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International Journal of Adhesion & Adhesives 19 (1999) 273–279

Adhesion & Adhesives

Influence of microwave plasma treatment on the wettability and the adhesive properties of polyamides films with an epoxy resin

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Accepted 19 November 1998

Abstract

Microwave plasma surface treatments of polyamides films, PA11 and PA12, have been carried out. Two treatments were used: ammonia and nitrogen/oxygen mixtures. Chemical and physical modifications of the surface were investigated by X-ray photoelectron spectroscopy and wettability measurements. The adhesion of the polyamide films with two epoxy adhesives was studied using a series of different tests in parallel: three-point bending test, pull-off test and lap-shear test. The wettability and adhesive properties were shown to improve greatly after plasma treatment, especially for the nitrogen/oxygen mixture. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Plasma; Polyamide; Epoxy adhesive; Wettability; Surface modification

1. Introduction

Due to their low surface energy, their poor chemical reactivity below melting point and the presence of a weak cohesion layer at the surface, polymer surfaces are often difficult to wet and have poor adhesion with other substrates. Surface treatments enable the nature of the chemical groups present at the surface to be modified and they may be used to modify the topography. Depending on the treatment used, the modification may be carried out without changing the bulk properties of the polymer. The alterations to the polymer may come under many different forms: removal of the weak cohesion layer or of the pollution present at the surface, introduction of new or an increased number of chemical functions, increase of the roughness of the surface. All these parameters can contribute to an improvement of the wettability and/or of the adhesive properties of the surface.

However, the efficiency of a surface treatment depends on the nature of the substrate and on the depth of treatment. There is often a compromise between the functionalisation and the degradation of the surface.

The methods used to treat a polymer surface are highly varied. They can be chemical, mechanical, thermal, photochemical or plasma.

The literature concerning the surface treatment of aliphatic polyamides is very limited [1–3]. Methods of chemical treatment include gaseous mixtures of fluorine, nitrogen and oxygen [1] and treatment with mixtures of iodine and potassium iodide [2, 3].

Plasma treatment of polyamides concerns essentially aromatic polyamides due to their particularly low surface energy and adhesive properties. Use of microwave plasmas in post discharge, as is used in this study, has the advantage of a less severe effect on the surface properties than treatments where the polymer is placed directly within the discharge [4]. In post-discharge, the polymer substrate is not exposed to high-energy entities such as electrons or high-energy ions which can have a highly destructive impact. The principal effects of a microwave post-discharge treatment are known to be the cleaning of the surface (removing pollution or a weak boundary layer), the crosslinking of the surface and the chemical

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PII: S0143-7496(98)00070-0

modification by introduction of functional groups. The modification of the roughness of the surface is generally less marked for this type of treatment but has been shown to occur in certain cases especially for drastic treatment conditions (high power and long treatment times) [5].

In this study, we will consider the plasma microwave treatment of polyamides using two gaseous systems. The first, using nitrogen/oxygen mixtures, has been shown to improve the wettability of polymers by introduction of oxygenated groups at the surface [6–9]. The second treatment using ammonia has also been shown to increase the surface energy of the polymer. This increase is generally attributed to the introduction of nitrogen functions [5] notably amine groups at the surface [8]. The characterisation of the surface will be carried out using wettability measurements and X-ray photoelectron spectroscopy. The adhesive properties of the treated films with respect to a typical epoxy adhesive will then be evaluated using a variety of mechanical tests including the three-point bending pull-off and lap shear tests.

2. Experimental

2.1. Materials and preparation

The substrates used in this study were prepared from polyamide 12 (Orgasol® 2002D) and polyamide 11 (Rilsan BD30) powders supplied by Elf Atochem. The films were prepared using two methods.

The films to be used for the wettability measurements and for spectroscopic analysis were prepared by coating of hot steel plates in a powder fluidised bed. The films are then carefully removed from the plates before use.

In order to measure the adhesion of the polyamide film with the epoxy resin, a rigid support was needed. The films were prepared by electrostatic propulsion of the powder onto steel plates coated with an adhesion promoter followed by rapid melting to form a smooth film which adheres well to the plate. Then the plates were stored in a desiccator until the preparation of the epoxy-PA assembly. Without this procedure, the properties of the assembly decrease from 40% due to the presence of water at the epoxy-PA interface.

Two epoxy adhesives were used in this study: an epoxy–anhydride system and an epoxy–amine system. In both cases, the epoxy prepolymer is a diglycidyl ether of bisphenol-A (DGEBA) of low molecular weight (DER 332). The anhydride hardener used is methyltetrahydrophthalic anhydride (MTHPA) with a polymerisation catalyst methylimidazole. The curing cycle used was 1 h at 100°C followed by 5 h at 160°C, determined as the cycle allowing to obtain the maximum glass transition temperature $T_{g\infty} = 130°C$ [10]. For the second system, the amine used is a polyoxypropylenetriamine known as Jeffamine T403 (TEXACO), used with stoichiometric conditions without a catalyst. The curing cycle used was 1 h at 100°C and 1 h at 150°C. It allows to reach the maximal glass transition temperature of the network: $T_{g\infty} = 83°C$.

Choosing these two kinds of system was interesting because they differ in their polymerization mode, the functional groups present in the reactive systems and the ductibility of the networks (the MTHPA based network was more brittle than the Jeffamine based network at room temperature). Another interesting fact is also that $T_{g\infty}$ is reached for both systems by keeping the cure temperature below the melting point of each PA used.

2.2. Microwave plasma treatment apparatus

The microwave apparatus consists of a 2.45 GHz microwave generator from Rayteck (RK L1200 LRT) which can supply power from 0 to 1200 W. The plasma is created by means of a surface guide in a quartz tube (diameter 16 mm) with the distance between the sample and the centre of the discharge in this case being 40 cm. The sample is therefore in post-discharge. The gas flow in the tube is controlled by mass flow regulators (Tylan FC280) over the range 0–200 $cm^3 min^{-1}$.

2.3. Contact angle measurements

The contact angle θ was calculted from the height h and the base diameter D of a sessile drop, by assuming the contour to be circular. Measurements using distilled water and methylene iodide allowed the calculation of both the dispersive and the non-dispersive components of the surface energy using Fowkes equations [11].

2.4. X-ray photoelectron spectroscopy (*XPS*)

XPS analysis was carried out on an ESCACOPE apparatus (vacuum generators) using an unmonochromatised A1 X-ray source ($h\nu = 1486$ eV). An X-ray power of 300 W was used to prevent degradation of the polymer during analysis. The binding energies are calibrated against a value of the C_{1s} hydrocarbon component centred at 285 eV. The surface region analysed is of some nanometers depth.

2.5. Adhesion measurements

Three tests were used for the adhesion measurements between the epoxy networks and the PA film covering a steel substrate; pull-off three-point bending and lap-shear tests.

For the pull-off test, an aluminium stud (20 mm in diameter) was adhesively bonded to the polyamide film substrate and a 4.9 N compression load applied to each stud. The excess of adhesive found around the stud trim, due to flow, was removed using a special trimmer. The pull-off test was performed using a tensile machine (DY25, Adamel Lhomargy-MTS) according to the standard NFT 30062 at a displacement rate of 10 mm/min. The average of the ultimate load and the rupture energy is reported.

The three-point failure test was carried out according to the standard NFT 30010. The epoxy adhesive was used as a stiffener on the polyamide coated substrates ($10 \times 50 \times 0.8$ mm^3) with a contact surface of 5×25 mm^2. The steel substrate used is thinner (0.8 mm) than that used for the other tests (3 mm) in order to avoid a too high rigidity of the substrate alone. The three-point bending test was carried out using the same tensile machine. The ultimate load (F), the ultimate displacement (Δl) and the subtended energy (W) were measured. The failure zone was studied using electron microscopy (Philips 515) coupled with an electron microphobe accessory (EDAX 9800).

The lap-shear test was carried out according to the standard NFT 76107. The epoxy adhesive present between the two films of polyamide has a constant thickness of 150 μm and the surface coverage is 12.5 mm × 25 mm. The same tensile machine was used to carry out the shear test but the tensile system was adapted in order to permit a perfect symmetrical tensile stress of the samples.

In all three cases, after curing, the samples were left in an air-conditioned room (22°C, 50% RH) for 24 h before testing (in the same room). No significant differences were noted between samples stored in a desicator before testing and samples left in an air-conditioned room.

3. Results and discussion

Firstly, the nature of the gas mixture, the influence of the power, the gas flow and the treatment time were evaluated on the surface modifications of the polyamides films. It was also verified by AFM, that no change in roughness was induced by the treatments. This study allowed us to choose, for each gas treatment, the optimal conditions for adhesion testing and it enables us to discuss later the influence of the surface modification on the adhesive properties of PA films with respect to the different adhesives used.

The use of nitrogen/oxygen mixtures for the plasma treatment of polymers is well-known and has been studied [6–9]. They are used to incorporate oxygen functions at the polymer surface, identified by ESCA and leading to an increase in the wettability. Several studies [12, 13] indicate that the use of a mixture of the two gases is more efficient than the use of oxygen alone as they lead to a higher concentration of atomic oxygen, the main active species in the oxygen plasma.

It therefore seemed of interest to study the influence of the proportions of the two gases in the plasma on the wettability of polyamide films. This study was carried out on PA11 using a gas flow level of 100 cm^3 min^{-1} and the results are presented in the Fig. 1. It can be seen that the improvement of the wettability depends not essentially on the quantity of oxygen in the mixture but simply on its presence. The surface energy is unchanged by treatment with nitrogen alone. Once oxygen is added, the wettability increases significantly with a reduction of the water contact angle on the PA11 from 75° to approximately 45°. However, contrary to the studies just mentioned, we did not notice any difference between the wettability or the O/C ratios (measured by ESCA) of the films treated in pure oxygen and those treated with the gas mixture. To study the influence of the other parameters on the polymer properties, we have chosen to use the gas composition 80% N_2/20% O_2, a mixture which approaches the composition of air.

Figs. 2 and 3 show the influence of the plasma power and the treatment time on the surface energies of the polyamides 11 and 12. An improved level of wettability is obtained for a 200 W treatment and raising the power does not amplify the effects. The surface energies show a rapid increase with treatment and the energies continue to rise between 100 and 360 s plasma exposure times. Whatever the power and the treatment time the two kinds of PA have similar behavior. The surface energy obtained after 360 s of treatment is over 60 mN/m compared to the value of 40 mN/m of the untreated films. As expected, it is essentially the non-dispersive component of the surface energy which is modified.

The ESCA analysis shows that whatever the plasma power, the oxygen/carbon atomic ratio increases with the treatment time (Table 1). The rise of the O/C ratio can be attributed to the creation of oxygenated chemical functions at the surface of nature COOR. The nitrogen/carbon

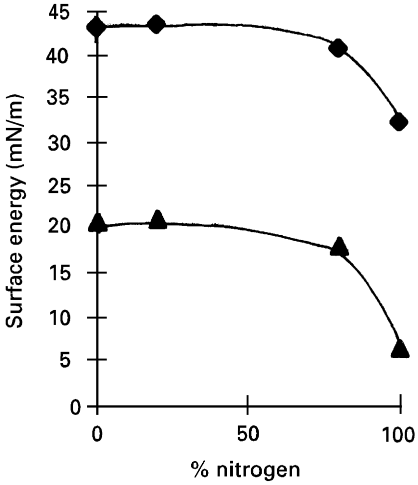

Fig. 1. (▲) Polar component and (◆) dispersive component of the PA11 surface energy as a function of the nitrogen % in the O_2/N_2 plasma (power = 800 W; gas flow = 100 cm^3 min^{-1}; treatment time = 120 s)

ratio also shows a slight increase with the plasma treatment, even in pure oxygen. This can be attributed to the presence of nitrogen trace present in the plasma reactor and/or to the reaction of the surface when it is exposed to air after removal from the plasma equipment, as it has been noticed in the literature [7].

Optimal treatment conditions with respect to the wettability and the chemical composition of the surface can therefore be determined as 100 cm^3 min^{-1}, 200 W, 360 s. These conditions were used to evaluate the adhesion improvement of the films, to be discussed later.

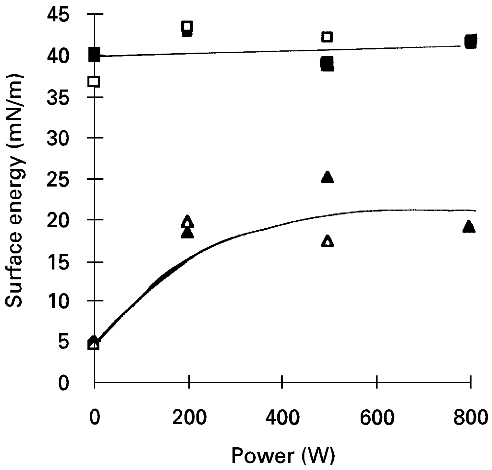

Fig. 2. Influence of the power of an O_2/N_2 plasma treatment (gas flow O_2: 20 cm^3 min^{-1}; N_2: 80 cm^3 min^{-1}; treatment time: 120 s) on the (△) polar and (□) dispersive components of the surface energy of polyamides: (△, □) for Orgasol® and (▲, ■) for Rilsan.

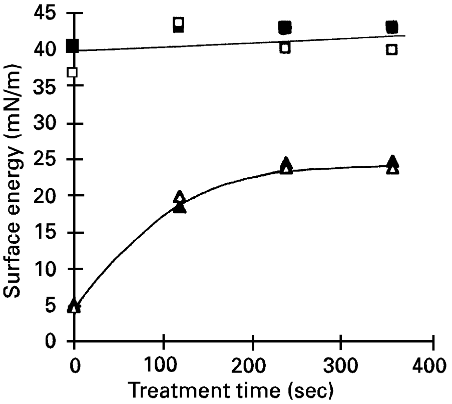

Fig. 3. Influence of the O_2/N_2 plasma exposure time (power = 200 W; gas flow O_2 = 20 cm^3 min^{-1}; N_2 = 80 cm^3 min^{-1}) on the (△) polar and (□) dispersive components of the surface energy of polyamides: (△, □) for Orgasol® and (▲, ■) for Rilsan.

Table 1
O/C and N/C ratio measured by ESCA on PA11 as a function of the plasma treatment conditions. The gas used is a O_2/N_2 mixture with the following gas flow. O_2: 20 cm^3 min^{-1}; N_2: 80 cm^3 min^{-1}

Power (W)	Treatment time (s)	O/C	N/C
0	0	0.18	0.07
200	120	0.46	0.09
200	360	0.63	0.08
800	120	0.48	0.13
800	360	0.54	0.13

3.1. Treatment of polyamides using ammonia

Fig. 4 shows the influence of the plasma power level on the surface energies of the polyamides films treated in an ammonia plasma. The treatment causes a rise in the surface energy of the films, notably for the non dispersive component which increases from 5 to approximately 10 mN/m. This improvement, although significant, is less great than that obtained using the nitrogen/oxygen mixture. Fig. 5 shows that the surface energy of polyamide varies little with the flow rate, though the highest values are obtained for 200 cm^3 min^{-1}. The influence of the

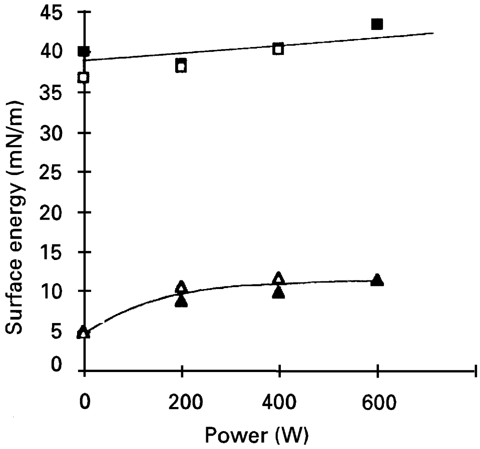

Fig. 4. Influence of the power of a NH_3 plasma treatment on the polar (△) and dispersive (□) components of surface energy of polyamides: (△, □) for Orgasol® and (▲, ■) for Rilsan.

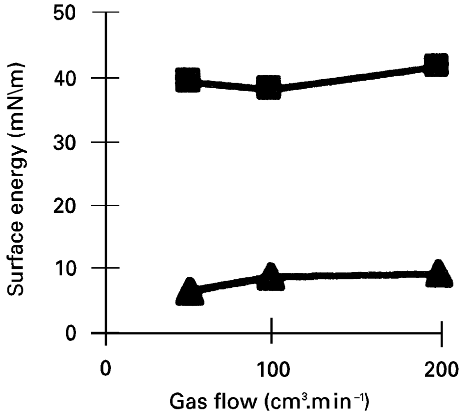

Fig. 5. Influence of the gas flow of a NH_3 plasma treatment on the (△) polar and (□) dispersive component of the surface energy of Rilsan.

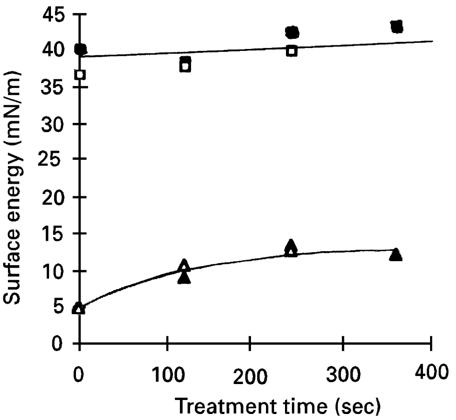

Fig. 6. Influence of the treatment time of a NH_3 plasma treatment on the (△) polar and (□) dispersive component of the surface energy of (△, □) Orgasol® and (▲, ■) Rilsan.

Table 2
O/C and N/C ratio measured by ESCA on PA11 as a function of the treatment time for a NH_3 treatment (gas flow: 200 cm^3 min^{-1} and power 600 W)

Treatment time (s)	O/C	N/C
0	0.18	0.07
180	0.19	0.19
360	0.17	0.19

treatment time on the superficial energy is shown in Fig. 6. As for the N_2/O_2 plasma treatment, the polar component of the surface energy shows a rapid increase in the first 120 s, and increases slightly for longer times. In the mean time an increase of the N/C ratio is observed (Table 2) and no great variations of the O/C ratio is noticed. From all these results, the optimum conditions can be taken as 200 cm^3 min^{-1} and 600 W.

3.2. Adhesion measurements

In order to connect the changes in surface energy due to the different plasma treatments with the adhesive properties of the films, adhesion measurements were performed on steel substrates covered by polyamides films (treated or not) as described before. Only Orgasol® was studied since no difference was observed between the two types of PA with respect to the plasma treatment.

We showed, in a preliminary study, that all the adhesion tests gave the same hierarchic order, but obviously not the same absolute values due to the different stress state and strain rate used.

The optimum conditions, determined with surface energy are maintained: O_2/N_2 with 20% O_2, 200 W, 100 cm^3 min^{-1} and for NH_3 plasma: 200 cm^3 min^{-1}, 600 W.

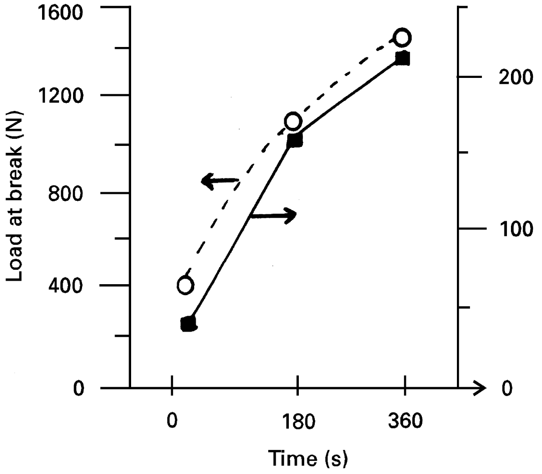

Fig. 7. Influence of treatment time on the pull-off test on the assembly constituted by O_2/N_2 plasma treated Orgasol 2002D and DGEBA/MTHPA/MIA (○: load at break; ■: work at break).

3.3. Influence of the treatment time and the plasma nature

The results using pull-off test on assembly constituted with O_2/N_2 plasma treated PA and epoxy/anhydride reactive system are presented in Fig. 7. It can be seen that the O_2/N_2 plasma treatment increases strongly the toughness of the PA/adhesive interface. The fracture surfaces are analysed by SEM with EDX accessory. With the EDX set-up, we can perform spectra for the metal surface pure or covered with the primary treatment for adhesion, the pure Orgasol® film, or the pure matrix and compare it with the EDX spectra recorded on the initiation zone or on the propagation zone. Thus the location of the failure was possible and in our conditions, the sensitivity of EDX was less than 500 Å. In each case the failure occurs at the interface between the two layers as confirmed by SEM with the EDX accessory.

The increase of rupture energy (by a factor of 5.4 for a treatment of 6 min and by a factor of 4 for a treatment of 4 min) is as much important as the O/C ratio increases (Table 1) This behaviour is in agreement with literature results for PA [8, 15] and other polymers [16, 17].

The comparison with the NH_3 plasma treatment was made with the optimum conditions already described, with the same exposure time (6 min) using the lap-shear test and the anhydride based system as adhesive. The results are presented in Fig. 8.

As regards, the adhesion of the NH_3-plasma-treated films shows an important increase compared to the untreated samples that can be attributed to the introduction at the surface of nitrogen species (N/C goes from 0.09 to 0.15 after 6 min of treatment).

These results are in a good agreement with those of Wertheimer et al. [15], who show that load for crack propagation during peel test is slighty higher for N_2/O_2 plasma treatment than with NH_3 one in the case of aromatic polyamides.

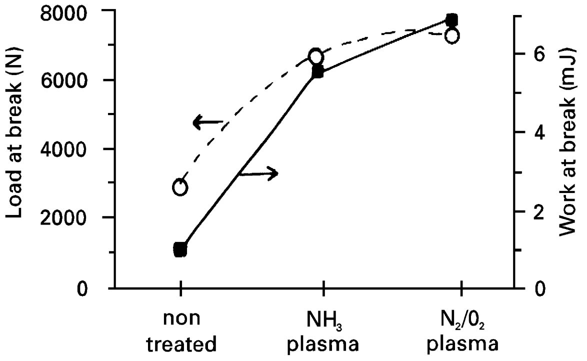

Fig. 8. Influence of the nature of plasma treatment on adhesive properties of Orgasol 2002D/ DGEBA-MTHPA by lap-shear test (○: load at break; ■: work at break).

3.4. Crack initiation and propagation

The mechanical tests previously described, demonstrate clearly the large improvement in the total work for failure induced by the NH_3 or N_2/O_2 plasma treatments. Nevertheless, no information from that test is available concerning crack initiation and propagation. So we performed Scanning Electron Microscopy experiments and EDX on fracture surfaces.

With SEM we can clearly identify the initiation and the propagation crack zone by evidence of different roughness (see Fig. 9) and with the EDX set-up we identify the location of these zones as previously described.

With the untreated Orgasol® 2002D, studied in three-point bending, both the initiation and propagation zone are located at the polyamide-epoxy interface (Table 3).

When the polyamide is plasma treated (both with NH_3 or N_2/O_2) the crack initiation is again located at the interface PA/epoxy but, undoubtly, the crack enters the polyamide film, near the interface PA/primary adhesive, showing clearly that the plasma treatment reinforces the PA/epoxy interface.

3.5. Comparison of the two different epoxy systems

In Fig. 10, the results of the adhesion tests (3-point bending) performed with each neat system (anhydride or amine hardener) are exhibited.

In the same experimental conditions, for the fully cured networks with the untreated Orgasol® 2002D both load and work at failure are higher for the T403 hardener compared with the anhydride. This clearly shows more interactions between PA and the triamine based network. The MTHPA based system is so brittle that the three-point bending specimen are broken when we push them off the mold, explaining that the work at break is nearly zero.

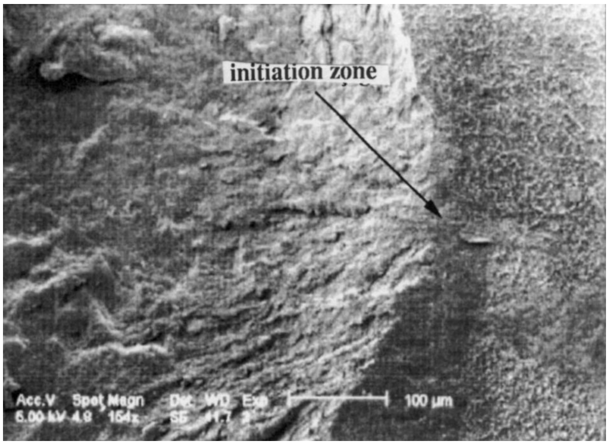

Fig. 9. SEM microscopy of a fracture surface of an Orgasol 2002D sample treated with NH_3 plasma (matrix DGEBA/T403).

Table 3
Ultimate load (F_r), ultimate displacement (Δl) and subtended energy (W) determined by three-point failure test on PA/epoxy-amine assemblies. Location of the failure: aE-PA at the epoxy/polyamide interface, aPA-Pr at the polyamide/primary adhesive interface

		F_r (N)	Δl (mm)	W_r (mJ)
Neat	aE-PA	40±15	0.11±0.03	2.0±1,3
O_2/N_2	aPA-Pr	154±7	0.42±0.06	27±9
NH_3 plasma	aPA-Pr	173±10	0.53±0.07	39±9

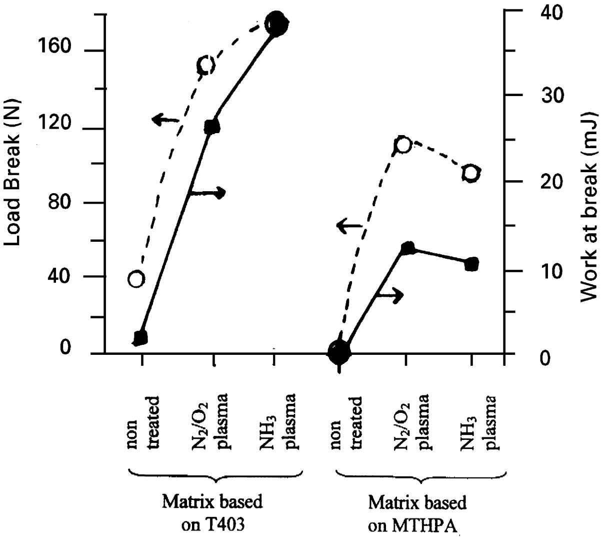

Fig. 10. Comparison of the plasma treatment effects on Orgasol 2002D with two different matrix (three-point bending test) (○: load at break; ■: work at break).

If plasma treatments are now performed on Orgasol® films, in both cases a strong improvement of the adhesive properties is shown and the same graduation is conserved with respect to the network types.

Contrary to the results obtained with the pull-off of test, the differences observed in Fig. 10, with the three-points bending test concerning the effect of the nature of the plasma treatment are in fact not statistically valid. The standard deviation of the measurements made the two sets of calculations the same, so we can conclude that, for the plasma treatment of polyamide films we did not evidence a clear gas effect with this adhesion test.

4. Conclusions

Surface modifications of two kinds of polyamides (PA11: Rilsan and PA12: Orgasol® 2002D) by microwave plasma downstream treatments were studied for O_2/N_2 mixtures and NH_3 gases.

Both plasma treatments principally lead to an increase of the non-dispersive component of the surface energy related for O_2/N_2 treatments to the increase of the O/C ratio and for NH_3 treatments to the introduction at the surface of nitrogen species. The study of different parameters such as power, gas flow and composition of the gas mixture in the case of O_2/N_2 treatment lead us to determine optimal treatment conditions with respect to the wettability: for O_2/N_2, a composition 20–80%, a power of 200 W with a gas flow of $100\,\mathrm{cm^3\,min^{-1}}$ during 180 s were chosen whereas for ammonia treatment the optimal conditions were $200\,\mathrm{cm^3\,min^{-1}}$ -600 W -180 s.

As the superficial modifications of the two kinds of polyamide were similar with respect to the plasma treatments, only Orgasol® adhesion properties were established.

After plasma treatment and whatever the gas used, a great increase of the adhesion properties was noticed whatever the epoxy reactive system. The propagation zone was located near the interface PA/primary adhesive showing clearly that the plasma treatment reinforces the PA/epoxy interface.

Work is now in progress to transfer these results to plasma treatments of Orgasol® powders in order to prepare toughened epoxy matrix with preformed particles, with a controlled and improved interphase with the matrix.

Acknowledgements

This research was supported by Elf Atochem. The authors would like to express their gratitude to Dr. E. Valot and Dr. O. Julien for fruitful discussions all along the thesis of P. Lennon.

They are also grateful to Dr. A. Roche for numerous advice and fruitful discussions and to Ph. Rivière and L. Blanchard for performing some adhesion tests.

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