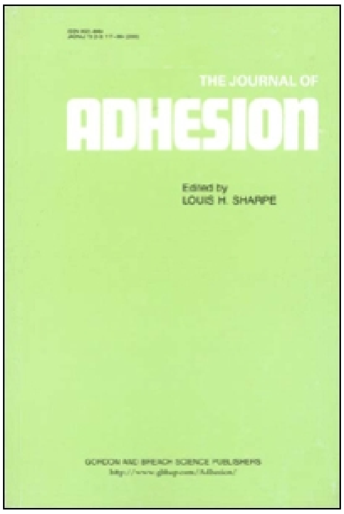

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Surface Modification of Fluorinated Polymers by Microwave Plasmas†

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We developed a new plasma treating method, incorporating the use of microwaves generated by an electronic cooking range. Using this method, polytetrafluorethylene (PTFE) and a copolymer of tetrafluoroethylene and hexafluoropropylene (FEP) were treated. Dialkylphthalates (DAP) were used as the standard liquids of contact angle measurements for evaluation of the wetting properties of plasma treated polymers. The components of surface tension (γ_L) due to the dispersion force (γ_L^d) and the polar force (γ_L^p) of DAP were calculated by Fowkes' equation from the contact angles (θ) on polypropylene. After plasma treatment cos θ of several standard liquids on PTFE and FEP increased. The linear relationship between $\gamma_L(1+\cos\theta)/(\gamma_L^d)^{\frac{1}{2}}$ and $(\gamma_L^p/\gamma_L^d)^{\frac{1}{2}}$ was verified. γ_S and γ_S^d and γ_S^p of the plasma treated PTFE and FEP also increased. From the results of ESCA analysis, it was found that a significant amount of oxygen was introduced to the polymer surface by the plasma treatment. Peel strengths of a pressure sensitive adhesive bonded to PTFE and FEP increased approximately two-to threefold if the plasma treatment was used prior to bonding.

KEY WORDS Fluorinated polymers; microwave plasmas; surface modification; contact angles; wetting; peel strength.

1 INTRODUCTION

In general, most polymer materials have low-energy surfaces, so that difficulties sometimes occur in the case of good quality printing, painting, adhesion and so forth. Many attempts are being made to improve these areas by means of surface modification, and one method which has been developed and which has come to be widely used involves the use of low-temperature plasma generated by irradiation with electromagnetic waves in a low-pressure atmosphere. However, this method requires the use of expensive equipment. In this paper, we report our development of a new and extremely simple method of plasma treatment which uses the microwaves generated by an ordinary domestic microwave oven.

In our method, all that is required is a very simple procedure whereby the test material is placed in a glass vessel, the pressure inside the vessel is then reduced to $0.2 \sim 1.0$ torr by means of a vacuum pump, and the valve shut and the vessel

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detached from the vacuum line, and then treated in a microwave oven for a period ranging from several seconds to several tens of seconds. Because it enables plasma treatment to be carried out easily in any laboratory using everyday utensils, if its effectiveness is confirmed, it is hoped that this method will enjoy wide application in research into the surface treatment of polymers.

In order to investigate the effectiveness of this method, fluororesin was treated according to the procedure described above, and extremely good treatment results were confirmed by taking contact angle measurements for various standard liquids, by conducting peeling experiments for pressure-sensitive adhesives, by *X*-ray photoelectron spectroscopy, and by scanning electron microscope observation.

2 EXPERIMENTS

2.1 Experimental materials

Two fluororesins, polytetrafluoroethylene (PTFE) and a copolymer of tetrafluoroethylene and hexafluoropropylene (FEP) were subjected to plasma treatment. The PTFE was in the form of commercially available Teflon sheet (thickness 0.5 mm), whilst the FEP was in the form of Daikin Manufacturing Ltd's Neoflon. After Soxhlet extraction by washing with acetone, the samples were vacuum dried at normal temperature. The reasons for selecting fluororesins as the test materials were as follows. Because wetting generally increases on a large scale as a result of plasma treatment, a standard liquid with a relatively high surface tension becomes necessary for the measurement of contact angles. If, from the outset, as far as possible polymers with low energy surfaces are used, then it becomes possible to employ the standard liquids used to measure contact angles under normal circumstances. Accordingly, we decided to use fluororesins because they are polymers with low energy surfaces.

The surface properties of the standard liquids used for the measurement of contact angles in the test materials are shown in Table I and Table II. The liquids shown in Table I are those commonly used to evaluate the wetting properties of solids. However, if these liquids are not used carefully, the Zisman plot does not always show good linearity. In order to obtain a Zisman plot with good linearity, it is better to use liquids of a homologous series with different surface tension (γ_L). In a previously published account[1] we have measured γ_L and θ on paraffin for dialkylphthalates (DAP) having varying alkyl chain lengths, calculated the polar component, (γ_L^p), and non-polar component, (γ_L^d) of γ_L by Fowkes' equation, and discussed their molecular weight dependency. In that case, γ_L decreased with the alkyl chain length (m), with its lowest value at C_1, and afterwards increased. γ_L^d maintained a steady value between C_1 and C_9, and decreased thereafter. γ_L^p decreased significantly until C_4, and thereafter remained more or less stable. DAP is thus a homologous liquid in which γ_L, γ_L^p, and γ_L^d vary greatly with m. The surface properties of DAP are shown in Table II.

In the current experiment DAP was used as the standard liquid for the evaluation of the wetting properties of plasma treated surfaces, but because there

TABLE I
Surface properties of standard liquids for contact angle measurement at 20°C

Standard liquids	γ (dyn/cm)	γ^a (dyn/cm)	γ^b (dyn/cm)	γ^c (dyn/cm)
n-Decane	23.9	23.9	0	0
n-Dodecane	25.4	25.4	0	0
n-Tetradecane	26.7	26.7	0	0
n-Hexadecane	27.6	27.6	0	0
1,1,2,2, Tetrachloroethane	36.3	33.2	3.1	0
Tricresyl Phosphate	40.9	37.4	3.5	0
1-Bromonaphthalene	44.6	44.4	0.2	0
1,1,2,2, Tetrabromoethane	47.5	44.3	3.2	0
Diethylene glycol	44.4	31.7	0	12.7
Ethylene glycol	47.7	30.1	0	17.6
Formamide	58.2	35.1	1.6	21.5

is concern about the compatibility of DAP and paraffin, it was decided this time to measure θ once again for polymers where this is not a matter for concern, and re-evaluate γ_L^p and γ_L^d. For this purpose polypropylene (PP, Mitsubishi Petrochemical Ltd's blown film) was used as the standard material. Although it is most appropriate to use polyethylene (PE) as a nonpolar solid standard material, because γ_L of DPB DAmP and DHP are close to γ_C (31 dyn/cm) of PE, θ on PE is extremely small, and accurate measurement is difficult.

For peel tests of pressure-sensitive adhesive, Scotch Tape #250 (width 25 mm) made by Sumitomo 3M Ltd was used.

2.2 Plasma Treatment

The microwave oscillator used in the plasma treatment was a domestic microwave oven with an output of 560 W at 2450 MHz. Test material cut to an appropriate size was placed in a glass vessel fitted with a suction valve (separable flask), pressure was reduced using a vacuum pump, and when the inside of the flask reached a pre-determined pressure ($P = 0.2 \sim 1.0$ torr), the valve was closed, the vessel placed in the microwave oven and treatment was carried out for $5 \sim 30$

TABLE II
Surface tension (γ) and its components due to the dispersion force (γ^d) and polar force (γ^p) for dialkyl phthalates at 20°C

Dialkyl phthalates	abbr.	γ (dyn/cm)	on paraffin γ^d (dyn/cm)	on paraffin γ^p (dyn/cm)	on polypropylene γ^d (dyn/cm)	on polypropylene γ^p (dyn/cm)	$X^p = \gamma^p/\gamma$
Dimethyl phthalate	DMP	39.5	32.0	7.5	30.4	9.1	0.23
Diethyl phthalate	DEP	36.6	32.4	4.2	31.3	5.3	0.15
Di-n-propyl phthalate	DPP	34.4	32.1	2.3	31.0	3.4	0.10
Di-n-butyl phthalate	DBP	33.1	31.4	1.7	30.9	2.2	0.07
Di-n-amyl phthalate	DAmP	32.0	30.6	1.4	30.3	1.7	0.05
Di-n-heptyl phthalate	DHP	30.0	28.6	0.8	28.9	1.1	0.04

seconds. Air was used as the plasma treatment atmosphere. In order to prevent the material from burning during the microwave treatment, continuous treatment for more than 10 seconds was avoided. When treatment for periods longer than 10 seconds was carried out, it was done intermittently, broken up into 10-second periods.

2.3 Measurement of contact angles

Contact angles were measured at 20 ± 1° using an Elmer Optics Ltd Goniometer contact angle measuring device. θ was measured from left to right five times apiece for each drop of liquid, five drops were so measured, and the average value determined.

2.4 Peel testing

30 × 150 mm sheets of PTFE and FEP film were subjected to plasma treatment, a pressure-sensitive adhesive conforming to JIS C2107 was affixed using a 2 kg roller, and a 180° peel test was conducted using a crosshead speed of 300 mm/min at 20°C.

2.5 ESCA spectrum measurement

The ESCA spectrum of the plasma-treated materials was measured using a Shimazu Manufacturing Ltd ESCA model 850 X-ray photoelectron spectrometer (X-ray voltage 8 KV, current 30 mA).

2.6 Electron scanning microscope examination

After the completion of the peel testing, the surface of the test materials was examined using an electron scanning microscope (Nippon Denshi KK model T-20).

3 RESULTS AND DISCUSSION

3.1 Assessment of the surface tension of dialkylphthalates

Figure 1 shows the relationship between cos θ and γ_L of DAP on untreated PP, PTFE and FEP (Zisman plot). Results with extremely good linearity were obtained for each material, and the effectiveness of DAP as standard liquids is demonstrated. In addition, the linear extrapolated values for cos $\theta \rightarrow 1$ (critical surface tension, γ_C) for PP, PTFE and FEP are 29.2 dyn/cm, 15.1 dyn/cm, and 13.2 dyn/cm respectively.

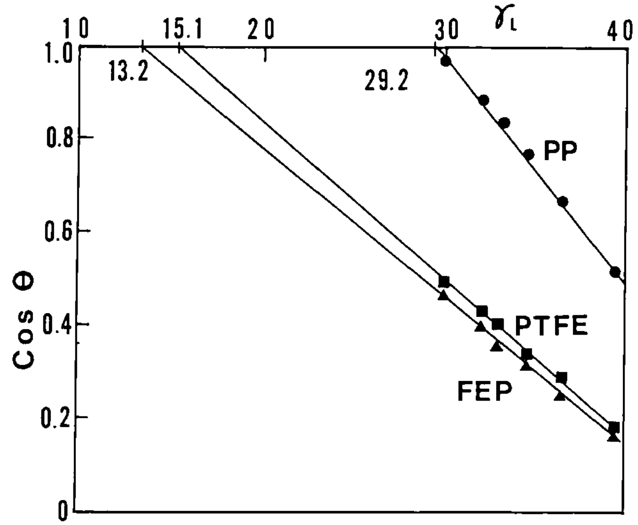

FIGURE 1 Contact angles (cos θ) of dialkylphthalates (DAP) on polypropylene (PP), polytetrafluoroethylene (PTFE) and tetrafluoroethylene-hexafluoropropylene copolymer (FEP) plotted against surface tension of DAP (Zisman plot).

In the case of PP it was close to recorded values, but for PTFE it was smaller than γ_C (18.5 dyn/cm) determined by using n-alkanes.

γ_L^p and γ_L^d were determined from the measured values of θ for DAP on PP by the following method.

Young's formula describes the relationship between contact angle (θ), liquid surface tension (γ_L), solid surface tension (γ_S) and solid/liquid interfacial tension (γ_{SL}) as follows:

$$\cos\theta = (\gamma_S - \gamma_{SL})/\gamma_L \qquad (1)$$

furthermore F. M. Fowkes[2] suggests that it is possible to divide surface tension into two components, that provided by the dispersion force (γ^d) and that provided by other forces (in this case the polar force), (γ^p):

$$\gamma = \gamma^d + \gamma^p \qquad (2)$$

Thus, it is thought that when a solid or liquid possessing these components ($\gamma_1 = \gamma_1^d + \gamma_1^p$) comes into contact with material possessing only the dispersion force ($\gamma_2 = \gamma_2^d$), only the dispersion force operates between the two, and only its geometric average appears in the form of a reduction in surface free energy. If this is the case, then interfacial tension (γ_{12}) becomes

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d\gamma_2^d)^{\frac{1}{2}} \qquad (3)$$

Furthermore F. M. Fowkes shows that from this equation and from Young's Equation 1, the relationship between θ and γ_L, γ_L^d, and γ_S^d is expressed by the following equation:

$$\cos\theta = -1 + \frac{2}{\gamma_L}(\gamma_S^d)^{\frac{1}{2}}(\gamma_L^d)^{\frac{1}{2}} \tag{4}$$

From this, in the case of materials where the solid body is formed solely by the dispersion force component, it is possible to determine the dispersion force component (γ_L^d) of a liquid if the surface tension ($\gamma_S = \gamma_S^d$) of the substrate possessing only the dispersion force component is known from the measurement of the contact angle.

From the measurement of θ on PP ($\gamma_S = 29.7$ dyn/cm), the values of γ_L, γ_L^d and γ_L^p for DAP calculated according to Equation 4 are shown in Table II. For the purpose of comparison, previously reported[1] results for paraffin have been included in the table. There is no change in the tendency of the changes in γ_L^d and γ_L^p accompanying the increase in m, but γ_L^d derived from θ on PP is smaller than that from paraffin, and γ_L^p is larger. This is thought to result from the compatibility between paraffin and DAP, and so from here on we will use the values for γ_L^d and γ_L^p for PP.

3.2 Effect of plasma treatment on wetting properties.

Figure 2 shows the relationship between $\cos\theta$ of dodecane, formamide and ethylene glycol on PTFE which has undergone our plasma treatment, and the pressure (P) inside the flask during the plasma treatment. In every instance, $\cos\theta$ is larger than that of untreated material. Accompanying the decrease in P from 1 torr to 0.2 torr, $\cos\theta$ increased, and the efficacy of the treatment increased in

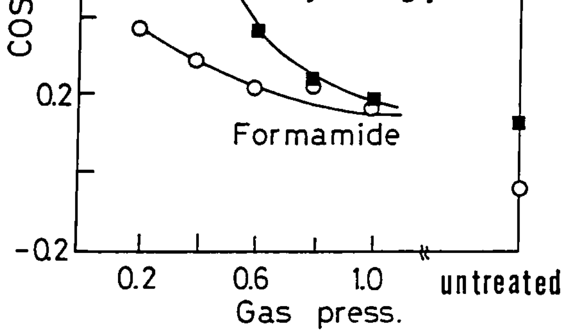

FIGURE 2 Contact angles ($\cos\theta$) of dodecane, ethylene glycol and formamide on plasma treated polytetrafluoroethylene (PTFE) plotted against plasma treating gas pressure.

line with the reduction of P. This demonstrates that the method described can be used satisfactorily for plasma treatment.

In order to evaluate quantitively the surface tension (γ_S) of plasma-treated surfaces, and their dispersion force component (γ_S^d) and polar force component (γ_S^p), we employed Kaelble's method shown below.

For contact between polar liquids, Owens[4] and Kaelble[5] expanded Fowkes' formula to obtain the following equation:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d\gamma_2^d)^{\frac{1}{2}} - 2(\gamma_1^p\gamma_2^p)^{\frac{1}{2}} \tag{5}$$

Substituting Young's Equation 1 for this, we get the following:

$$\frac{\gamma_L(1+\cos\theta)}{(\gamma_L^d)^{\frac{1}{2}}} = 2(\gamma_S^d)^{\frac{1}{2}} + 2(\gamma_S^p)^{\frac{1}{2}}\frac{(\gamma_L^p)^{\frac{1}{2}}}{(\gamma_L^d)^{\frac{1}{2}}} \tag{6}$$

With this equation, if θ is measured for various liquids with different values for γ_L, γ_L^d and γ_L^p and $\gamma_L(1+\cos\theta)/(\gamma_L^d)^{\frac{1}{2}}$ is plotted against $(\gamma_L^p)^{\frac{1}{2}}/(\gamma_L^d)^{\frac{1}{2}}$, the result is a straight line; from the gradient of this line γ_S^d is derived, and from the extrapolated value of $(\gamma_L^p)^{\frac{1}{2}}/(\gamma_L^d)^{\frac{1}{2}} \to 0$, γ_S^p is derived. Figure 3 shows the relationships produced for θ of DAP on plasma treated and untreated PTFE and FEP. The data fall more or less entirely on a single straight line, from which we understand that Equation 6 is valid. Figure 4 shows the relationship between gas pressure (p) and γ_S, γ_S^d and γ_S^p for PTFE and FEP so derived. As a result of plasma treatment, γ_S, γ_S^d and γ_S^p increased greatly. Additionally, accompanying the reduction in P from 1.0 torr to 0.2 torr, γ_S^p increases, but the change in γ_S^d is small, and we find that the increase in γ_S is dependent on the increase in γ_S^p.

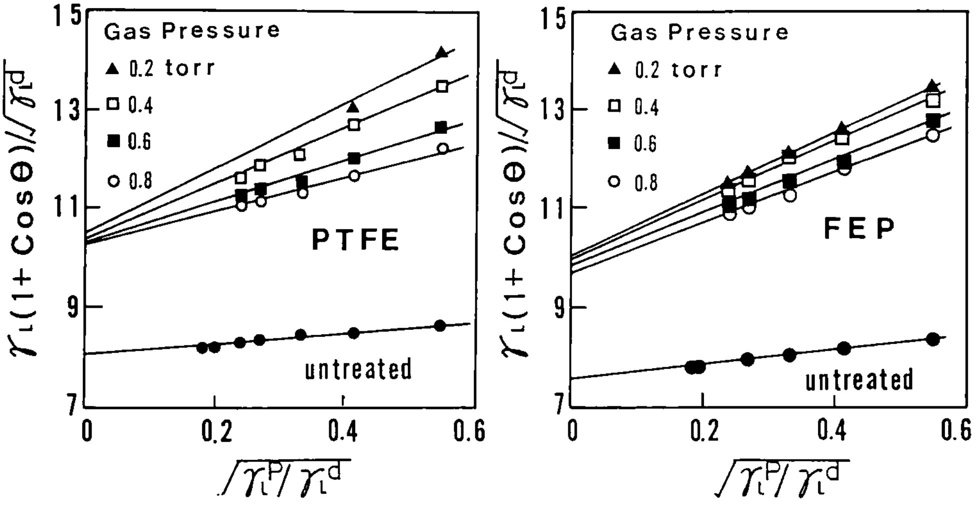

FIGURE 3 Relation of $\gamma_L\ (1+\cos\theta)/\sqrt{\gamma_L^d}$ to $\sqrt{\gamma_L^p}/\sqrt{\gamma_L^d}$ for plasma treated polytetrafluoroethylene (PTFE) and tetrafluoroethylene-hexafluoropropylene copolymer (FEP).

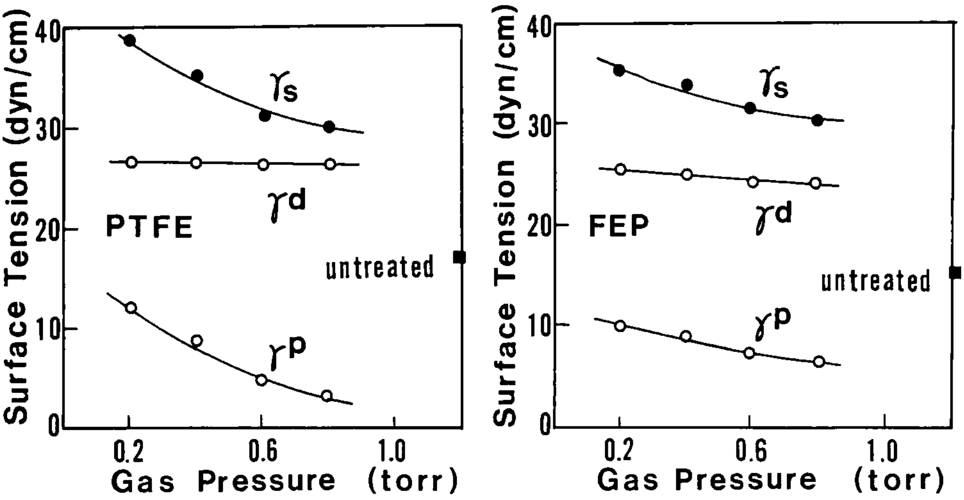

FIGURE 4 Surface tensions (γ_S) and their components due to dispersion force (γ_S^d) and polar force (γ_S^p) of plasma treated polytetrafluoroethylene (PTFE) and tetrafluorethylene-hexafluoropropylene copolymer (FEP) plotted against plasma treating gas pressure.

3.3 ESCA Analysis of plasma-treated surfaces

Figure 5 shows the ESCA spectra of FEP and PTFE subjected to 10 seconds of plasma treatment at 0.2 torr, as well as those of untreated FEP and PTFE. For all materials, peaks can be seen for C_{1S} (the signal of carbon chemically-shifted by CF_2) in the vicinity of 292.5 ev, and F_{1S} in the vicinity of 689 ev. For plasma-treated materials, a large O_{1S} peak appears in the vicinity of 532.5 ev for both FEP and PTFE, and a broad spectrum spanning from 292.5 ev to 285 ev for C_{1S}.

The broad spectrum for C_{1S} is brought about by the overlapping of signals chemically shifted by CF, CO, COO, etc. For the results described above it is apparent that as a result of plasma treatment a significant amount of oxygen has been introduced into the surface of the test materials. In the O_{1S} of untreated FEP a small signal was observed, and it may be that this is because the surface was oxygenated when the film was formed. In the case of untreated PTFE, almost no oxygen was detected because we measured the spectrum of a surface which had been cut off with a knife immediately beforehand.

3.4 The effect of plasma treatment on peel strength

Figure 6 shows the relationship between gas pressure (P) and peel strength of pressure-sensitive adhesive affixed to PTFE and FEP, with the duration of treatment as a parameter. For both FEP and PTFE, peel strength increased greatly as a result of plasma treatment, with the degree of the increase proportional to the duration of the treatment. It is clear that, as a result of the plasma treatment, polar groups have been introduced, wetting has improved, and

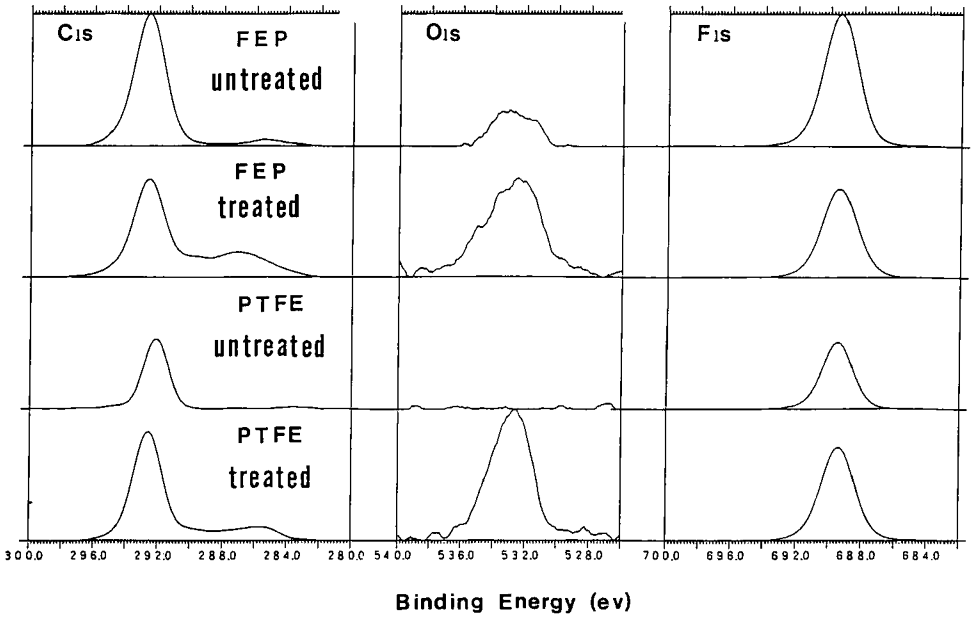

FIGURE 5 ESCA spectrum of untreated and plasma treated polytetrafluoroethylene (PTFE) and tetrafluoroethylene-hexafluoropropylene copolymer (FEP).

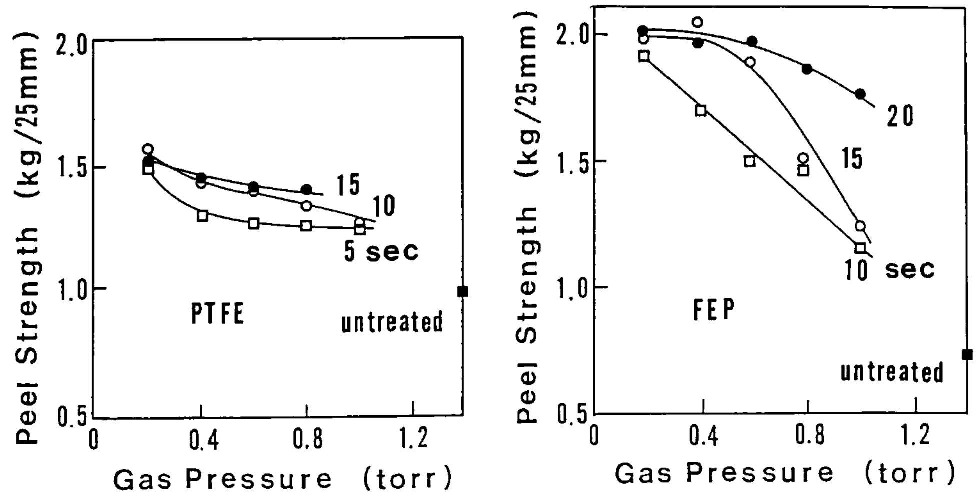

FIGURE 6 Peel strength of pressure sensitive adhesive bonded to plasma treated polytetrafluoroethylene (PTFE) and tetrafluoroethylene-hexafluoropropylene copolymer (FEP) plotted against plasma treating gas pressure.

the bonding and adhesion between adhesive and adherend has increased. In order to observe more clearly the effect of polarity on peel strength, if we plot peel strength against the ratio ($x^p = \gamma_S^p/\gamma_S$) of the polar component (γ_S^p) to surface tension (γ_S), we obtain a result such as that shown in Figure 7. As x^p increases, peel strength rapidly increases, from which we understand that the increase in x^p contributes greatly to the increase in peel strength.

Here there are large differences in the peel strength behaviour of FEP and PTFE. For untreated material, PTFE peel strength, at 0.99 kg/25 mm, is greater than that of FEP, which is 0.72 kg/25 mm. However, after plasma treatment, the peel strength of FEP attains a maximum value of 2.0 kg/25 mm, whereas PTFE peel strength reaches only 1.6 kg/25 mm, reversing the situation. This can be explained in the case of untreated material by the fact that the value of γ_S is higher for PTFE, but in the case of plasma-treated material, conversely, the value of γ_S for FEP is lower (see Figure 4), and this phenomenon of the reversal of peel strengths cannot be explained simply by the advantages and disadvantages of wetting. It is thought that surface morphology has a large influence on this, and so the surfaces of the test materials were observed using a scanning electron microscope after the pressure-sensitive adhesive was peeled off. Figure 8 shows scanning electron microscope photographs of the resin surface after pressure-sensitive adhesive was peeled off in the case of untreated FEP and PTFE, and FEP and PTFE plasma-treated for 10 seconds at 0.2 torr. In the treatment PTFE, granular unevenness can be observed, and this may be partly attributed to the fact that PTFE is produced by the compression sintering of a powder. Some

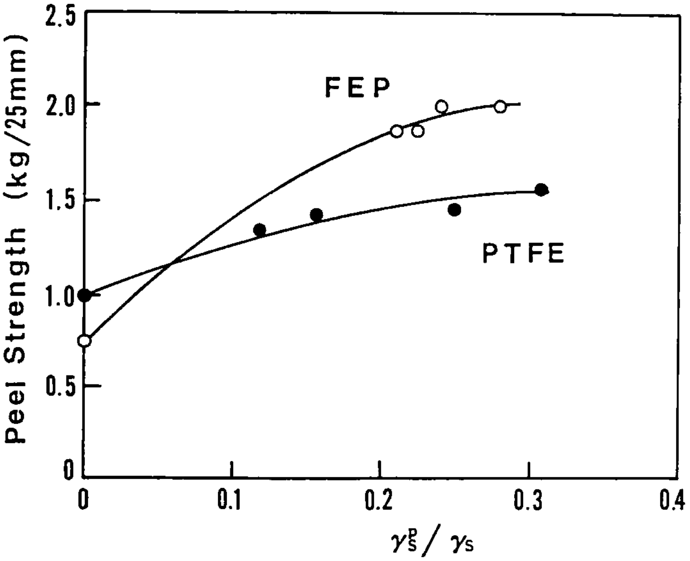

FIGURE 7 Peel strength of pressure sensitive adhesive bonded to plasma treated polytetrafluoroethylene (PTFE) and tetrafluoroethylene-hexafluoropropylene copolymer (FEP) plotted against polarity ($X^p = \gamma_S^p/\gamma_S$) of plasma treated polymers.

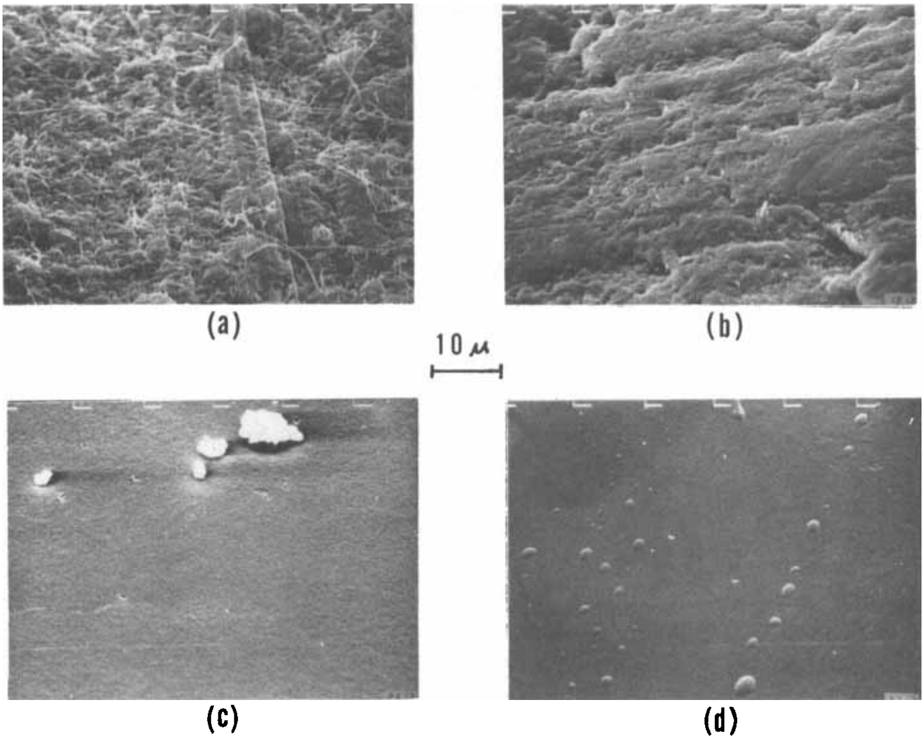

FIGURE 8 Scanning electron micrographs of fracture surface after peel test for polytetrafluoroethylene (PTFE) and tetrafluoroethylene-hexafluoropropylene copolymer (FEP).
(a) untreated PTFE, (b) plasma treated PFTE, (c) untreated FEP, (d) plasma treated FEP.

fibrous matter is stuck on a disorderly fashion, but this is fibrillated tacky adhesive which has become attached at the time of peeling. Irregularities in the surface structure of plasma-treated PTFE were reduced and smoothed out as a result of ablation during the plasma treatment. On the other hand, the surface of untreated FEP is smooth, and no structures at all can be seen. Even after plasma treatment there is almost no change in the state of the surface, although a number of small particles of roughly 1 μm diameter can be observed; these are thought to be tacky adhesive.

From the above scanning electron microscope observations, the following matters can be understood. The fact that the peel strength of untreated PTFE is larger than that of FEP is because, as well as having better wetting, there is also the added anchor effect of the tacky adhesive sticking to the irregularities on the surface. The surface of PTFE is somewhat smoothed out by the plasma treatment, and wetting also improves, but because the layer of tacky adhesive on the tape is thin, the tacky adhesive can no longer infiltrate sufficiently into the indentations remaining after plasma treatment, and adherence with the adherend is incomplete (i.e., the contact surface area is smaller than apparent). Accordingly, even after plasma treatment, the peel strength of PTFE does not increase in comparison with that of FEP. In contrast to this, because the surface of FEP is extremely smooth, the effect of plasma treatment is completely reflected in peel strength, and so peel strength increases greatly.

4 CONCLUSIONS

We have developed an extremely simple new method of plasma treatment using the microwave energy produced by an ordinary domestic microwave oven. In order to study the effectiveness of this method, two types of fluororesin, PTFE and FEP, were treated, and extremely good treatment results were confirmed by measuring the contact angles of various standard liquids, conducting peel tests for pressure-sensitive adhesive, X-ray photoelectron spectroanalysis and scanning electron microscope observation.

The cosine of the angle of standard liquids ($\cos\theta$) was in every case larger than that for untreated material. Additionally, as the gas pressure during treatment (P) reduced from 1.0 torr to 0.2 torr, $\cos\theta$ increased, and the effectiveness of the treatment improved as P grew smaller. γ_S, γ_S^d, and γ_S^p all increased greatly as a result of plasma treatment.

The results of ESCA analysis of the surfaces of plasma-treated materials showed that a significant amount of oxygen was introduced.

The peel strength of a pressure-sensitive adhesive tape placed on these fluoropolymers increased greatly as a result of plasma treatment, with the amount of increase directly proportional to the duration of the treatment.

The above results show this method is suitable as a method of plasma treatment.

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