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Adhesion activation of Twaron® aramid fibres studied with low-energy ion scattering and x-ray photoelectron spectroscopy

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The properties of the interphase between Twaron® aramid fibres and polymer matrix systems can be optimized by a surface treatment process of the fibres. In this work, x-ray photoelectron spectroscopy and low-energy ion scattering have been used to analyse the surface layers, whereas the adhesion was measured by a bundle pull-out experiment. From the results, we succeeded in establishing a relation between the surface treatment, the resulting chemical/elemental surface composition and the adhesion to an epoxy matrix. Copyright © 2001 John Wiley & Sons, Ltd.

INTRODUCTION

Polymeric fibres, such as poly (paraphenylene terephthalamide) ('aramid fibre'), are very suitable to reinforce high-performance composite materials because they combine a high specific modulus and strength with a high thermal resistance, high chemical inertia and low electrical conductivity. In order to transfer loads and stresses from matrix to fibre, the fibre–matrix interphase must be designed in such a way that optimal adhesion and composite mechanical properties are combined.

For this reason, Twaron® aramid fibres are 'adhesion activated' commercially by the application of an epoxy-based finish to their surface and subsequent curing thereof.[1–3] The resulting fibre surface has improved interfacial adhesion to, for example, epoxy and rubber matrices.[4,5] Better understanding of the adhesion mechanism is important for the design of a more optimal surface treatment. Therefore, the complete process of adhesion activation has been followed with a combination of analytical techniques.[5–8]

This work describes the characterization of differently treated Twaron fibre surfaces, both before and after solvent extraction. Twaron fibre samples without any treatment, after a standard (non-adhesion-active) finish treatment and after adhesion activation treatment were selected. Using x-ray photoelectron spectroscopy (XPS), chemical information from a depth down to 3–5 nm was collected. Moreover, by using low-energy ion scattering (LEIS), the composition of the outermost atomic surface layer of the samples was

analysed.[9–12] This type of analysis provides information on the coverage of the finish over the fibre surface. Finally, the surface composition of the samples has been correlated with the adhesion performance in an epoxy matrix, as measured in bundle pull-out tests.

EXPERIMENTAL

Fibre materials

P-aramid yarn from Teijin Twaron b.v., Arnhem, The Netherlands, was used for the investigation. One basic yarn type (Twaron 2200, 1680 dtex, f1000) was selected, which was studied in three different forms: without any finish or surface treatment (coded as HM), with a standard finish (coded as HMF) and with an adhesion activation treatment (coded as HMA). The standard finish is present on commercial material and consists of a non-ionic emulsifier containing ethylene oxide and propylene oxide tails. It was developed to improve the processability of the fibres. The adhesion-active finish is based on an epoxy–amine system. For this particular study a watery model system was applied, containing the diglycidyl ether of glycerol as epoxy and piperazine as amine, in a mass ratio of 9 : 1. This finish aims to improve the adhesion properties and contains, in addition, an oily component for processability reasons. After application (0.3 wt.% epoxy–amine, based on weight of yarn) and drying (2 s, 70 °C), the adhesion-active finish is cured on the yarn by drawing the finished yarn over a hot metal plate (240 °C) for 5 s. More details about the preparation of adhesion active samples and the chemistry involved are given in Ref. 3.

X-ray photoelectron spectroscopy (XPS)

The XPS measurements were carried out on a VG Escalab Mk II instrument, making use of non-monochromated Al

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$K\alpha$ radiation from a dual Al–Mg anode. The analyser was operated in constant analyser energy (CAE) mode with a pass energy of 50 eV for elemental quantification purposes and 20 eV for C 1s peak shape comparison purposes. Intensities were converted to elemental concentrations using Wagner sensitivity factors.[13] Data processing was performed with VG Eclipse software. All three Twaron aramid samples were analysed both *per se* and after Soxhlet extraction (4 h) with ethanol.

Low-energy ion scattering (LEIS)

The LEIS experiments were performed in a Calipso instrument equipped with a double toroidal energy analyser.[9,10] The high sensitivity of this analyser makes it possible to perform *static* LEIS experiments, i.e. the ion dose needed is so low (typically $<10^{14}$ He ions cm^{-2}) that the samples to be measured are not noticeably damaged. As projectile ions, we used ^{3}He^{+} ions of energy 3 keV. These provide good mass resolution and the best sensitivities for the elements of interest (C, N and O). The ion beam was scanned over 1×1 mm^{2} of the fibre bundles. The pressure in the analysis chamber was determined by the inlet of He in the ion source chamber and was typically $\sim 1 \times 10^{-8}$ mbar. The base pressure of the system is of the order of 10^{-10} mbar.

In the course of this investigation we found that the surface of the Twaron samples to be analysed contained a (very) thin layer of contamination. In order to remove this contamination we used a dose of 8×10^{15} He ions cm^{-2} prior to the actual measurement. The sputter yield Y, i.e. the number of target atoms sputtered per impinging primary ion, is not known exactly but is estimated to be $Y = 0.1$. In such a case, a dose of 8×10^{15} He ions cm^{-2} would be equivalent to remove less than one atomic layer. Later, it appeared that the contamination had been caused by our practice of sputter cleaning a Cu reference sample to be used for calibration purposes. Since then, these experimental routines have been performed in the absence of the sample(s) to be measured.

Adhesion measurements

The adhesion of a bundle of filaments to an epoxy matrix was evaluated using a 'bundle pull-out' (BPO) test. This test is described also in Ref. 3. A twisted bundle (50–100 turns per metre) of aramid yarn is threaded through a hole in a metal plate. A pre-tension of ~ 1–2 N is applied to the bundle. This results in a tightly packed and nearly circular arrangement of filaments. A layer of 2–4 mm of epoxy resin is cast into a mould around the hole and cured at room temperature for 72 h. On one side of the resin tablet, the bundle itself is impregnated with the resin in order to provide a rigid ensemble. On the other side of the tablet, the bundle is cut off just above the resin surface. The bundle then is drawn from the cured resin tablet using a tensile tester. To correct for differences in contact surface between bundle and matrix, the force per millimetre thickness of the thermoset matrix required to pull the bundle out of the matrix is calculated and expressed in newtons per millimetre. Penetration of the resin into the bundle of filaments, which changes the above—mentioned contact surface, is low and assumed to be independent of the Twaron fibre type. In general, four pull-out experiments per situation are carried out. The resin is a cold-curing epoxy-hardener system (Araldite HY 5052 / Hardener LY 5052 from Ciba). Adhesion measurements were carried out using the fibres both *per se* and after Soxhlet extraction (4 h) with ethanol.

RESULTS AND DISCUSSION

Analysis by XPS

The results of XPS analysis of the three Twaron samples, measured before as well as after extraction, are given in Table 1. Comparisons between the shapes of the C 1s, N 1s and O 1s signals before and after extraction are provided in Fig. 1 (HM), Fig. 2 (HMF) and Fig. 3 (HMA).

The atomic percentages of the Twaron sample without finish (HM) are very close to the theoretical percentages of aramid. Part of the deviation is caused by the presence of a minor amount of Na_2SO_4 originating from the spinning process. This contamination is largely removed by the Soxhlet extraction with ethanol. The cleanness of the HM sample follows also from the shape of the C 1s, N 1s and O 1s signals. Already before extraction, but even more after extraction, the shapes are very close to the theoretical peak shapes of aramid. In the C 1s signal, the $-C(\!=\!O)-$NH$-$groups are clearly visible. The small shoulder at the high-binding-energy side of the oxygen signal points to the presence of some singly bonded oxygen (C$-O-$H or C$-O-$C), possibly caused by a slight finish contamination. It is removed by extraction, resulting in one oxygen signal from only doubly bonded oxygen, as expected for clean aramid.

Table 1. The XPS results of Twaron aramid fibres before and after extraction with ethanol

Sample		Atomic%						
Code	Description	C	O	N	Na	S	Cl	Si
HM	Without finish	76.0	12.6	10.6	0.5	0.2	0.0	0.1
HM-e	Without finish, extracted	76.4	11.6	11.8	0.1	0.1	0.0	0.0
HMF	Standard finish	72.6	25.1	2.0	0.1	0.0	0.0	0.1
HMF-e	Standard finish, extracted	77.6	11.4	10.9	0.1	0.1	0.0	0.0
HMA	Adhesion activated	78.3	18.2	2.5	0.3	0.1	0.5	0.2
HMA-e	Adhesion activated, extracted	69.4	23.5	5.7	0.1	0.7	0.6	0.1
Aramid	Theoretical	77.8	11.1	11.1				

Figure 1. Overlay of the XPS C 1s, N 1s and O 1s signals of the Twaron aramid sample without finish, before and after extraction.
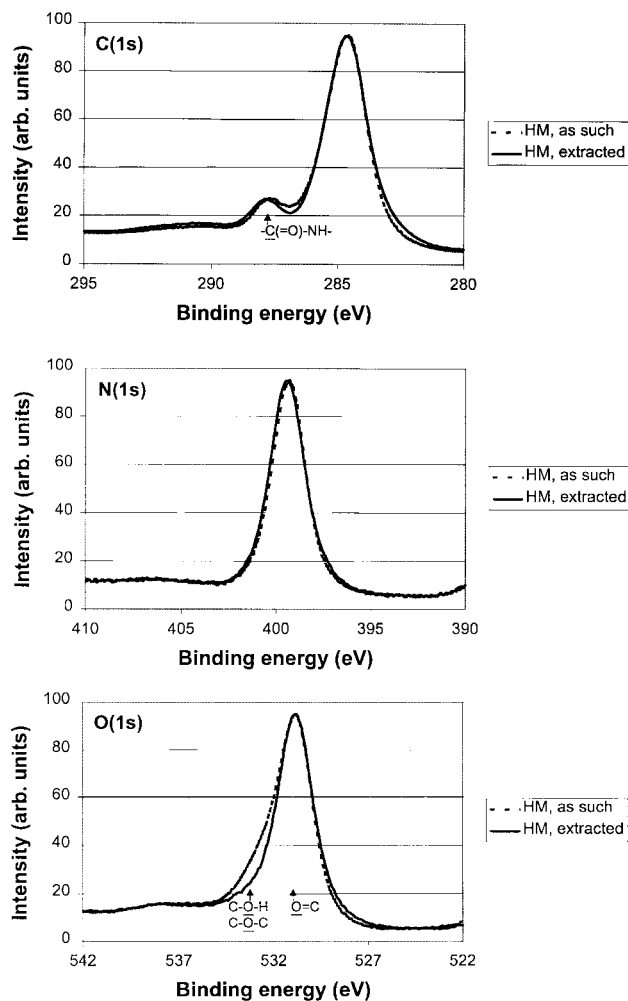

Figure 2. Overlay of the XPS C 1s, N 1s and O 1s signals of the Twaron aramid sample with standard finish, before and after extraction.

Initially, the elemental composition of the sample with the standard finish (HMF) deviates strongly from the theoretical aramid composition (Table 1). This is because the standard finish has a high oxygen content, due to the ethylene oxide (EO) and propylene oxide (PO) tails, which raises the oxygen percentage of this sample substantially. Furthermore, a small amount of nitrogen was detected. Because the pure finish does not contain a significant amount of nitrogen, it should be attributed to aramid, so at least part of the analysed surface is uncovered or covered with a finish layer thinner than the information depth of XPS. After extraction, the elemental composition of the HMF sample comes very close to the composition of clean aramid. This implies that most of the finish is removed by the extraction process, which is not unexpected because the finish is soluble in the extraction solvent. Apparently, the interaction between the standard finish and the aramid surface is not strong enough to keep a significant (in 'XPS terms') amount of finish bonded to the fibre surface. These results are confirmed further by the shape of the XPS signals for the HMF sample shown in Fig. 2. Initially, the C 1s signal contains a strong contribution of $C-O$ that can be attributed to the carbon of the EO/PO tails. Extraction removes this contribution and the peak shape of
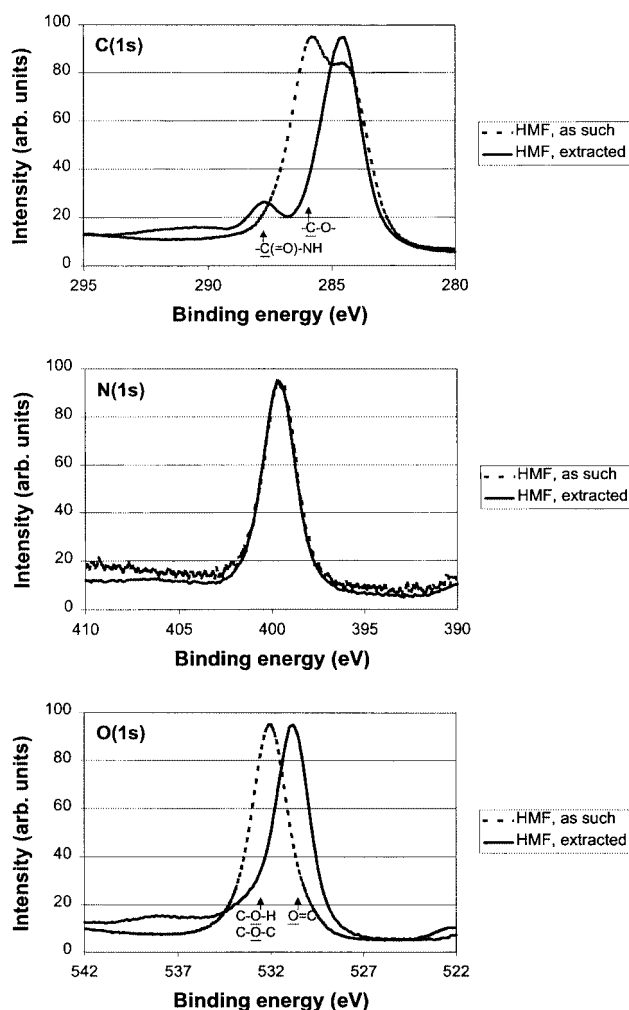
clean aramid is reappearing. The oxygen signal clearly shifts from the position of singly bonded oxygen, as expected for EO/PO, to the position of doubly bonded oxygen, as expected for aramid. Note also the appearance of the shake-up satellites in both the carbon (~291 eV) and oxygen (~538 eV) signals, due to removal of the standard finish.

The sample with the adhesion-active finish (HMA) also deviates initially (before extraction) from clean aramid (Table 1). However, in contradiction to the HMF sample, solvent extraction does not result in complete removal of the finish. Apparently, the epoxy−amine part of the adhesion-active finish is fixed to the Twaron surface and cannot be removed anymore by extraction. This fixation can be explained by a combination of curing and hydrogen bond formation with the aramid surface. During curing of the epoxy−amine mixture, hydroxyl groups are formed, e.g. by the reaction of the epoxy with piperazine and by hydrolysis.[3] These hydroxyl groups are able to form hydrogen bonds with the aramid surface. The cross-linked structure enables interaction of the epoxy−amine reaction product with the surface at multiple points, resulting in a strong fixation. A small contribution of covalent bonding of the epoxy groups with amine end-groups of the aramid fibres is not excluded.
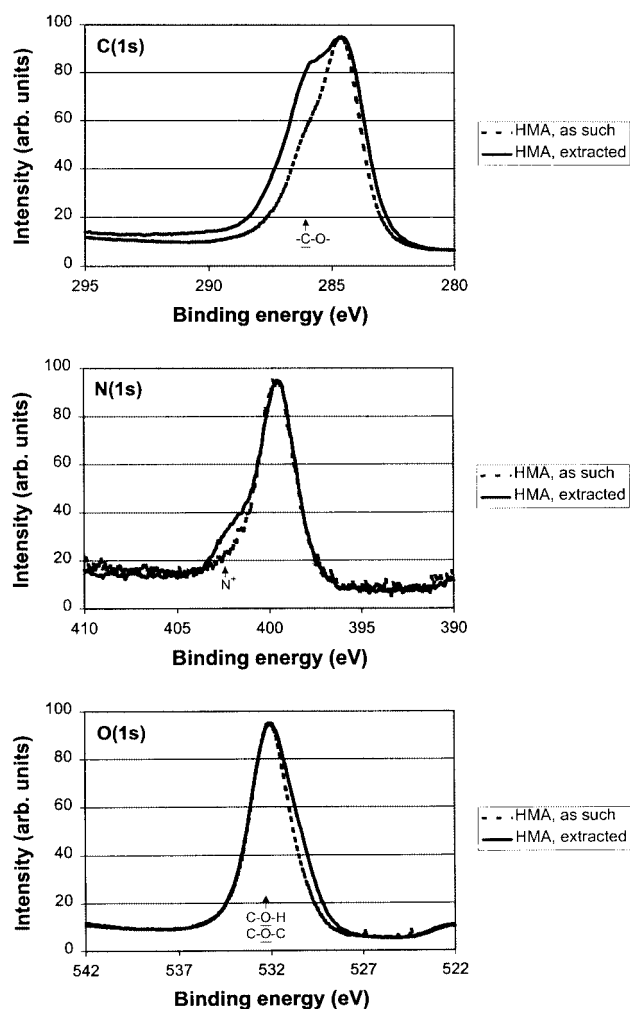
Figure 3. Overlay of the XPS C 1s, N 1s and O 1s signals of the Twaron aramid sample with the adhesion-active finish, before and after extraction.

The increase of oxygen after extraction can be explained by removal of the 'oily part' of the adhesion-active finish, which is relatively oxygen poor. The cured epoxy–amine structure that remains behind on the surface raises the oxygen percentage. The nitrogen can, at least partly, be attributed to the amine hardener, and chlorine is present in the epoxy compound used. In Fig. 3 the shape of the XPS signals is given. The $C-O$ contribution in the carbon signal can be attributed to the cured epoxy compound (hydroxyl and ether groups). In the nitrogen signal, a contribution of quaternary nitrogen is visible, which is already formed during maturation of the adhesion-active finish.[3] The position of the oxygen signal corresponds to singly bonded oxygen, which is expected for the cured epoxy compound. The small shoulder at the low-energy side of the oxygen signal after extraction might be attributed to doubly bonded oxygen, from underlaying or bare aramid, or to sulphate, because some unexplained sulphur is detected after extraction.

Analysis by LEIS

To analyse the composition of the outermost surface of the samples, a selection of them were measured with
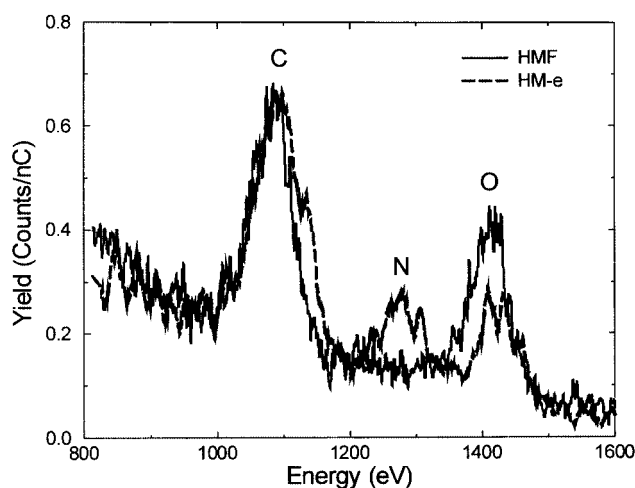

Figure 4. Typical LEIS spectra of samples HMF (standard finish) and HM-e (without finish, extracted). Carbon, nitrogen and oxygen peaks are clearly visible.

LEIS. As discussed earlier, surface contamination had to be removed prior to the actual analysis. Examples of LEIS spectra measured are shown in Fig. 4. For all samples, significant signals for carbon and oxygen were obtained. For most samples, either relatively small nitrogen signals or no nitrogen signals at all were obtained. In fact, the strongest nitrogen signals were measured for the Twaron sample without finish, which can be explained by the relative high nitrogen content of the aramid structure.

Concentrating on O/C signal ratios (Table 2) and on the presence or absence of a nitrogen signal, the following results are found. The samples without finish treatment but additionally 'cleaned' by extraction (HM-e) show O/C values of 0.34 and 0.33, respectively. For these samples, a significant nitrogen peak is found, which can be attributed to the aramid. The O/C ratio of 0.33/0.34 will be taken as reference for clean aramid fibre.

The Twaron sample treated with the (EO/PO-based) standard finish (HMF) shows, without being extracted, a much higher O/C signal ratio, viz. 0.65. This sample does not show a (significant) nitrogen signal, which indicates that

Table 2. The LEIS results of Twaron aramid fibres after sputtering of 0.8 ML

Sample		O/C ratio	
		First	Second
Code	Description	sample	sample
HM-e	Without finish, extracted	0.34	0.33
HMF	Standard finish	0.65	
HMF-e	Standard finish, extracted	0.36	
HMA-e	Adhesion activated, extracted	0.49	0.44/0.49[a]
HMA-e (ref)	Reference adhesion activated	0.54	

[a] This sample was measured twice (on two different measuring spots).

the standard finish covers the fibres (almost) completely. Consequently, the ratio of 0.65 can be considered to represent the standard EO/PO-based finish material.

Analysing comparably treated fibres after being extracted (HMF-e), the nitrogen signal appears to be present again and the O/C ratio drops to a value of 0.36, which is very close to the reference value of clean aramid. Thus, again, it can be concluded that the extraction procedure used has efficiently removed the bulk of the EO/PO-based standard finish. Within the accuracy of our data, we estimate that roughly 10% of the fibre surface still might be covered with the standard finish.

Finally, the adhesion-active samples have been analysed after extraction (HMA-e) and O/C ratios of 0.49 and 0.44/0.49 have been found. These values are considerably higher than those of the unfinished samples (0.34 and 0.33), implying that after extraction the adhesion-active samples are still covered, at least partly, by the adhesion-active finish. The presence of a significant nitrogen signal is not further conclusive because it can be attributed both to adhesion-active material on the surface of the fibres (i.e. cured epoxy/amine) and to bare, i.e. uncovered, aramid material.

In order to interpret the results on the adhesion-active sample further, e.g. to estimate the percentage of surface coverage, a reference measurement on a fully covered adhesion-active sample is required. For this reason, a bare aramid sample was treated, under controlled conditions in the laboratory, with a threefold excess of the adhesion-active finish and then cured. To ensure complete coverage, this treatment was carried out twice. The sample then was extracted with ethanol and investigated using LEIS. The result obtained after removal of surface contamination is given in Table 2. Besides carbon and oxygen, a nitrogen signal is present that can be attributed to the amine hardener. Based on the O/C signal ratio measured for this 'fully covered' reference sample (0.54), we conclude that at least two-thirds of the HMA-e fibre surface (O/C = 0.49) is covered with the adhesion-active finish.

Adhesion measurements

Measurement of the adhesion strength to an epoxy matrix was carried out with the bundle pull-out (BPO) test. The three Twaron fibre samples were tested *per se* and after Soxhlet extraction with ethanol. Because of a high standard deviation, three complete series of measurements (each consisting of four pull-out experiments per situation) were carried out. In all series, a reference sample of a standard type of Twaron was included. This reference sample (Twaron 1000) is always included in the BPO test because of corrects for possible experimental variations between different measurement series. The results of the BPO measurements are expressed as percentage of the adhesion reached for the reference sample. Table 3 shows an overview of the average adhesion values, including the standard deviation ($n = 12$). A graphical representation is given in Fig. 5, from which it is clear that the adhesion to epoxy of both the HM sample and the HMF sample, before as well as after extraction, is on the same level and close to the reference Twaron. This implies that, within the accuracy of this test, there is no significant effect
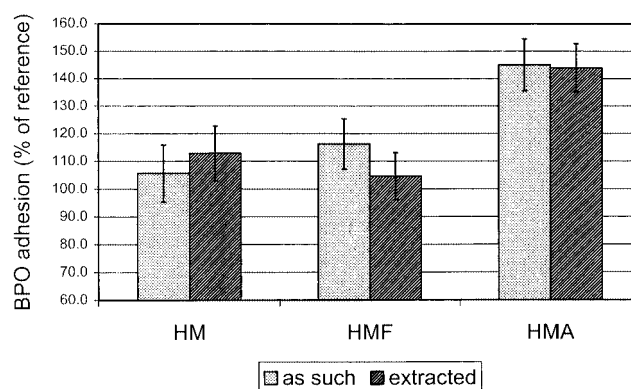

Figure 5. Results of the bundle pull-out (BPO) adhesion test.

Table 3. The BPO results of Twaron aramid fibres before and after extraction with ethanol

	Sample	BPO adhesion	Standard
Code	Description	(% of reference)	deviation
HM	Without finish	105.6	10.3
HM-e	Without finish, extracted	112.9	9.9
HMF	Standard finish	116.3	9.1
HMF-e	Standard finish, extracted	104.6	8.4
HMA	Adhesion activated	145.0	9.5
HMA-e	Adhesion activated, extracted	143.9	8.8

of the standard (non-adhesion-active) finish on the adhesion. Thus, there are no indications for the formation of a weak boundary layer by the standard finish.

The adhesion of the HMA sample is clearly on a higher level. The force required to pull the fibres out of the epoxy matrix increases to ~140% of the value for the reference Twaron. Apparently, the hydroxyl groups of the cured and surface-bonded adhesion-active finish act as effective fixation points for the epoxy matrix material. Again, there is no significant effect of the extraction procedure on the adhesion. Thus, the adhesion performance is not reduced significantly by the extractable part of the adhesion-active finish. However, the large standard deviation of the BPO test hinders the observation of possible small effects of the interphase composition on the adhesion performance.

CONCLUSIONS

Differently treated Twaron aramid fibres were characterized using XPS and LEIS, thus yielding both chemical and elemental information. The surface composition of the upper 3–5 nm, as measured with XPS, can be understood easily and related to the treatment of the fibres. Presence of a standard finish or an adhesion-active finish on the fibre surface can be detected clearly. Solvent extraction removes most of the standard finish, indicating only a weak interaction with the

aramid surface. This is in contrast with the cured adhesion-active finish, which is fixed to the aramid surface and cannot be removed by solvent extraction. This fixation can be explained by a combination of curing, through which a cross-linked structure with hydroxyl groups is formed, and multiple-point hydrogen bond formation with the aramid surface. The LEIS results confirm the XPS observations. Moreover, owing to the high surface sensitivity of this technique, it provides information on the degree of coverage of the fibre surface with the finishes. Based on the LEIS results, it can be concluded that, after solvent extraction, roughly 10% of the (HMF-e) fibre surface still may be covered with the standard finish. In the same way, it can be concluded that at least two-thirds of the HMA-e fibre surface is covered with the adhesion-active finish.

Measurements of the adhesion to an epoxy matrix show (within the accuracy of the test) no significant differences between the HM and the HMF fibres, either before or after solvent extraction. Obviously, the standard finish does not *decrease* the strength of the fibre–matrix interphase. Hence, there are no indications for the formation of a weak boundary layer by the finish. Possibly, the finish migrates into the epoxy matrix. On the other hand, no *increase* of adhesion is found. This is not unexpected because the interaction between standard finish and aramid fibre surface is so low that most of the finish is removed by the solvent extraction.

The adhesion of the HMA sample is clearly on a higher level. Strong fixation of the adhesion-active layer to the aramid surface together with a high degree of coverage, both following from the XPS and LEIS measurements, result in an optimized surface structure for further adhesion to matrix materials. This explains the improved adhesion properties of the HMA sample.

Summarizing, the combination of solvent extraction and surface analysis has proved to be very powerful in analysing the effect of adhesion promoters. In future, possible adhesion promoters will be pre-screened with this combination of techniques.

Acknowledgements

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