

# Plasma Modification of Cellulose Fibers: Effects on Some Polymer Composite Properties

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## SYNOPSIS

Cellulose fibers have been surface-modified by selected cold, microwave plasma treatments. Inverse gas chromatographic (IGC), XPS, and SEM analyses showed surface treatment to be incomplete, but, nevertheless, effective in controllably altering the acid/base interaction balance of fiber surfaces. Surface-modified fibers were used in composites with polystyrene (PS), chlorinated polyethylene (CPE), and polypropylene (PP) as, respectively, basic, acidic, and neutral matrices. Favorable acid/base interactions led to enhanced mechanical properties and increased glass transition temperatures of composites. Acid/base interaction appears to be an important, though not the sole consideration, in the design of superior systems using cellulose fibers as reinforcing agents. As expected, in the case of PP composites, acid/base considerations proved to be irrelevant. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

The purpose of this work was to modify the surfaces of cellulose fibers by exposing them to selected cold microwave plasma environments. Surface-modified fibers were then used as reinforcing agents in composites with selected polymer hosts, in the related objective of further studying the contribution of specific (acid/base) interactions to the properties of composites.

Cellulose fibers are recognized as economically attractive candidates for application in multicomponent polymer systems. However, when used in combination with many plastics, their strong polarity implies compatibility problems, leading to compromised performance. The negative implications can be moderated by modifying the surface structure of either component, thereby also affecting the interaction balance at contacts between host and included fiber.<sup>1-7</sup> An example of this is found in a report<sup>7</sup> that describes the use of corona discharges to alter the surfaces of cellulose fibers and of poly-

olefin hosts, with positive consequences on rheological and mechanical properties of the composites. Further, we have reported recently on the use of various coupling (compatibilizing) agents for enhancing the adhesion at interfaces in composites with cellulose and polypropylene (PP), polystyrene (PS), and chlorinated polyethylene (CPE).<sup>8</sup> In the earlier work, it was found that acid/base interactions, evaluated by inverse gas chromatography (IGC), if not necessarily a predominant factor, cannot be neglected when designing surface treatments intended to optimize the performance of these composite materials. The results motivated the use of more powerful tools for surface modification, exemplified by cold plasma discharges.

A cold plasma is generated when a gas at low pressure and near-ambient temperature is exposed to an electromagnetic field, e.g., at radio- or microwave-frequency. A fraction of the gas is excited by the high-energy (hot) electrons of the field, causing the formation of radicals, ions, photons, and other excited species capable of initiating and propagating reactions at surfaces of solids positioned in the plasma. A great variety of surface effects can be generated by controlling plasma variables, notably the chemistry of the gas used to sustain the plasma, the

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gas flow rate and pressure, applied power, and treatment time. Extensive reviews of plasma technology elaborate on these procedures.<sup>9,10</sup>

Cold plasma treatments have been used extensively and successfully to modify the surfaces of synthetic polymers.<sup>11-13</sup> On cellulose fibers and other wood products, however, the use of plasmas has been more restricted, in part because of the susceptibility of cellulose and related materials to degradation in the plasma environment.<sup>14</sup> Nevertheless, significant surface modification of cellophane was reported some time ago from our laboratories.<sup>15</sup> The use of oxygen plasmas to alter the wettability of cotton cellulose was explored by Benerito and co-workers,<sup>16</sup> and similar plasmas were applied to paper by Chan Tang and Bosisio<sup>17</sup> and by Carlsson and co-workers.<sup>18</sup> Oxidative plasmas also have seen use in the enhancement of adhesion between paper and polyethylene.<sup>19,20</sup> A further inquiry into the potential usefulness of plasma modifications therefore seemed warranted.

## EXPERIMENTAL

### Materials

Three host polymers were used in this study. As in the earlier case,<sup>8</sup> these were the polypropylene (PP) Trespaphan NNA 30, from Hoechst AG, Germany, and polystyrene (PS) and chlorinated polyethylene (CPE), both from Dow Chemical Co., Canada. The PP is considered able to exert only dispersion forces, whereas acid/base forces can be associated with the latter two polymers.

The cellulose fiber, again as in earlier work,<sup>8</sup> was supplied by Nymolla AB, Sweden. The fiber was obtained from 60% beechwood/40% birchwood and consisted of 86% cellulose, 13% hemicellulose, and a very small lignin fraction. The fiber was extracted with toluene and vacuum-dried. It was then used, in part, to formulate reference composites and, in part, for plasma treatments. Plasma-treated fibers were then used to prepare composites matching the reference set. All composites contained 40 wt % fiber. They were prepared by compounding fiber and matrix in a Brabender mixer under a nitrogen blanket. Mixing was at 180°C for PP compounds, at 160°C for PS matrices, and at 140°C for CPE-based materials. Throughout, a rotor speed of 50 rpm was used and mixing was continued to the establishment of equilibrium torques, generally for periods of about 5 min. Specimens for mechanical property evaluation were made by compression-molding the com-

posites at their respective mixing temperatures under 3 metric tons of applied pressure. Samples were then transferred to another press at room temperature and cooled under the stated applied pressure.

### Plasma Modification

The effectiveness of surface modifications by plasma treatments is influenced by the "line-of-sight" character of the technique. Surfaces in direct contact with the constituents of an active plasma (the glow discharge) tend to be affected far more rapidly than are underlying regions of a solid placed in the plasma. When the surfaces in question are those of particulates or fibers, this raises difficulties, since only a fraction of the total available surface will be exposed to the plasma environment at any moment. The cited difficulty applied in the current instance, where the fiber specimens were aggregates with diameters of about 25  $\mu\text{m}$ . Designs of plasma reactors are needed, therefore, which attempt to palliate the problem. An evolutionary path is being followed in our laboratories, with the reactor used in the present case shown schematically in Figure 1.

The cylindrical glass reactor vessel was 24 cm long and had an i.d. of 8.5 cm. It was fitted with an agitator with dimensions close to those of the reactor, so that in operation the reactor wall was scraped by the stirrer surface. The agitator was driven by a rotary motor connected through a vacuum seal and was operated normally at 10 rpm. This motion promoted the breakup of aggregates and favored the presence of free-flowing fibers. Other components of microwave plasma equipment were those fully described in previous literature.<sup>10</sup> Fiber treatment involved the following sequence: About 60 g of fiber was placed in the reactor vessel, and the assembly was evacuated to below 0.06 Torr. Samples were placed toward the center of the cylinder, away from the ends of the stirrer where preliminary tests showed the plasma glow discharge to be weaker. After 30 min of evacuation, the reactor chamber was flooded with the gas to be used in plasma treatment, at gas flow rates of 50 mL/min, elevating the pressure to near atmospheric and permitting the fiber to be saturated with respect to the treatment gas. Saturation was followed by a second evacuation to below 0.06 Torr, whereupon the plasma medium was reintroduced to generate a steady-state pressure of 0.80 Torr at a gas flow rate of 50 mL/min for  $\text{NH}_3$  and  $\text{N}_2$  and 15 mL/min for methacrylic acid (MAA). A 2.45 GHz power generator was then activated to produce a visible glow discharge. The applied power was held at 200 W,

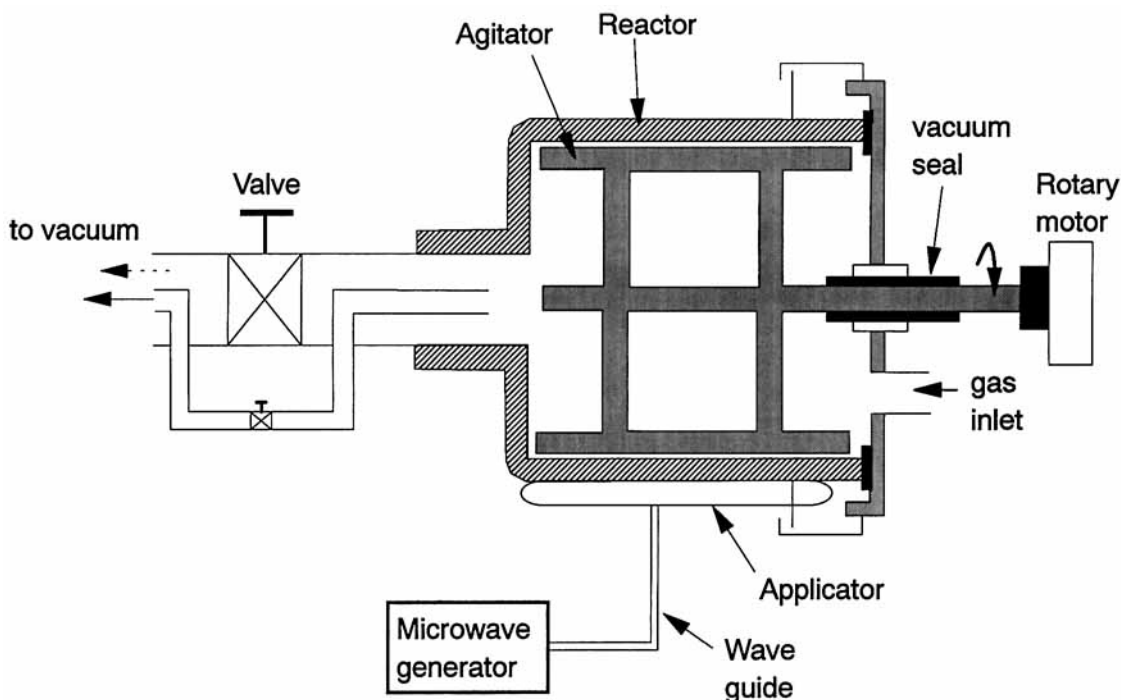


Figure 1 Schematic view of plasma reactor vessel, showing design of internal agitator.

and treatment times were 5, 15, and 60 s. Throughout these steps, the agitator was operated at 10 rpm. After quenching the plasma, gas flow and stirring was continued for 2 h, so as to minimize reactions between freshly treated surfaces and atmospheric gases and to reduce the risk of self-aggregation of freshly treated fibers. Finally, the reactor was brought to atmospheric pressure, and plasma-treated specimens were stored in desiccators for subsequent use.

As inferred above, the gases used for plasma treatments were ammonia, nitrogen, and methacrylic acid (MAA). The first two media were intended to enhance the basicity of the cellulose fiber surface by introducing electron donor groups into the material's surface. The MAA was expected to produce an acidic plasma polymer layer on the cellulose surface by the process of plasma deposition.

### Diagnostics and Property Evaluation

The effects of plasma treatments were studied by XPS and scanning electron microscopic (SEM) analyses. The apparatus and techniques used for XPS diagnoses were those described in our preceding article.<sup>8</sup> They were based on the use of a vacuum generator ESCALAB 3 MK II with monochromated  $MgK\alpha$  radiation. The take-off angle throughout was  $90^\circ$ , and curve fitting of the results was carried out

on smoothed data following a Shirley background correction. SEM analyses made use of a Jeol JSM 5300 installation, operating at 15–25 kV.

Interaction characteristics of control and surface-modified fibers and of host polymers were determined by the method of inverse gas chromatography (IGC).<sup>21</sup> The protocols leading to the evaluation of acid/base interaction parameters and of dispersion surface energies for solids in the IGC experiment have been discussed in considerable detail in contemporary articles.<sup>22–24</sup> These approaches were adopted for the work reported in Ref. 8 and for the present research. The solids were housed in stainless-steel columns; from 3.12 to 3.65 g of cellulose fiber was packed directly into the columns. The columns containing host polymers were those described in Ref. 8. IGC data were collected to conform with the requirements of the expression

$$RT \ln V_n = 2Na(\gamma_l^d)^{1/2} \cdot (\gamma_s^d)^{1/2} + \text{const} \quad (1)$$

where  $V_n$  is the net retention volume;  $N$ , Avogadro's number;  $a$ , the diameter of cross section of vapor probe molecules, and  $\gamma^d$ , the dispersion surface energies of the vapor ( $l$ ) and solid ( $s$ ) phases in the IGC experiment. Vapors representing dispersion-force materials were the  $n$ -alkanes from  $C_6$  to  $C_9$ ; following the acid/base theories of Gutmann,<sup>25</sup> chloroform was selected as the reference acid vapor

probe and diethyl ether as the reference base. The temperatures involved were 40, 50, 60, and 80°C. Multiple injections of the vapors produced symmetrical elution peaks. From these, retention times and volumes were obtained with a standard deviation less than 3.5%. Linear plots of  $RT \ln V_n$  vs.  $a(\gamma_f^d)^{1/2}$  for the alkane probes yielded values of a dispersion surface energy parameter for the stationary phases.<sup>†</sup> The results for polar probes were used to compute acid and base interaction parameters,  $K_a$  and  $K_b$ , respectively. The method described in Ref. 8 was again applied. However, in the earlier article, the units of acid and base parameters differ, a difficulty implicit in the application of Gutmann's theory.<sup>25</sup> The units problem can be resolved by applying the suggestions of Riddle and Fowkes,<sup>26</sup> as followed recently by Panzer and Schreiber<sup>23</sup> and again in this work. Thus, values of  $K_a$  and  $K_b$  quoted here can be used as a direct measure of the acidity/basicity balance of any one stationary phase.

Mechanical properties of composites were determined by stress/strain and by dynamic mechanical measurements. For stress/strain measurements, an Instron 1122 tester was employed, at a traction speed of 50 mm/min. At least five determinations were made for each composition. Maximum standard deviations were 5.1% for PS composites, 3.1% for PP composites, and 1.9% for those based on CPE. A Rheometrics RSA II instrument was used for dynamic mechanical measurements. The frequency was 0.5 Hz, and the heating ramp 2°C/min. Three samples of each composite were analyzed. Standard deviations throughout were < 3% and did not affect the relative position of curves.

## RESULTS AND DISCUSSION

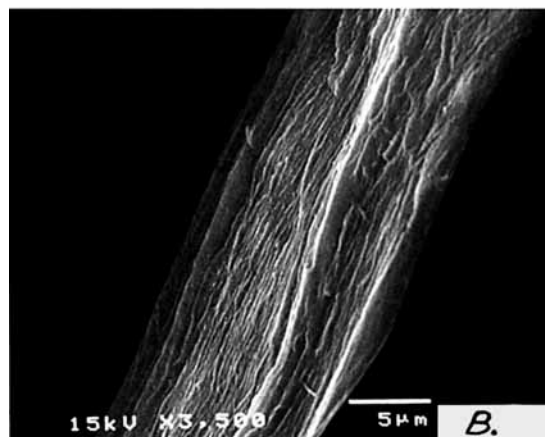
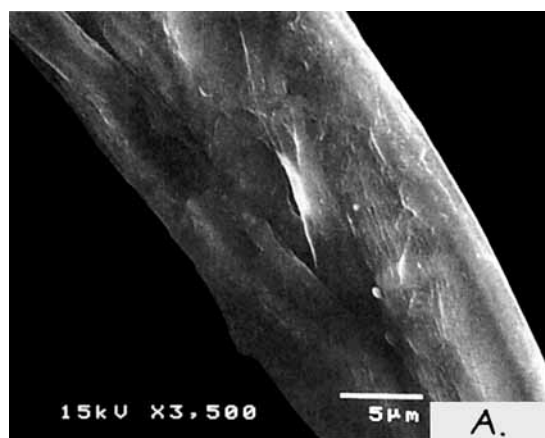
### Plasma Treatment Effectiveness

Earlier we noted limitations to the effectiveness of modifying the surfaces of particulates and fibers by plasma treatments. Treatment conditions for the present cellulose specimens were defined by preliminary experiments, which showed evidence of thermal degradation when microwave power input exceeded 300 W. The power used in all treatments was therefore limited to 200 W. Moreover, dynamic

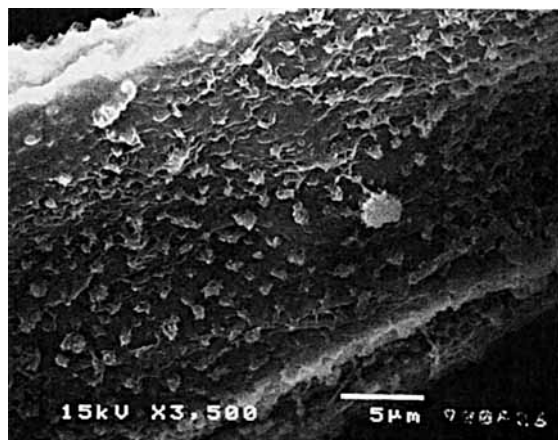
<sup>†</sup> Surface energies from IGC determinations will not necessarily agree with measurements made by conventional methods (e.g., contact angle), in part because at the very high dilutions used in IGC the vapor molecules may not interact randomly with surface sites and in part because local plasticization of the surface by contacting bulk liquids may affect contact-angle measurements.

pressures were also kept constant (0.8 Torr) and flow rates were set, as noted in the preceding section, so as to maintain a stable glow discharge. Treatment time was therefore the only variable retained for the present study.

The consequences of plasma treatment on the composition and appearance of cellulose fibers are summarized in Tables I and II and in Figures 2 and 3. Tables I and II refer to XPS analyses, with C, O, and N concentrations reported in Table II. These data derive from spectra illustrated in Figure 4 for untreated cellulose and fiber plasma-modified by 15 s treatment in MAA vapor. The composition of the untreated cellulose is reasonably close to theoretical expectations, deviations presumably being due to the presence of some lignin residues. Plasma treatments



**Figure 2** Comparing SEM views of cellulose fibers: (A) untreated control; (B) fiber following 60 s plasma treatment in nitrogen.

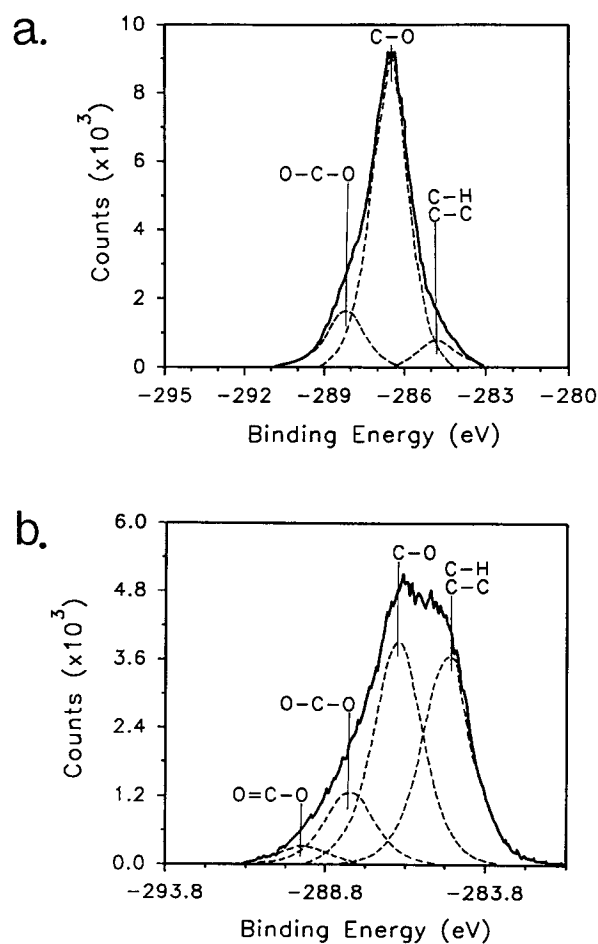


**Figure 3** SEM view of cellulose fiber following 60 s plasma treatment in MAA.

result in significant compositional changes: The appearance of nitrogen is characteristic of treatments with  $\text{NH}_3$  and nitrogen, whereas MAA plasmas reduce the O/C ratio, as might be anticipated. More detailed analyses of XPS results are shown in Table II. Evidently, nitrogen implanted by plasma exposure is associated with C—N, C=N, and N—C=O linkages. The data in both tables indicate that the generation of the nitrogen linkages is most effective in the first 15 s of plasma treatment. During that time, the dominant reaction appears to be that between activated species of nitrogen and cellulose, accompanied by the release of oxygen. At longer exposure times, the influence of other processes, which decrease the surface nitrogen concentration, become significant. These processes likely include (thermal) degradation and ablation of the modified surface layers. The topography of treated fibers is consistent with the suppositions. Figure 2 compares the surface of untreated cellulose fiber with one that had undergone extended  $\text{N}_2$  plasma treatment. Surface etching, in the form of uniaxial rowlike cavitations, is visible on the plasma-treated specimen.

MAA plasma treatments produce analogous results. Treatment times of 15 s appear to be best suited for effective surface modification. Marked increases in C—C content and corresponding diminutions in C—O linkages are observed. The contribution of carboxylic moieties to the C(1s) peak is evident, suggesting the deposition of MAA or of its plasma polymer. Lengthier treatment again seems counterproductive: The O/C ratio approaches that of untreated cellulose and once more implies loss of the surface-modifying layer deposited during shorter treatments. The O/C value of 0.6, obtained

after 15 s of treatment, leads to the following speculation: If the fiber surface were covered uniformly by PMAA, then the O/C value should be 0.5. Plasma polymers, however, are known to be structurally distinct from their conventional counterparts,<sup>27</sup> and we would expect the plasma polymer to have a somewhat lower O/C ratio than its conventional counterpart. Accepting a value in the range of 0.3–0.4 as reasonable, it would follow that the surface coverage attained by plasma treatment is only in the range of 40%. This incomplete coverage is consistent with the micrograph of Figure 3, which shows the deposit of MAA plasma treatment to be in the form of aggregates, rather than as a smooth layer. It is possible that the incomplete coverage attained is due partly to the heterogeneity of the cellulose surface, making it variably susceptible to plasma treatment. A more likely explanation for the findings in Tables I and II and Figures 2 and 3 is that the



**Figure 4** XPS spectra showing the C(1s) peaks for cellulose fibers: (a) unmodified cellulose; (b) MAA plasma-treated, 15 s exposure.

**Table I Chemical Composition as Obtained by ESCA of the Sample Surfaces**

Fiber Treatment (Medium and Time)	O/C Ratio	N/C Ratio	Relative Mol Percentages of		
			C	O	N
Untreated	0.77	—	56.5	43.5	—
Theoretical value	0.83	—	55.0	45.0	—
MAA					
15 s	0.60	—	62.5	37.5	—
60 s	0.69	—	59.2	40.8	—
N <sub>2</sub>					
15 s	0.62	0.10	58.7	34.2	7.1
60 s	0.72	0.06	56.2	40.4	3.4
NH <sub>3</sub>					
15 s	0.58	0.12	58.2	36.0	5.8
60 s	0.74	0.09	54.6	40.4	5.0

reactor used in this work still falls short of designs ideally suited to optimize surface modifications in fibers or particulates. Any changes in properties of composites using the present plasma-modified fibers

should therefore be considered as trend indicators. More drastic property modifications should be expected when improved reactors are able to produce more uniformly treated cellulose fibers.

**Table II Percentage of Different Carbons in Untreated and MAA Plasma-treated Sample and in N<sub>2</sub> and NH<sub>3</sub> Plasma-treated Samples**

(A) Percentage of Different Carbons in Untreated and MAA Plasma-treated Samples				
Fiber Treatment (Medium and Time)	C (1s)			
	C—H C—C 285.0 eV	C—O 286.5 eV	C=O O—C—O 288.0 eV	O=C—O 289.5 eV
Untreated	7.2	78.0	14.8	—
MAA				
15 s	39.7	42.9	13.9	3.5
60 s	4.1	74.8	15.3	5.8
(B) Percentages of Different Carbons in N <sub>2</sub> and NH <sub>3</sub> Plasma-treated Samples				
Fiber Treatment (Medium and Time)	C (1s)			
	C—H C—C 285.0 eV	C—N 285.8 eV	C=N C—O 286.9 eV	N—C—O O—C—O 288.6 eV
NH <sub>3</sub>				
15 s	19.2	21.4	47.4	12.0
60 s	4.4	6.1	74.2	15.3
N <sub>2</sub>				
15 s	14.6	14.1	56.2	15.1
60 s	6.1	8.3	79.4	6.2

### Acid/Base and Surface Energy Parameters

The acid/base indicators,  $K_a$  and  $K_d$ , and the dispersion surface energies ( $\gamma_s$ )<sup>d</sup> for cellulose fibers are stated in Table III (a)–(c); those for the host polymers are given in Table III(d). The temperature throughout is 60°C. The ( $\gamma_s$ )<sup>d</sup> of untreated cellulose is in good agreement with values for bleached kraft pulp reported by Gurnagul and Gray<sup>28</sup> determined by an IGC technique similar to the present. Nitrogen and ammonia plasmas have relatively little effect on the datum, the slight decreases with increasing treatment time being attributed, presumably, to ablation and degradation processes. MAA plasmas lead to a more pronounced decrease in ( $\gamma_s$ )<sup>d</sup>. The presence of plasma polymer (P-PMAA) would be a logical cause, with the effect being lessened by the incomplete surface coverage attained in these experiments (see Fig. 3).

The acid/base parameters are noteworthy. As noted in the previous publication,<sup>8</sup> cellulose is highly

interactive, with acid and base functionalities in near balance. This is evident from the ratio  $K_d/K_a$ , which is close to unity. The effects of various plasma treatments are more conveniently viewed via this ratio. As shown in Table III (a) and (b), treatments to 15 s by nitrogen and ammonia shift the interaction balance toward basicity, ammonia being the more effective medium, as might be expected. These changes are due to systematic increases in  $K_d$  and decreases in  $K_a$ . The longer 60 s treatment reverses the trend and leads to ratios again approaching unity. As shown previously by the XPS data, short exposure times are to be preferred, at least with the present plasma apparatus.

The flexibility of the plasma route to surface modification is illustrated in Table III(c). Here, MAA plasmas produce a sharp shift to surface acidity. Here, also, the systematic increase in  $K_a$  and decrease in  $K_d$  is not interrupted when going beyond 15 s treatment times. Clearly, the degradation products due to extended plasma treatment are strongly

**Table III Acid–Base Characteristics of NH<sub>3</sub>, N<sub>2</sub>, and MAA Plasma-treated Cellulose Fibers (I = 60°C) and of Host Polymers Used in This Study**

Treatment Time (s)	$\gamma_s^d$ (mJ/m <sup>2</sup> )	$K_a$	$K_d$	$K_d/K_a$
(A) Acid–Base Characteristics of NH <sub>3</sub> Plasma-treated Cellulose Fibers				
0	45.1	0.25	0.23	0.93
5	43.2	0.14	0.28	1.94
15	42.5	0.09	0.31	3.43
60	40.7	0.16	0.22	1.35
(B) Acid–Base Characteristics of N <sub>2</sub> Plasma-treated Cellulose Fibers				
0	45.1	0.25	0.23	0.93
5	43.7	0.22	0.27	1.25
15	43.1	0.16	0.30	1.80
60	41.0	0.19	0.22	1.16
(C) Acid–Base Characteristics of MAA Plasma-treated Cellulose Fibers				
0	45.1	0.25	0.23	0.93
5	40.1	0.30	0.20	0.69
15	36.9	0.33	0.15	0.44
60	38.2	0.39	0.10	0.25
(D) Acid–Base Characteristics of Host Polymers Used in the Study*				
Polystyrene (PS)	37.2	0.06	0.35	5.69
Polypropylene (PP)	32.8	0.01	0.00	—
Chlorinated polyethylene (CPE)	33.3	0.35	0.06	0.18

\* Based on data obtained in a previous study.<sup>8</sup>

acidic. Nevertheless, the shorter, 15 s period remains preferable for useful surface modification, as indicated by the XPS results discussed above.

The availability of  $K_a$  and  $K_d$  values with identical units for host polymers and fibers permits the calculation of pair interaction parameters. These might be useful for the interpretation of changes in composite properties due to plasma modifications. Following the precedent of our preceding report,<sup>8</sup> we obtain the pair interaction parameter  $P_{ad}$  from

$$P_{ad} = [K_{a,f} \cdot K_{d,m}]^{1/2} + [K_{d,f} \cdot K_{a,m}]^{1/2} \quad (2)$$

where the subscripts  $f$  and  $m$  denote fiber and matrix, respectively. The expression is to some extent arbitrary, other averaging methods being possible. Parameter values, valid for the temperature range studied, are listed in Table IV.

Although the changes in net acidity and basicity due to plasma treatments of cellulose are manifest [Table III(a)–(c)], the overall impact on  $P_{ad}$  is slight. In the case of PP, the  $P_{ad}$  data are of questionable significance given the (expectedly) very low values of  $K_a$  and  $K_d$  for this polymer. This matrix should interact at interfaces primarily through dispersion forces. The strong base PS and the acidic CPE generate high  $P_{ad}$  indexes, suggesting that acid/base forces exert considerable influence at contacts between matrix and inclusion. With PS, the highest  $P_{ad}$  parameters are produced when acidic, MAA-modified fibers are involved. In contrast, 15 s ammonia and nitrogen surface modifications of cellulose lead to maximum parameter values when the acidic CPE is the matrix.

**Table IV** The Specific Interaction Parameter,  $P_{ad}$ , for Various Fiber/Polymer Pairs

Fiber	Polymer		
	PS	PP	CPE
Untreated	0.41	0.07	0.40
NH <sub>3</sub> -treated			
5 s	0.35	0.07	0.41
15 s	0.32	0.07	0.42
60 s	0.35	0.06	0.38
N <sub>2</sub> -treated			
5 s	0.40	0.07	0.43
15 s	0.37	0.07	0.43
60 s	0.37	0.07	0.39
MAA-treated			
5 s	0.43	0.07	0.40
15 s	0.43	0.07	0.37
60 s	0.44	0.07	0.34

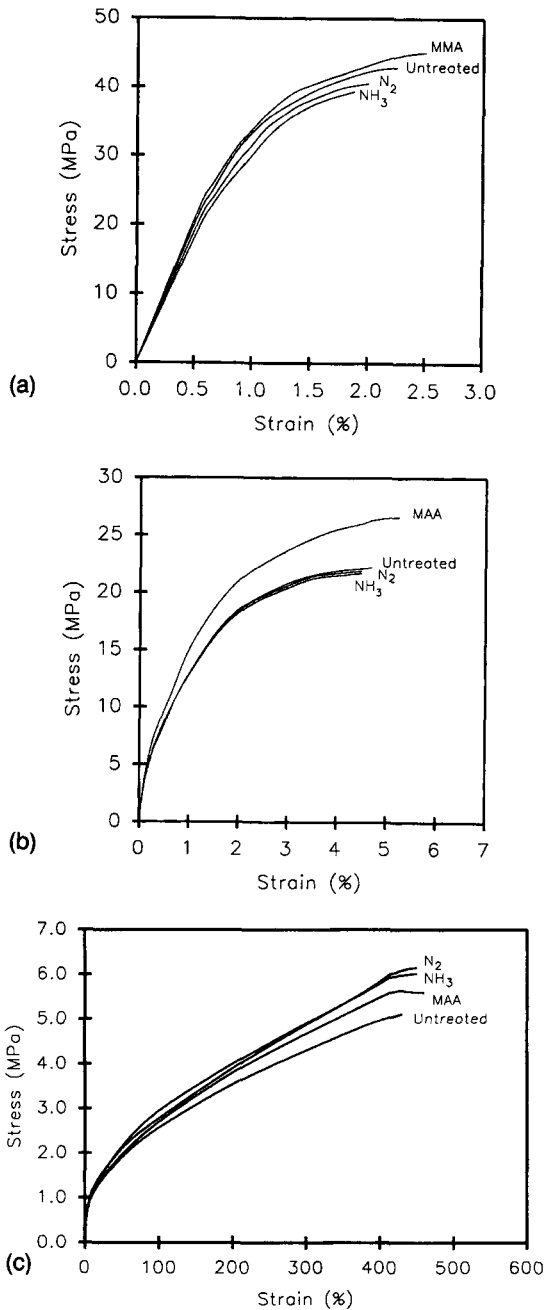
## Mechanical Property Analyses

The effects of plasma modification on mechanical properties of composites using the cellulose fibers are illustrated by the stress–strain curves in the various sections of Figure 5. In keeping with the evidence presented above, the composites with modified cellulose fibers use samples that had been given 15 s plasma treatments. In the case of PS [Fig. 5(a)], the sequence of curves follows expectations based on the contribution of acid/base forces, with the acidic MAA-modified fiber producing optimum changes in modulus and ductility. Plasma treatments leading to fibers with enhanced basic surfaces are counterproductive. The case of PP [Fig. 5(b)] also follows expectation to a degree, with nitrogen and ammonia plasmas ineffective. Unexpectedly, however, MAA modification leads to a preferred result, again with noticeable increases in elastic modulus and ductility. Indeed, regardless of the matrix, even when that is the acidic CPE of Figure 5(c), it is MAA modification that produces the preferred composite properties. Other factors than acid/base interactions must come into consideration, one being the presence of the discontinuous MAA plasma-polymer layer seen in Figure 3. The possibility then exists for local mechanical coupling (entanglement) between chains of the matrix polymer and those of the plasma deposit.

A broadly analogous situation exists when dynamic mechanical properties are under consideration. Typical results are given in Figure 6(a), showing the loss tangent/temperature plot for the series of PS composites, and in Figure 6(b) for CPE composites. The effects of plasma-surface modification are evident in the peak temperature as well as in the position of the peak in the  $y$ -axis. Increasing acid/base forces or the possibility of chain interpenetration should shift the peak temperature,  $T_{\delta_{max}}$  to higher values and might also be expected to lower the position of the peak,  $\tan \delta_{max}$ . These trends are evident in Figure 6.

Finally, an attempt can be made to separate the postulated acid/base and mechanical coupling factors by use of the  $P_{ad}$  parameter. To this end, the elastic modulus,  $E$ , the ultimate ductility,  $\epsilon_b$ , and  $T_{\delta_{max}}$  have been plotted against relevant  $P_{ad}$  values in the parts of Figure 7. The utility of acid/base considerations as a guide to property evolution in composites of this type varies substantially from matrix to matrix. In the case of PS composites [Fig. 7(a)], the relationship appears to be strong, and a further enhancement of the fiber-surface acidity predictably would lead to composites with more





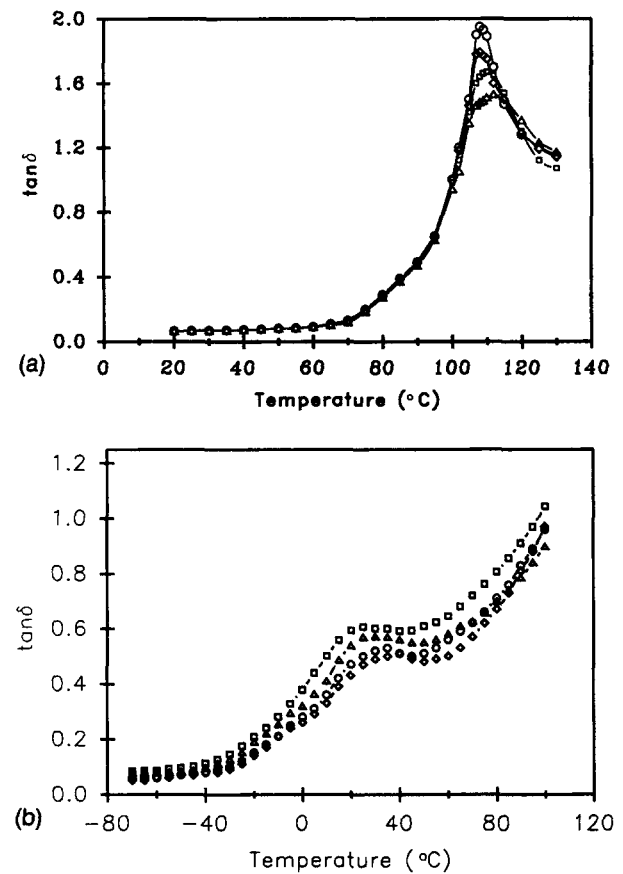
**Figure 5** Stress/strain curves for composites with untreated and plasma-modified cellulose fibers: (a) PS matrix; (b) PP matrix; (c) CPE matrix

substantially enhanced mechanical properties and with greater tolerance to elevated temperatures. The inference is put forth that analogous effects may be obtained with other basic matrices, such as polyamides and polycarbonates. The situation with the acidic CPE matrix is more complex, as shown in Figure 7(b). Introducing donor sites into the cellulose surface is unquestionably beneficial to the

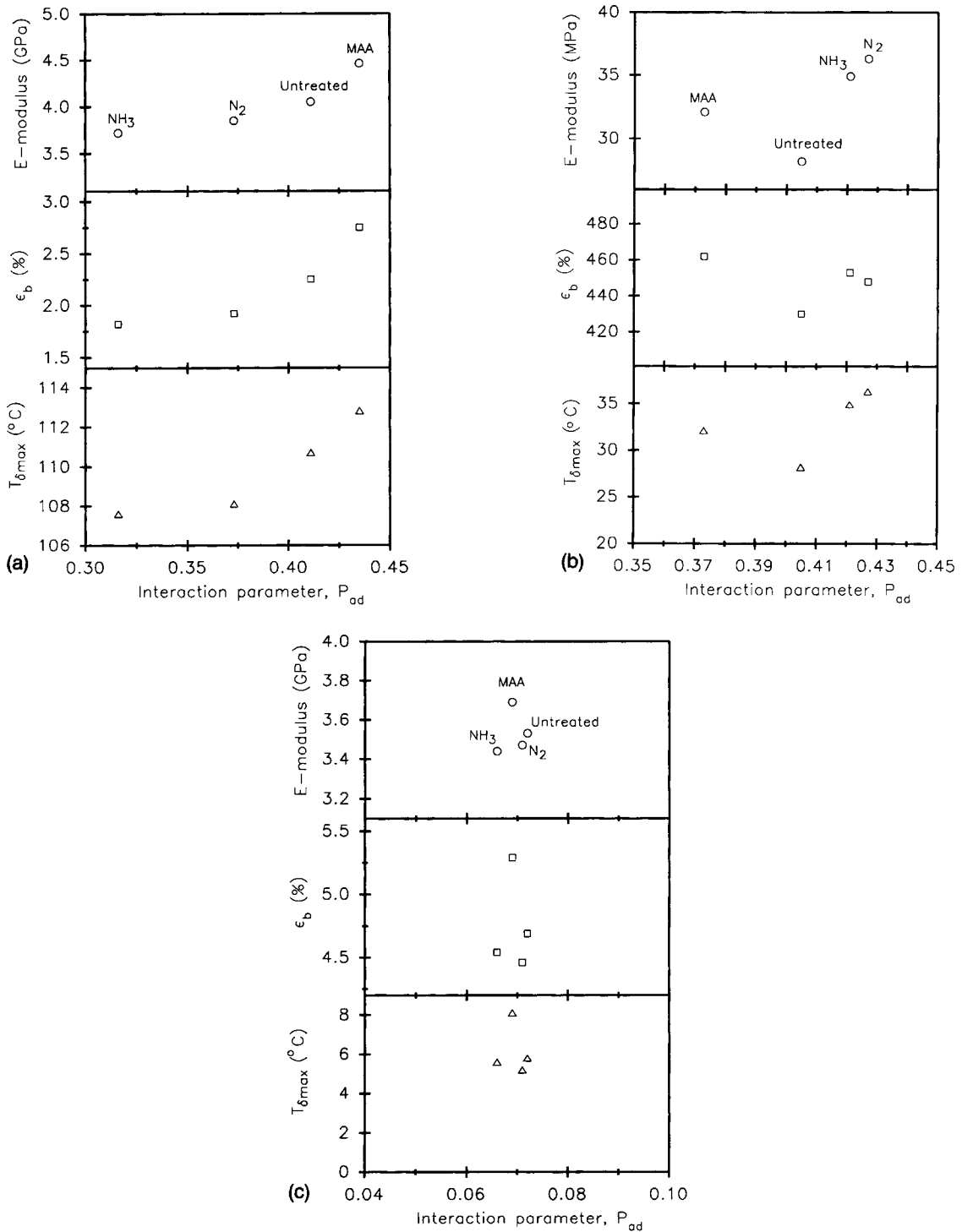
composite modulus and to the position of the apparent  $T_g$  value. The behavior of composites with MAA-modified cellulose fibers is anomalous, however, as noted above, and requires the introduction of additional mechanisms to account for observations. The acid/base concept therefore should be applied as a guide to superior composites, but the application carries the caution inherent in these analyses. Finally, and not surprisingly, there is no evident relationship between properties and  $P_{ad}$  for PP composites [Fig. 7(c)]. Again, extension of the conclusion can be made to other polyolefins and other dispersive-force matrices.

**CONCLUSIONS**

Microwave plasma treatments have been applied to cellulose fibers. By controlling the plasma environ-



**Figure 6** Illustrating dynamic mechanical responses. (a)  $\tan \delta$  vs.  $T$  for PS composites with control and 15 s plasma-treated fibers: ( $\square$ ) control; ( $\circ$ )  $\text{NH}_3$ ; ( $\diamond$ )  $\text{N}_2$ ; ( $\Delta$ ) MAA. (b)  $\tan \delta$  vs.  $T$  for CPE composites with control and 15 s plasma-treated fibers: ( $\square$ ) control; ( $\circ$ )  $\text{NH}_3$ ; ( $\diamond$ )  $\text{N}_2$ ; ( $\Delta$ ) MAA.



**Figure 7** Testing relevance of relationships between selected mechanical properties of composites and acid/base interaction parameter,  $P_{ad}$ : (a) modulus, ductility, and  $T_{\delta_{max}}$  for PS composites; (b) modulus, ductility, and  $T_{\delta_{max}}$  for CPE composites; (c) modulus, ductility, and  $T_{\delta_{max}}$  for PP composites.

ment, the acid/base interaction balance of cellulose fiber surfaces can be shifted toward acidity or basicity. The former effect was produced by treatments

with MAA, and the latter, by treatments with nitrogen or ammonia as reactive gases. Only partial surface modification can be claimed, however, due

either to limitations in current reactor design and/or to the limited susceptibility of the fibers to effective plasma modification.

Techniques including IGC, XPS, and SEM have proven to be valuable in evaluating the effectiveness of plasma treatments. The IGC protocol again proved to be a valuable tool for the quantification of acid/base interactions at matrix/fiber contacts.

Mechanical properties of composites based on PS and CPE, and using plasma-modified cellulose fibers, were improved when strong acid/base interaction between matrix and fiber was favored. Acid/base factors, however, are not the sole determining criterion in the development of composite mechanical properties. The properties of PP-based composites were unaffected by acid/base considerations.

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