

Adhesion of Microwave-Plasma-Treated Fluoropolymers to Thermoset Vinylester

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ABSTRACT: Poly(tetrafluoroethylene) and a fluoroethylene copolymer were surface treated with a 2.45-GHz microwave plasma to enhance their adhesion to a vinylester thermoset. The plasmas were generated with an inert gas (Ar) and with reactive gases (H₂, O₂, and N₂). The lap-joint shear stress was measured on fluoropolymer samples glued with the vinylester. In general, the stress at failure increased with increasing plasma-energy dose. The H₂ plasma yielded the best adhesion, and X-ray photoelectron spectroscopy revealed that it yielded the highest degree of defluorination of the fluoropolymer surface. The defluorination efficiency de-

clined in the order H₂, Ar, O₂, and N₂. Contact angle measurements and scanning electron microscopy revealed that the surface roughness of the fluoropolymer depended on the rate of achieving the target energy dose. High power led to a smoother surface, probably because of a greater increase in temperature and partial melting. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 838–842, 2005

Key words: poly(tetrafluoroethylene); poly(fluoroethylene-co-fluoropropylene); vinylester thermoset; adhesion; plasma

INTRODUCTION

Fiber-reinforced polyester products are sometimes laminated with fluoroplastics for chemical protection in the pulp and paper and chemical industries.^{1,2} Laminating the hydrophobic fluoropolymer and the more hydrophilic polyester is not trivial. A mechanical procedure is commonly employed in which a glass-fiber backing is melted into the fluoropolymer prior to lamination.¹ It is important to obtain sufficient adhesion with the most simple method possible. Only a few studies have reported on the adhesion properties of fluoropolymers treated with microwave plasma, and they consider the adhesion between fluoropolymers and “epoxy adhesives.”^{3,4} This article focuses on the possibility of using the microwave-plasma technique to enhance the adhesion between fluoropolymers and the fiber-reinforced polyester type of vinylester resins, without using any “adhesive.”

Although poly(tetrafluoroethylene) (PTFE) is generally considered to be negatively affected by high-energy radiation,⁵ Tutiya⁶ showed in 1972 that this is not necessarily the case when it is irradiated in the melt.

Since then, major efforts have been devoted to determining the optimal conditions for the irradiation crosslinking of PTFE and other fluoropolymers in order to increase their stiffness and strength.^{7–9} Irradiation techniques include γ -irradiation and electron irradiation, but the plasma technique may also generate modified/crosslinked materials.¹⁰

Yasuda et al.¹¹ introduced the concept of crosslinking via activated species of inert gases (CASING). It involves the use of inert-gas plasma to activate the surface and create radicals or unsaturations. This method is studied here and generalized to include reactive gases. We present the results of the effects of plasma treatment of fluoropolymers on the surface adhesion, surface topology, and contact angle. PTFE and poly(fluoroethylene-co-fluoropropylene) (FEP) are treated. To evaluate the effectiveness of reactive and “inert” plasma and the size of the plasma gas molecules, plasma of both reactive (H₂, N₂ and O₂) and inert (Ar) gases are used. The effects of the plasma-energy dose and dose effect are also studied.

EXPERIMENTAL

Materials

The materials were 2 mm thick sheets of PTFE with a melting point of 330°C and FEP with a melting point of 264°C. A bisphenol A epoxy-based vinylester resin (Atlac 430 type, DSM Composite Resins, Zwolle, The Netherlands) was applied to the fluoropolymers. The vinylester was cured using a formulation of 100 mL of

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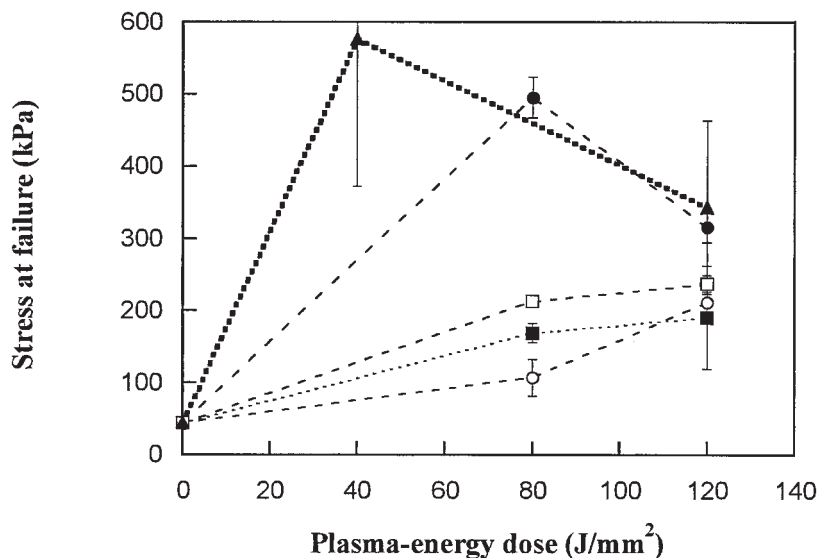


Figure 1 The stress at failure as a function of the plasma-energy dose at 100 W for PTFE (●) H₂, (○) O₂, (■) N₂, and (□) Ar and for FEP (▲) H₂.

resin, 0.5 mL of 1% cobalt solution, and 1.0 mL of methylethyl ketone peroxide (Butanox M-50).

Plasma treatment

A Plasma-Finish V15-G (Plasma-Finish GmbH) apparatus with a regulated magnetron with radial ventilator and microwave coupling system was used for the plasma treatment. The microwave generator operates at a maximum adjustable power of 300 W and a frequency of 2.45 GHz.

Adhesion test

A method based on the ASTM D-3165 standard was used. Two specimens, with surface areas greater than $50 \times 25 \text{ mm}^2$, were treated simultaneously in the plasma oven. After 1–4 h, the two surfaces were subsequently glued together with a vinylester polymer on a $25 \times 25 \text{ mm}^2$ square to yield a lap-joint. This sandwich was cured for 24 h in air at ambient temperature, for 24 h at 80°C, and finally for 12 h at ambient temperature.

The lap-joint shear force on the cured sandwiches was recorded using a tensile testing machine. The actual glue surface area was measured after the failure. Because of the liquidlike nature of the uncured resin, the glued area could increase well during the curing process. The failure stress was calculated from the actual size of the glued area and the failure force.

Contact angle

The contact angles were measured immediately after the samples had been taken out of the plasma appa-

atus, according to the method of Dahlgren and Sunqvist¹² using limonene as a liquid.

X-ray photoelectron spectroscopy (XPS)

The XPS spectra were recorded using an AXIS-HS XPS spectrometer (Kratos Analytical, Manchester, UK) with a monochromatic Al K α X-ray source operating at 15 kV and 20 mA. The take-off angle was 90° with respect to the sample surface. The analysis area was approximately 1 mm². The pressure was below 10⁻⁷ Pa during the measurements and the pass energies of the spectra used to determine the elemental composition and curve resolution were 80 and 20 eV, respectively. These data were supplied by Kratos Analytical. The XPS spectrum was recorded approximately 1 day after the plasma treatment.

RESULTS AND DISCUSSION

The stress at failure of the PTFE/vinylester/PTFE laminates is shown in Figure 1 as a function of the plasma-energy dose. The adhesion increased almost continuously with an increasing energy dose, hydrogen being the exception. For comparison, the stress at failure of hydrogen-plasma-treated FEP was also determined. Interestingly, the pattern was similar to that of PTFE with a peak in adhesion at intermediate doses. Visual inspection of the fracture surfaces of the hydrogen-plasma-exposed PTFE specimens showed that the amount of vinylester left on the fluoropolymer surface increased with increasing plasma-energy dose, suggesting that the fracture was not always located in the interlayer between the fluoropolymer and the vinylester. The greatest improvements in adhesion were

obtained with the hydrogen plasma and these amounted to 11 and 13 times that of the untreated PTFE and FEP, respectively. This may be compared to improvements in adhesion between PTFE and epoxy adhesives, which are on the order of 16–22 using NH_3 , N_2 , or $\text{H}_2\text{O}/\text{Ar}$ plasma gases.^{3,4} It is interesting that, as observed here for H_2 , the optimal adhesion has also been reported to occur at intermediate plasma times/doses in the case of NH_3 and N_2 plasma.⁴ The relative effectiveness of O_2 , N_2 , H_2 , and Ar plasma gases is discussed in the literature. A higher content of oxygen-containing groups in PTFE was obtained with Ar than with N_2 or O_2 in radio frequency (RF) plasma.¹³ It was also shown that the defluorination efficiency increased in the order $\text{O}_2 < \text{N}_2 < \text{Ar}$.¹⁴ Takashima and Oda¹⁵ observed a different relative defluorination efficiency, using a home-built low-pressure discharge plasma-processing device: $\text{air} < \text{Ar} < \text{N}_2$. Yu et al.¹⁶ showed that Ar was more efficient than H_2 in modifying the PTFE surface using either an RF or a low-temperature cascade-arc torch plasma. This is in contrast to our finding with the microwave plasma. These examples show that the “ranking” of a plasma gas, in terms of its defluorination efficiency, depend on the actual plasma processing conditions and techniques employed.

The limonene contact angles after the plasma treatment are given in Figure 2. The limonene contact angle increases with increasing surface polarity and decreases with increasing surface roughness.¹⁷ As observed in Figure 2, these two factors were competing. At small doses, and for PTFE at the highest dose, the surface roughening/etching seemed to dominate, as indicated by the low contact angles.

The surfaces of PTFE sheets exposed to different doses of H_2 plasma are shown in Figure 3. The surface clearly became rougher with increasing energy doses. Liu et al.^{18,19} observed that the “etching effect,” and consequently the surface roughness, increased with increasing energy dose using either an RF plasma or a dielectric barrier discharge plasma. As suggested by Matienzo et al.,²⁰ the roughening may partly be a consequence of different etch rates in the amorphous and crystalline parts of the polymer.

XPS showed that hydrogen plasma was the most effective medium to reduce the content of CF_2 groups (Figure 4). It also produced slightly higher contents of oxygen-containing carbon groups than the other plasma gases. It is known that hydrogen plasma generates intense vacuum UV radiation^{21,22} and that PTFE and FEP absorbs mainly in this region.²³ This, in combination with its reactivity, could be, at least to some extent, the reason for its high efficiency here. As expected, the highest content of oxygen and ether or keto groups was obtained with the oxygen plasma. Again the differences were small between the different plasmas. The differences in adhesion efficiency of the Ar,

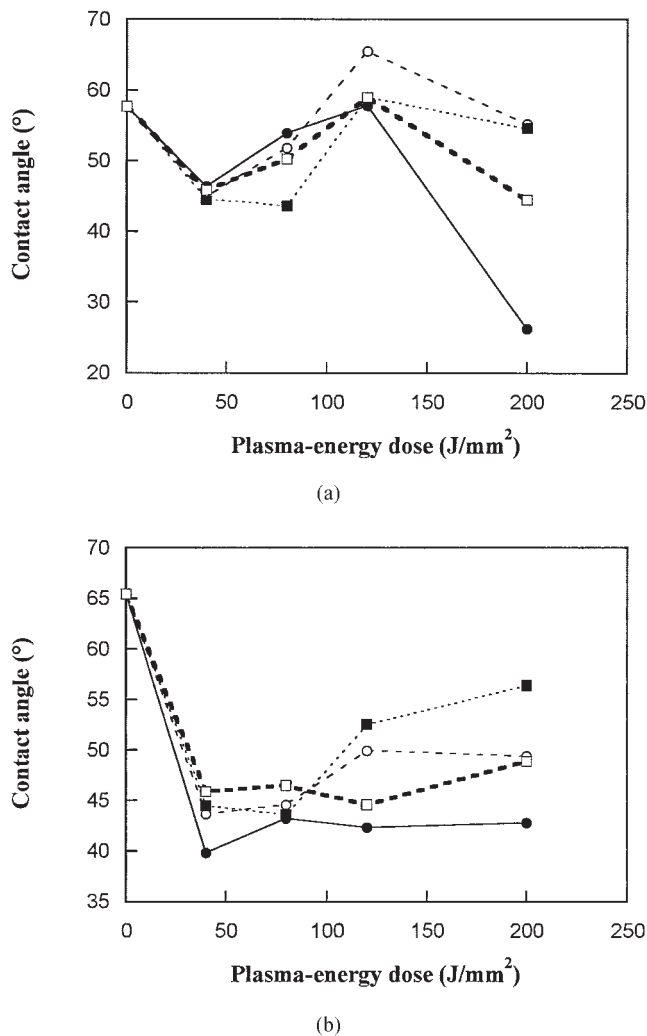


Figure 2 The contact angle as a function of the plasma-energy dose at 100 W (a) for PTFE (●) H_2 , (○) O_2 , (■) N_2 , and (□) Ar and (b) for FEP (●) H_2 , (○) O_2 , (■) N_2 , and (□) Ar.

O_2 , and N_2 plasmas were small, but their efficiencies were significantly lower than that of hydrogen. As observed in Figure 4, in general, the reduction in CF_2 content yielded an increase in adhesion (increase in stress at failure). The Ar XPS and adhesion data showed that the inert gas, through the CASING/pool effect, produced adhesion properties and chemical changes similar to the reactive oxygen and nitrogen gases. The kinetic energy of the Ar plasma and possibly its vacuum UV emission²⁴ is presumably sufficient to create radicals at the surface, which later, outside the reactor, react with oxygen to form a more stable polar surface. Carbon radicals, in the crystalline component or in the crosslinked component, can be stable for weeks, perhaps in the form of peroxy radicals.^{9,25} Consequently, the plasma-treated polymer may be readily oxidized after the vacuum is removed.^{15,26,27}

It is well known that the efficiency of the plasma treatment slowly decays in air through molecular re-

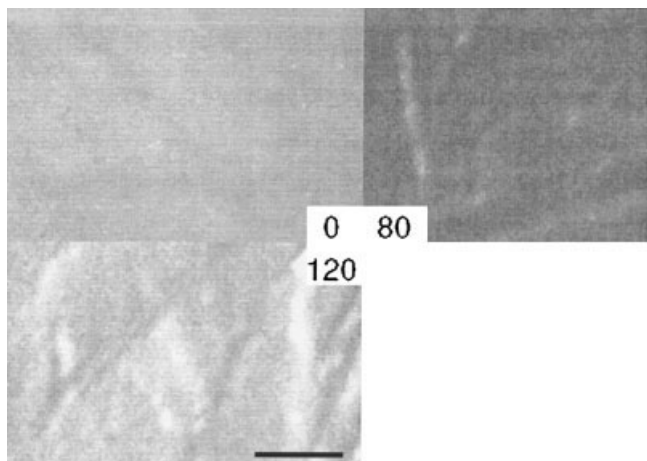


Figure 3 The surface structure of plasma-treated PTFE. The treatment was carried out with H₂ at 100 W. The numbers are the doses (J/mm²).

laxation.^{3,16,27-30} The relative efficiency of the different plasma gases was therefore determined after approximately the same amounts of time after plasma treatment (see Experimental section).

The oxygen and nitrogen plasmas gave the smallest reduction in CF₂ content and the smallest improvements in adhesion. In order to reveal the effects of the plasma dose, XPS was also run on a PTFE surface exposed to hydrogen plasma at a dose of 80 J mm⁻². The content of -CF₂- carbons was reduced to 67% at 80 J mm⁻² as compared to 27% at 200 J mm⁻² of the content of the unexposed material. There was no minimum in -CF₂- content at intermediate energy doses, similar to that reported for pulsed RF H₂ plasma.²⁶ Thus, this could not explain the peak in adhesion at intermediate doses (Fig. 1).

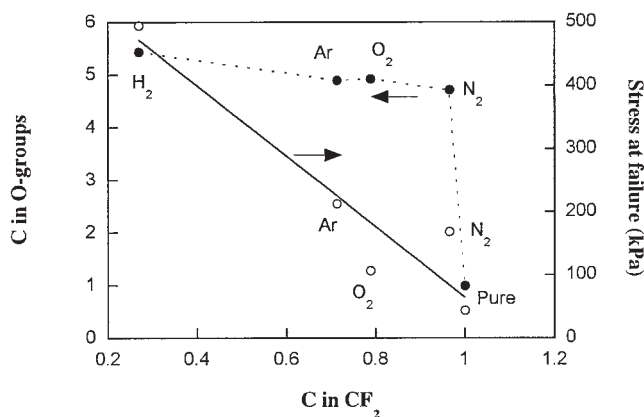


Figure 4 (●) The amount of carbon in oxygen-containing groups, relative to that of (●) the unexposed (pure) material (200 J mm⁻²) and (○) the stress at failure at 80 J/mm² for PTFE at 100 W as a function of the amount of carbon in fluoro-containing groups relative to that of the unexposed material.

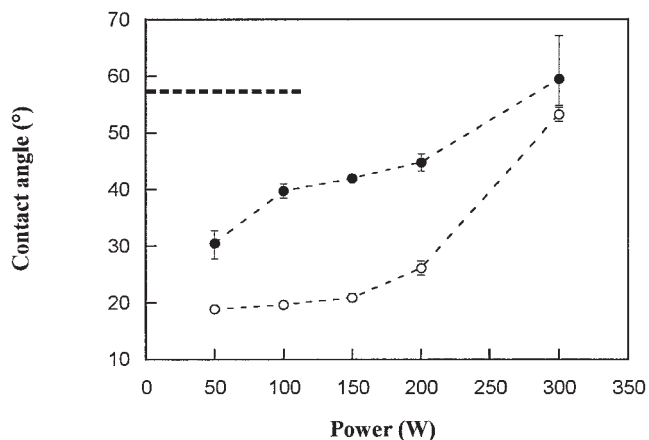


Figure 5 The contact angle of limonene on PTFE as a function of power using (●) Ar and (○) H₂. The energy dose is 200 J/mm². The contact angle of untreated PTFE is represented by the bold broken line.

Because the surface roughness increased with plasma treatment time, the effect of using different powers to achieve the same plasma-energy dose was studied. Figure 5 shows that the contact angle decreased more at low power under both the hydrogen- and argon-plasma treatments. Figure 6 shows that the surface roughness decreased with increasing power. Hence, a lower power, and consequently a longer plasma-exposure time, led to a greater increase in surface roughness and a lower contact angle. Thus, the processes involved in surface etching/roughening were strongly time dependent. Although adhesion tests were not conducted at different powers, it is

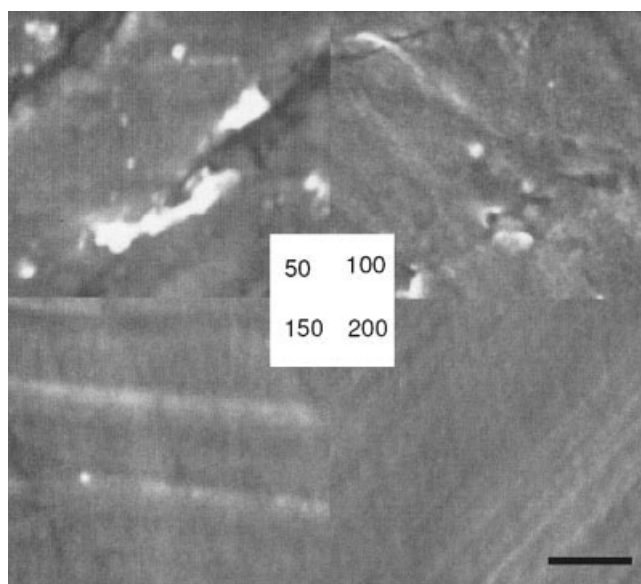


Figure 6 The surface structure of plasma-treated PTFE (H₂, 200 J/mm²). The numbers refer to the power (W); scale bar = 10 μm.

evident that a rougher surface leads to better adhesion.

CONCLUSION

The hydrogen microwave plasma yielded the greatest defluorination and the best fluoropolymer–vinylester adhesion. Interestingly, the inert Ar plasma gas was as efficient as the reactive O₂ and N₂ gases. The reason for a peak in adhesion at intermediate H₂ plasma-energy doses for both PTFE and FEP was not obvious and could not be explained by variations in defluorination (PTFE) or surface roughening (PTFE). Except for H₂, the stress at failure increased with increasing plasma-energy dose. The limonene contact angle showed a complex pattern as a function of the energy dose because of the competing effects of increasing defluorination and increasing surface roughness. It was demonstrated that a low plasma power (i.e., a long treatment time) yielded a rougher surface than a higher power for the same energy dose.

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