# Analysis of Glass Fibre Sizing

**H. N. Petersen*,**
Department of Micro- and Nanotechnology,
Technical University of Denmark,
Ørsteds Plads Building 345E,
DK-2800 Kgs. Lyngby, Denmark.

**Y. Kusano, P. Brøndsted,**
Department of Wind Energy,
Section of Composites and Materials Mechanics,
Technical University of Denmark, Risø Campus,
Frederiksborgvej 399, DK-4000 Roskilde, Denmark.

**K. Almdal**
Department of Micro- and Nanotechnology,
Technical University of Denmark,
Ørsteds Plads Building 345E, DK-2800 Kgs. Lyngby, Denmark.
**\***Email: hnpe@dtu.dk

## Abstract

Glass fibre reinforced polymer composites are widely used for industrial and engineering applications which include construction, aerospace, automotive and wind energy industry. During the manufacturing glass fibres, they are surface-treated with an aqueous solution. This process and the treated surfaces are called sizing. The sizing influences the properties of the interface between fibres and a matrix, and subsequently affects mechanical properties of composites.

In this work the sizing of commercially available glass fibres was analysed so as to study the composition and chemical structures. Soxhlet extraction was used to extract components of the sizing from the glass fibres. The glass fibres, their extracts and coated glass plates were analysed by Thermo-Gravimetric Analysis combined with a mass spectrometer (TGA-MS), and Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy. Commercially available silane coupling agents were also analysed by ATR-FTIR in order to identify components in the sizing. The results indicate that the analysed fibres have both bonded and physisorbed sizing, containing a film former and a coupling agent.

## 1.0. Introduction

Fibre reinforced composites are materials that consist of components with different mechanical properties; a matrix and a reinforcement. Usually the reinforcement is mechanically strong and stiff so that introducing it into the matrix will yield a new type of material that has the elastic properties often associated with the matrix and the mechanical strength from the reinforcement. The matrix can be ceramics, metal, and more often thermosetting and thermoplastic polymers. The reinforcements are generally fibres made of, for example, glass, carbon, cellulose, and polyethylene. The outstanding advantage of using fibre reinforcement is efficient stress transfer between the fibre and the matrix so that the composite can carry more load than the components alone[1]. Carbon fibres are superior to other fibres in stiffness and strength, but the raw material and manufacturing process are much more expensive and complicated than glass fibres. This is certainly the reason why around 95% of fibre reinforced composites are made with glass fibres[3]. Glass fibres are commonly used in composite materials for wind turbine blades, where high stiffness is one of crucial properties that glass fibre reinforced composites can fulfill[1].

During the manufacturing of glass fibres a surface treatment called sizing is carried out. This is a necessary step to ease the handling and improve the performance of glass fibres. Otherwise they will be very brittle and fragile. The sizing is considered crucial for the mechanical properties of composites as it is believed that sizing affects the adhesion between glass fibres and a matrix. Despite the importance of sizing, however, little is known about the behaviour and effect of the sizing. In particular, dedicated study on the interface between a glass fibre and a matrix is rarely reported in literature[2].

Sizing consists of a number of components such as a silane coupling agent, a film former, an antistatic agent, and a lubricant. The role of the film former is to protect glass fibres during manufacturing and handling, while the silane coupling agent is considered to be primarily responsible for the adhesion between glass fibres and a matrix[3]. It is reported that approximately 10 wt.% of sizing is a silane coupling agent and around 79 wt.% is a film former[4]. The lack of information about the exact chemical composition of sizing makes a determination of reactions and an overall structure difficult. So far, a simplified structure has been suggested, consisting of a mixture of silane polymers bonded and/or physisorbed to the fibre surface and a film former entangled in the silane network [5,6]. Without a known full recipe, most experiments associated with sizing are conducted with focus on one component: the silane coupling agent and its sol-gel reaction with the glass surface.

The choice of a film former and a silane coupling agent depends highly on the type of matrix to be used. Film formers typically contain polyurethane, polyvinyl acetate, polyester, polyalkene, and/or epoxy resins[7,8]. Organosilanes are obvious choice for coupling agents as they have an inorganic silica part and an organic functional group that can react with the glass surface and the matrix, respectively[9,10]. A long list of organosilanes has been investigated for their effect on adhesion in composite materials[11]. Organosilanes with an amino or epoxy functionality have been suggested to work especially well with epoxy matrices[4,10].

In this paper analysis of glass fibre surfaces and sizing is presented. Sizing extracted from the surface of glass fibres is compared to commercially available organosilanes and their coatings on glass plates identify common functional groups.

## 2.0. Experimental Methods

The fibres used in this investigation were E-glass fibres (tex number of 1200, 17 μm diameter of monofilament, moist content ≤ 0.10% and sizing content in the range of 0.45-0.70%) supplied by Jushi (Chengdu, China).

The soxhlet extraction was based on the work of Tanoglu et al. [12]. Similar extractions have been conducted [3,5,13]. The extraction was carried out with approximately 10 g of fibre bundles with a length of around 10 cm by soxhlet extraction in 200 mL spectroscopic grade acetone (Sigma-Aldrich, Steinheim, Germany) for 24 h and subsequently left to dry for at least 24 h. Acetone is assumed to be unreactive when used as a solvent for the extraction of sizing. The fibres were weighed before and after extraction in order to calculate the amount of extracted sizing. The extract was concentrated to a volume of about 20 mL.

Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy was conducted on a Perkin Elmer spectrum 100. The analyses were performed from 4000 to 800 cm$^{-1}$ with a resolution of 4 cm$^{-1}$ and 16 scans per sample. Extracted samples were dissolved in acetone before placed on the ATR crystal. The acetone was subsequently evaporated on the ATR crystal prior to analysis.

Thermo-gravimetric Analysis with subsequent Mass Spectrometry (TGA-MS) analysis was conducted on a STA 409 CD with a QMS 403 D both from Netzsch. The tests were performed with a heating rate of 10°C/min from room temperature to 600°C in air. The glass fibres were cut to small pieces and approximately 100 mg of them were added to a crucible. The extracts dissolved in acetone were prepared by adding a few droplets to the crucible and left the acetone to evaporate. This was repeated until a mass of a residual solid became at least 14 mg.

Two organosilanes were used as reference materials to help identify characteristics in ATR-FTIR results: 3-aminopropyltrimethoxysilane, abbreviated APTMS (97%) and 3-glycidoxypropyltrimethoxysilane, abbreviated GPTMS (≤ 98%) both from Sigma-Aldrich (Steinheim, Germany).
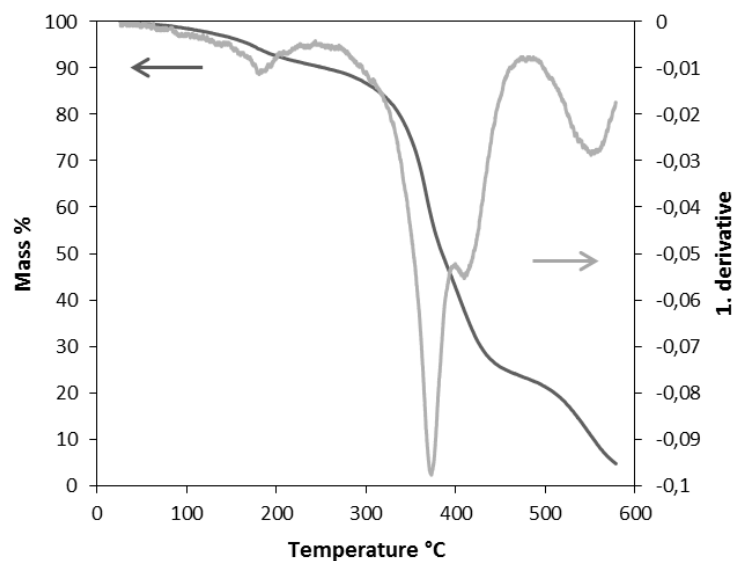
Glass plates (Plain Micro Slides, 2947-75x25, from Corning Incorporated, USA) were cleaned prior to the dip-coating by sonication in acetone for 2 x 5 minutes. The plates were dip-coated by submerging them in a boiling 1v/v% APTMS or GPTMS aqueous solution for 5 minutes. The coated plates were subsequently dried at 130 °C for 3h.

## 3.0. Results and Discussion

### 3.1. Extraction of sizing

Extraction of sizing was performed in combination with a burn-off experiment to evaluate the amount of sizing and its distribution between sizing removable by burning and sizing extractable by a solvent[14]. The same fibres, as used in the present work, were analysed and they were found to contain an amount of removable sizing of 0.63 ± 0.01 wt.% where the extractable part constituted 80-90% of the amount of the removable sizing, both values are similar to ones found in literature[12,14].

It is noted that the acetone extraction can remove the physisorbed parts of sizing e.g. film former and free organosilanes. The weight measurements in the present work indicate that the mass loss after the extraction was 0.64 ± 0.08 wt.% of the total mass of the as-received fibre. This looks a somewhat higher value than the previously measured value of 0.50 ± 0.10 wt.%[14], but still within standard deviation. The difference can be explained by the high variation in the distribution of sizing along the fibres[15] as only around 10 cm of fibre bundle samples were used for each measurement.

**Fig. 1:** TGA graph for an extracted sizing sample displaying the mass % and the first derivative of the mass % with separate axis as a function of temperature

The application of sizing is a rapid process conducted by dragging the fibres across a roll resulting in a thickness of the sizing layer in the range of 1nm-1μm[5,15]. After the extraction the fibres were observed to be softer and electrostatically charged, which indicate the removal of antistatic agents and the film former.

The fibres were analysed by ATR-FTIR before and after extraction[14]. The spectra obtained from fibres after extraction displayed no absorption besides from Si-O-Si, while the spectra from fibres before extraction had several other bands[14]. The absence of bands was interpreted as a complete extraction. The extract was also analysed and is used in the later analysis of coated glass plates.
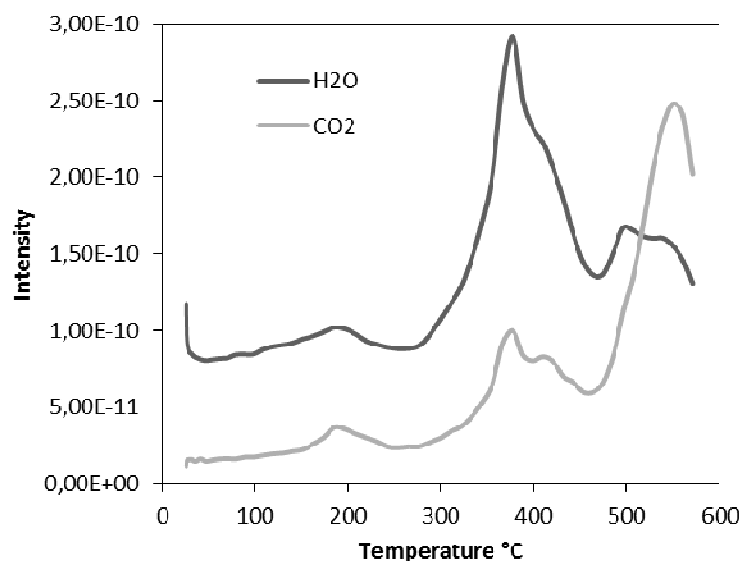
### 3.2. TGA-MS analysis

TGA-MS was conducted on the extract by soxhlet in acetone as shown in Figs. 1 and 2 and on as-received sized fibres as shown in Figs. 3 and 4. The analysis of both sized fibres and extracted sizing were repeated three times. All the samples showed the same peaks at the same temperatures. One of the three samples is displayed here. The analysis of the mass loss is carried out based on the first derivative as the mass losses can be difficult to distinguish visually.

The graph in Fig. 1 exhibits a major peak at 372 °C with a shoulder peak at 409 °C and a peak at 551 °C. The first peak could correspond to a film former as polyurethane or uncured epoxy resin [8]. The shoulder peak can be of a similar polymer type since film formers are often a mixture of different polymers. The third peak can be assigned to organosilanes with higher thermal stability than γ-aminopropyltriethoxy silane [8]. The mass losses of first peak and the shoulder peak together add up to around 67% of the total mass loss in the temperature interval analysed. The mass loss of the third peak accounts for approximately 19% of the total mass loss. This distribution is not very far from the reported one between film former and silane coupling agent of 79 and 10%, respectively [4].

In Fig. 2 there is a clear difference in the intensities of $H_2O$ and $CO_2$ between the two major peaks at approximately 390 °C and 550 °C, indicating that the degenerated components at these temperatures differ significantly.

**Fig. 2:** The MS spectra for an extracted sizing sample displaying m/e equal to $H_2O$ (m/e=18) and $CO_2$ (m/e=44) as a function of the temperature corresponding to the temperature of the TG analysis at the time of measurement

TG measurements confirm that the mass loss of the fibres were in the range of what was found with the burn-off experiment previously presented[14]. 0.59% ± 0.1. The standard deviation is higher due to the very small samples for TGA compared to the 10 grams of sample in the burn-off experiment.
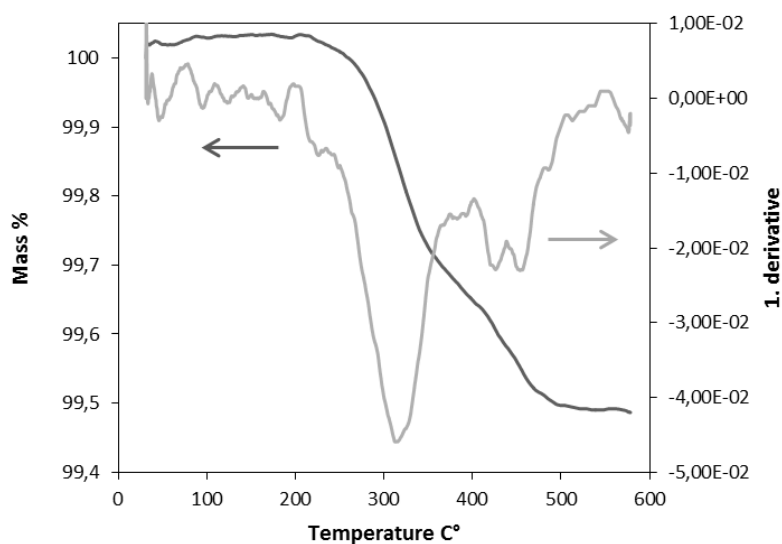
The mass loss and its 1st derivative of the glass fibres are shown in Fig. 3. At 320 °C, dominant mass loss of approximately 63% of the total mass loss is observed, most likely corresponding to a film former. Furthermore, mass loss at 420 and 460 °C is detected with a magnitude of around 35% of the total mass loss that could correspond to organosilanes[8]. It is noted that the peaks are located at lower temperatures than the ones in Fig. 1. A similar shift of the temperatures is reported in literature[8]. The explanation of the shift can be the difference in sample size and concentration, where extract samples were around 15 mg of sizing and fibre samples were around 100 mg but with only around 0.6 wt.% sizing. Furthermore the surface-volume ratio is very different for the two types of samples.

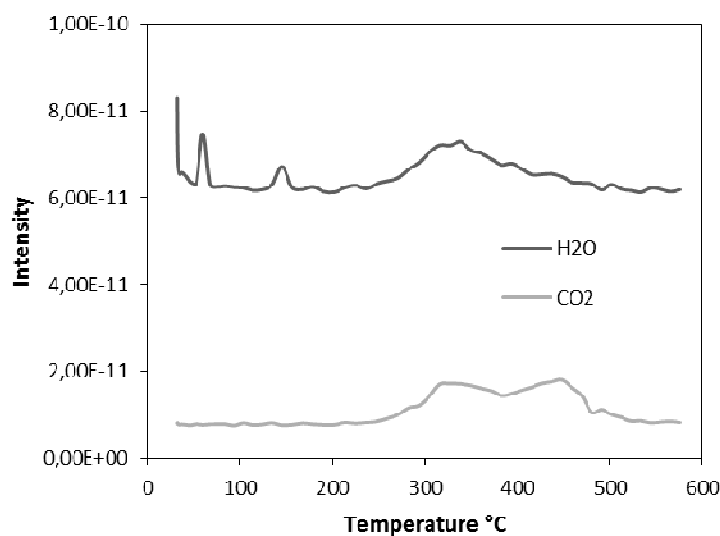The mass loss distribution between the peaks is, however, less convincingly similar to the reported values in literature than the ones found from the extract analysis. This can be explained by the small amount of sizing in the fibre samples making the characterization directly on the fibres very difficult and less accurate. Despite the less accurate values, the TG curve obtained is still similar to the one from the extract analysis, indicating that the results are in some extent reproducible[8,16]. Fig. 4 shows the corresponding MS spectra of the mass-to-charge ratio equivalent to $H_2O$ and $CO_2$ at the temperatures corresponding to the sample at the time of degradation. There are broad peaks of $H_2O$ and $CO_2$ centred at around 320 °C. The $CO_2$ spectrum shows another broad peak over 400 °C, while the $H_2O$ spectrum does not contain a noticeable peak at this range, which can be caused by the low sensitivity of the measurement and/or partial oxidation of silicone groups[16].

### 3.3. ATR-FTIR analysis

Literature indicates that the organosilanes with an amino or epoxy group are commonly used in sizing for glass fibres aimed for epoxy resin based composites [2].

5

**Fig. 3:** TGA graph for a glass fibre sample displaying the mass % and the first derivative of the mass % with separate axis as a function of temperature
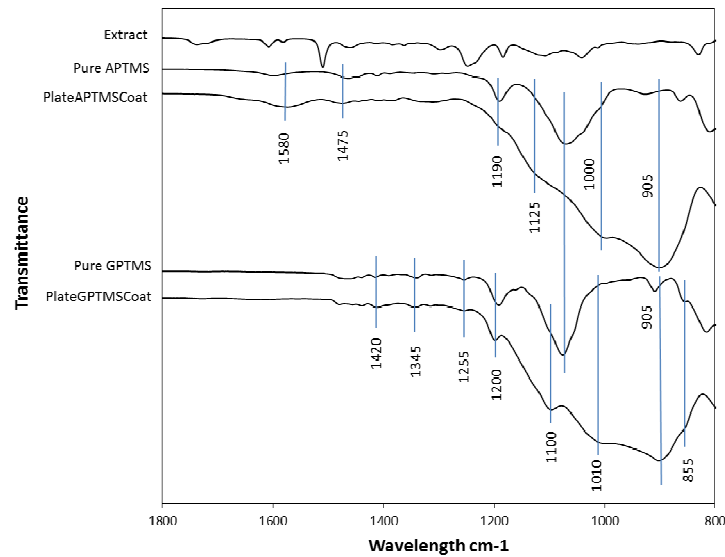


**Fig. 4:** The MS spectra of m/e equal to $H_2O$ (18) and $CO_2$ (44) as a function of the temperature corresponding to the temperature of the TGA analysis at the time of measurement

3-aminopropylsilane, 3-glycidopropylsilane, 3-aminoethylaminepropylsilane and chlorine-substituted aminosilane have been reported to enhance the adhesion between glass fibres and epoxy resin matrices[5,9,10]. Two organosilanes chosen for dip-coating were used as references in the IR analysis. FTIR spectra of the analysed plates and references are illustrated in Fig. 5. The sizing extracted from commercially available fibres was also analysed with ATR-

FTIR for comparison. The spectrum is also shown in Fig. 5.

The spectra are not shown in the range of 1800-4000 $cm^{-1}$ since only bands originated from stretching in N-H/O-H (bonded to C and/or Si) at 3200-3600 $cm^{-1}$ and stretching in C-H of CH, $CH_2$ and $CH_3$ (both in aromatic and aliphatic compounds) at 2965-2873 $cm^{-1}$ were detected in that range.

**Fig. 5:** FTIR spectra of glass plates coated with APTMS and GPTMS. The two organosilanes used are also shown as references as well as the spectrum recorded for the extracted sizing from the analysed fibres

The spectra from analysis of all the coated glass plates exhibit strong absorption from Si-O-Si bonds which obstruct other signals in the area around 900-1100 cm$^{-1}$. The Si-O-Si bonds give rise to a high and broad band since the amount of glass is much higher than the one of applied organosilane which makes it difficult to identify bands in the area.

Comparison of coated glass plates and the sizing from extraction clearly determines that the sizing is complex and contains more components than just organosilanes. Some of the bands that are associated with an epoxy resin were detected in the extract: bands at 1248 and 1183 cm$^{-1}$. Similar bands were found in the GPTMS coated glass plates: 1255 and 1200 cm$^{-1}$. These bands are slightly shifted compared to the reference. The APTMS coated glass plates exhibits bands that are slightly shifted compared to the reference: 1580 and 1475 cm$^{-1}$ which are assigned scissor vibration in N-H and deforming vibration in CH$_2$-NH, respectively. The spectra of both the pure APTMS and GPTMS references display very strong broad bands with centre around 1070-1080 cm$^{-1}$ which seems to have shifted to 1100-1125 cm$^{-1}$ for the coated samples. The bands are less visible as the large band from absorption of the Si-O-Si bonds covers this area[4,7,8,13,17-19]. The shifting of some of the bands detected on the coated glass plates could indicate that the organosilanes are not only physisorbed to the glass surfaced but rather bonded.

## 4.0. Conclusion

- The analysed fibres contained an extractable amount of sizing of 0.63 wt.% which is considered common in commercially glass fibres.
- Samples of 10 cm fibre bundles might be too short for definitive determinations of the sizing content of glass fibres due to large variation of the amount of sizing along the fibres.
- Thermo-gravimetric analysis indicated the presence of two major components with different decomposition temperatures: film

7

former and organosilanes with the distribution of 67 and 19%, respectively.

- Similarities between sizing extract and glass plates coated with organosilanes were detected by ATR-FTIR. Some bands were shifted compared to references indicating a change in the bonds.

## 5.0. Acknowledgements

## 6.0. References

1. Brøndsted, P.; Lilholt, H.; Lystrup, A.; Annu. Rev. Mater. Res., 2005, vol. 35, p. 505.
2. Thomason, J.L.; Glass Fibre Sizings – A Review of the Scientific Literature. University of Strathclyde, Scotland, 2012.
3. Plonka, R.; Mäder, E.; Gao, S.L.; Bellmann, C.; Dutschk, V.; Zhandarov, S.; Compos. Part A-Appl. S., 2004, vol. 35, p. 1207.
4. Gorowara, R.L.; Kosik, W.E.; McKnight, S.H.; McCullough, R.L.; Compos. Part A-Appl. S., 2001, vol. 23, p. 323.
5. Jones, F.R.; J. Adhes. Sci. Technol., 2010, vol. 24, p. 171.
6. Liu, X.; Thomason, J. L.; Jones, F.R.; J. Adhes., 2008, vol. 84, p. 322.
7. Dwight, D.W.; Glass Fiber Reinforcements. In: Comprehensives Composite Materials, edited by Kelly A., Zweiben C. (Elsevier, Amsterdam), vol. 1, p. 231, 2000.
8. Rudzinski, S.; Häussler, L.; Harnisch, Ch.; Mäder, E.; Heinrich, G.; Compos. Part A-Appl. S., 2011, vol. 42, p.157.
9. Plueddemann, E.P.; Int. J. Adhes. Adhes., 1981, vol. Oct., p. 305.
10. Shokoohi, S.; Arefazar, A.; Khosrokhavar, R.; J. Reinf. Plast. Comp., 2008, vol. 27, p. 473.
11. Ivaschenko, E.A.; Technol. Polym. Comp. Mat., 2009, vol. 43, p. 511.
12. Tanoglu, M.; Ziaee, S.; McKnight, S.H.; Palmese, G.R.; Gillespie, J.W.; J. Mater. Sci., 2001, vol. 36, p. 3041.
13. Zhuang, R.-C.; Burghardt, T.; Mäder, E.; Compos. Sci. Technol., 2010, vol. 70, p. 1523.
14. Petersen, H.N.; Kusano, Y.; Brøndsted, P.; Almdal, K.; Proce. of the 34th Risø Int. Symp. on Mat. Sci., ed.: Madsen, B.; Lilholt, H.; Kusano, Y.; Fæster, S.; Ralph, B., p. 333, 2013.
15. Thomason, J.L.; Dwight, D.W.; Compos. Part A-Appl. S., 1999, vol. 30, p. 1401.
16. Dupont, A., Characterization of Silicones in Inorganic Polymers, Nova Science, ed.: De Jaeger, R. and Gleria, M., 2007.
17. Macan, J.; Ivanković, H.; Ivanković, M.; Mencer, H.J.; Thermochim. Acta, 2004, vol. 414 p. 219.
18. Öhman, M.; Persson, D.; Surf. Interface Anal., 2011, vol. 44, p. 133.
19. Salmon, L.; Thorminette, F.; Pays, M.F.; Verdu, J.; Compos. Sci. Technol., 1997, vol. 57, p. 1119.