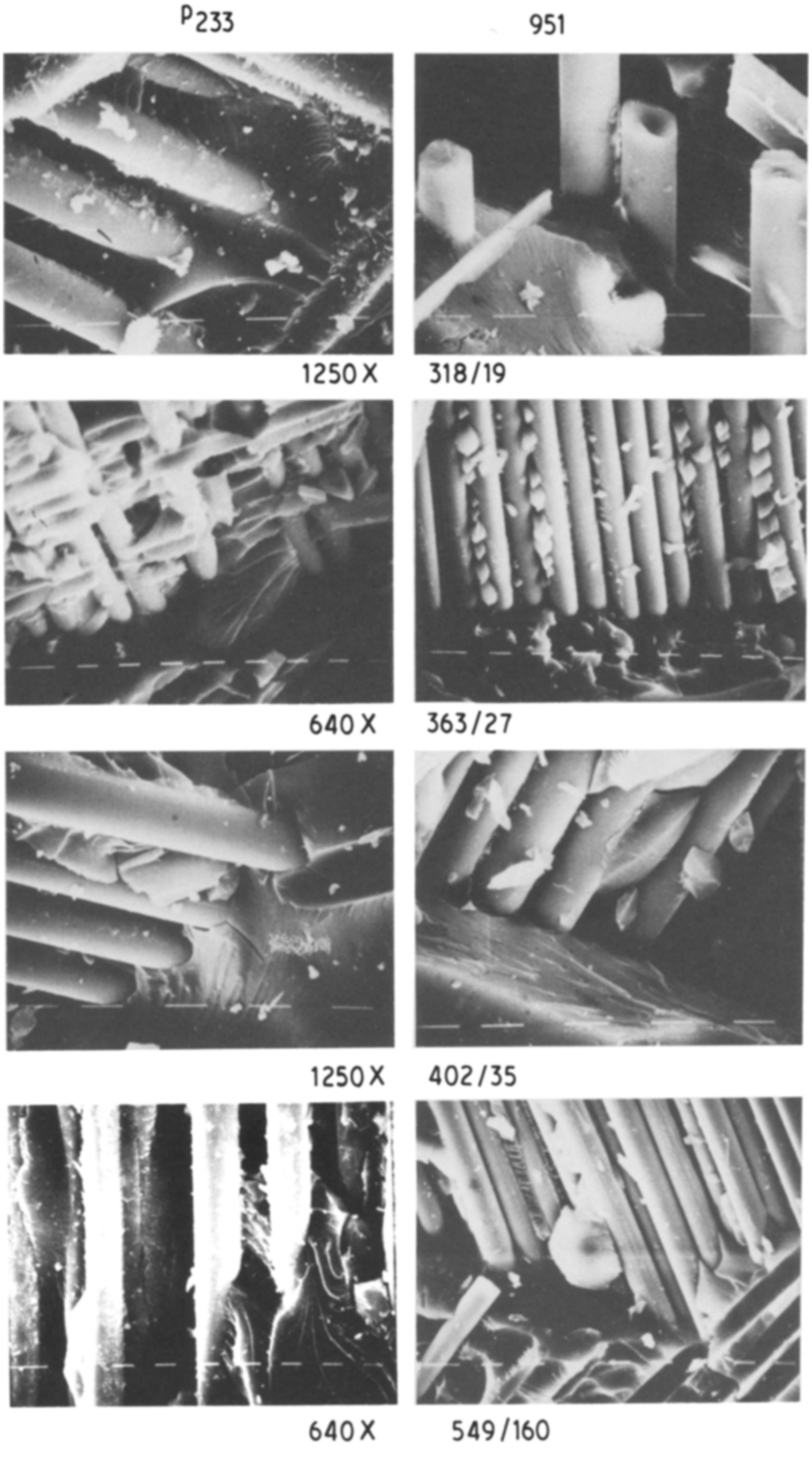


Figure 7 Electron photomicrographs of fracture surfaces of laminates broken in tensile strength tests.

(c) At relatively low styrene levels, it appears that the resin structures do not have much influence on the θ angle, both for the insoluble and of the soluble glass.

(d) At relatively high styrene levels, the values of the θ angles tend to be very close, both for the soluble and for the insoluble glass.

(e) The values of the α angle, the drop length/drop diameter ratios (DL/DD) and the equatorial length/axial length ratios (EL/AL) cannot be correlated with the styrene levels. Only glass P233 shows an almost regular average increase of such parameters, when styrene level is increased. This is in accordance with the theory that a drop with good wettability, spreading on the fibre, has a length/diameter ratio higher than that of a drop with poor wettability.

3.2. Scanning electron microscopy

Figs 7 and 8 show the electron photomicrographs of

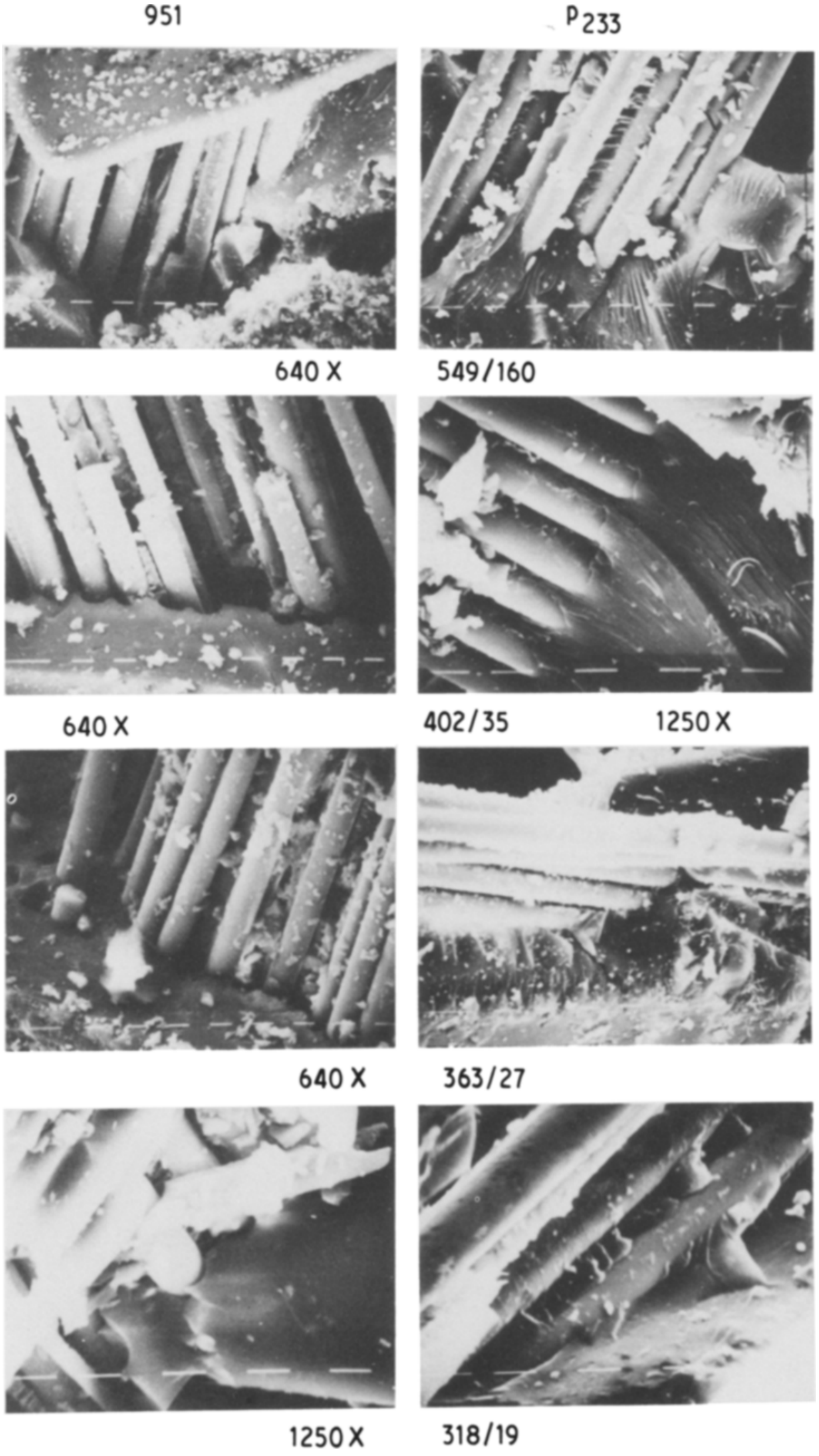


Figure 8 Electron photomicrographs of fracture surfaces of laminates broken in flexural strength tests.

the fracture surfaces of specimens used for testing mechanical properties (see Section 2.4). It can be noticed that, on average, the adhesion in the specimens reinforced with soluble glass (P233) is better than with the insoluble type (951); this difference is more noticeable on the fracture surfaces of the specimens broken in flexural strength tests.

As regards the performance of the resins reinforced with the same type of glass fibre, from an examination of the photomicrographs of the surfaces obtained in tensile strength tests, it is possible to list the resins in decreasing order of adhesion, as follows:

$$549/160 \geqslant 318/19 > 363/27 > 402/35$$

The same trend was observed with the insoluble glass, even if the differences between the resins 549/160 and

318/19, and the resins 363/27 and 402/35, are less noticeable.

From the data given in Table II, it appears that the adhesion property of the various resins might be correlated with the calculated values of cohesive energy density (*CED*). It would be advisable to check this correlation by synthesizing resins with a wider range of *CED* values.

3.3. Mechanical properties

The examination of the mechanical properties of the four resins reinforced with soluble glass (P233) and insoluble glass (951) shows, in general, a better performance of the resins reinforced with soluble glass. This aspect is shown above all by tensile and flexural strength tests, in agreement with data in the literature [7].

4. Conclusions

The following conclusions can be drawn from the present work:

1. The method is quite complicated for measuring the contact angle θ at the interface between the glass fibre and the unsaturated polyester matrix in styrene, but the experimental values obtained in this way fall into a very narrow range, unlike the values often given in technical literature.

2. The wettability of the glass fibres by the unsaturated polyester resins in styrene solution, evaluated in composite materials such as SMC and BMC, depends mainly on the nature of the sizing of the fibres and on the styrene level of the resin. The styrene-soluble sizings give contact angles lower than those of the insoluble sizings, and consequently the glass fibres sized with soluble products have a better wettability.

3. The influence of the chemical structure of the resins on the θ angle appears less strong; nevertheless, at least for the resins investigated in the present work, a certain correlation appears between the cohesive energy density (*CED*) and the adhesion properties.

4. Finally, electron microscopy investigations show that, by improving the adhesion between the glass fibres and the polyester matrix, and improvement is also obtained in the mechanical properties (such as tensile and flexural strength) of reinforced materials.

References

1. W. D. BASCOM and J. B. RAMANO, *Ind. Eng. Chem. Prod. Res. Develop.* 7 (1968) 172.
2. R. J. GOOD, *Poly. Sci. Tech. – Adh. Sci. and Tech.* **9A** Lieng-Huang Lee (1975) 107.
3. D. W. VAN KREVELEN and P. J. HOFTYZER, *"Properties of Polymers"*, (Elsevier, New York, 1976).
4. S. WU, "*Polymer interface and adhesion*" (Marcel Dekker Inc., New York and Basel, 1982).
5. K. WOLF, R. E. FORNES, J. D. MEMORY and R. D. GILBERT, *Chem. Phys. Carbon* **18** (1982) 93.
6. J. I. YAMAKI and Y. KATAYAMA, *J. Appl. Polym. Sci.* **19** (1975) 2897.
7. R. BURNS, "*Polyester Molding Compounds*", (Marcel Dekker Inc, New York and Basel, 1982).

Received 16 June
and accepted 18 August 1986