PII: S0032-3861(97)00587-9

Surface modification of polymer films by graft copolymerization for adhesive-free adhesion

E. T. Kang[a,*], K. G. Neoh[a], Z. F. Li[a], K. L. Tan[b] and D. J. Liaw[c]
[a]*Department of Chemical Engineering, National University of Singapore, 119260 Kent Ridge, Singapore*
[b]*Department of Physics, National University of Singapore, 119260 Kent Ridge, Singapore*
[c]*Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan, R.O.C.*

The surfaces of low density polyethylene (LDPE), poly(carbonate) (PC), polytetrafluoroethylene (PTFE) and emeraldine (EM) base films of poly(aniline) are modified by graft copolymerization with N,N-dimethylacrylamide (DMAA), Na salt of styrenesulfonic acid (NaSS), 3-dimethyl(methacryloylethyl)ammonium propanesulfonate (DMAPS) and acrylic acid (AAc). Two surface graft copolymerized films are capable of exhibiting 'adhesive-free' adhesion or auto-adhesion when brought into contact in the presence of water and subsequently dried. The development of the lap shear adhesion strength depends upon the concentration of the surface graft, the contact adhesion (drying) time, the nature of the substrate, the microstructure of the graft copolymerized surfaces and the extent of molecular interaction (dispersive, electrostatic, etc.) at the lapped junction. Lap shear adhesion strengths in excess of 90 N cm^{-2} were readily achieved between films graft copolymerized with the amphoteric DMAPS, as well as between a DMAPS graft copolymerized EM film and an AAc graft copolymerized PTFE film. X-ray photoelectron spectroscopy (x.p.s.) analysis of the delaminated surfaces suggests that the failure mode involves the fracture of the graft chains at the substrate–graft interface. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: graft copolymerization; adhesive-free adhesion; x.p.s.)

INTRODUCTION

In most engineering applications, a polymer is selected because of its favourable bulk properties, such as mechanical strength, electrical properties, thermal stability and processability. Often, however, the selected polymer may have surface characteristics that are less than optimum for the intended application. For example, the surfaces of most engineering polymers in use today are all fairly hydrophobic. As a result, it is difficult to directly bond the hydrophobic polymer surfaces with other substances, such as adhesives, printing inks and paints which generally consist of polar groups or components. The problem can be overcome to a large extent through controlled modification and functionalization of polymer surfaces via molecular design[1-3]. Physical and chemical methods for the modification of polymer surfaces, which have direct relevance to adhesion improvement of enhancement, have also been summarized[4-6].

Although plasma treatment is probably the most widely used technique in the surface modification of polymers[3,5,7-11], the physicochemical characteristics of the modified polymer surfaces are time-dependent. Furthermore, the chemical compositions of the plasma-modified surfaces can vary widely with the glow discharge conditions, such as plasma power, oscillator frequency, sample-electrode configuration, gas pressure and sample surface preparations, etc. One method of eliminating the time- and condition-dependent effects of plasma and other physical

treatments is to subject the physically modified polymer films to further modification, for example via surface grafting or surface graft copolymerization.

In the present work, some pristine, argon plasma and ozone pretreated polymer films were subjected to further surface modification via thermally or near-u.v. light induced graft copolymerization with water-soluble ionic and amphoteric monomers. The surface composition and microstructure of the graft copolymerized films were characterized by angle-resolved X-ray photoelectron spectroscopy (x.p.s.). The possibility of achieving an 'adhesive-free' condition between two surface-modified films from graft copolymerization is demonstrated. In comparison with adhesive-promoted adhesion, 'adhesive-free' adhesion may provide several advantages, such as simple and convenient bonding operation, absence of an adhesive layer and uniform adhesion junction thickness.

EXPERIMENTAL

Materials

Low density polyethylene (LDPE) film, polytetrafluoroethylene (PTFE) film and poly(carbonate) (PC) film with a thickness of about 125, 100 and 75 μm, respectively, were obtained from Goodfellow Inc. of Cambridge, UK. The films were purified by Soxhlet extraction with methanol for 6 h before use. The electroactive poly(aniline) (PANi) in its emeraldine (EM) base form was first prepared by the oxidative polymerization of aniline by ammonium persulfate in 1 M HCl according to the method reported in the

literature[12]. It was then converted to the neutral EM base by treatment with excess 0.5 M NaOH. Free standing and lightly crosslinked EM films of about 30 μm in thickness were prepared by heating the concentrated N-methylpyrrolidinone (NMP) gel solution (containing 8% EM base by weight) at 150°C for about 6 h, followed by exhaustive pumping under reduced pressure[13]. The EM base so prepared has a tensile yield strength of about 120 N cm^{-2}. The two anionic monomers, acrylic acid (AAc) and sodium salt of 4-styrenesulfonic acid (NaSS), and the two cationic monomers, N,N-dimethylacrylamide (DMAA) and acrylamide (AAm) were obtained from Aldrich Chem. Co. of Milwaukee, USA. The amphoteric monomer, 3-dimethyl-(methacryloylethyl)ammonium propanesulfonate (DMAPS) was prepared according to the method reported earlier[14]. The DMAPS molecule has the following chemical structure: $CH_2=C(CH_3)COOC_2H_4N^+(CH_3)_2C_3H_6SO_3^-$.

Surface pretreatment and graft copolymerization

Ozone pretreatment of LDPE and PC films was carried out in the Fisher Model 500 ozone generator operating at 100 V with the pure oxygen inlet flow rate fixed at 100 l h^{-1} to give an ozone production rate of about 3 g h^{-1}. The ozone exposure time of the films was fixed at 20 min. This treatment time has been found to be sufficient in activating the polymer film surfaces without causing excessive surface oxidative degradation. Due to the reactive nature of the conjugated polymer surfaces, surface graft copolymerization on emeraldine (EM) film was carried out in the absence of any surface pretreatment. In fact, surface pretreatment of EM film by ozone[15] and Ar plasma[16] may be accompanied by other side reactions, in addition to surface oxidation. Thermal graft copolymerization of LDPE, PC and EM films was carried out by immersing films strips of about 4 cm × 6 cm in size in aqueous monomer solution of a predetermined concentration. The reaction mixture was thoroughly purged with nitrogen and then kept in a 65°C (for the ozone-pretreated LDPE and PC films) or a 80°C (for EM films) water bath for about 1 h. After the thermal graft copolymerization, each film strip was removed from the viscous homopolymer solution and washed with a jet of doubly distilled water. Thereafter, it was subjected to repeated rinsing and soaking in a gently stirred water bath for at least 48 h to remove the residual adsorbed homopolymer. Due to the chemical inertness of the PTFE films, they were pretreated with Ar plasma before graft copolymerization. Argon plasma pretreatment was carried out on a bell-jar-type glow discharge cell (Model LCVD 12, manufactured by Shimadzu Corp., Kyoto, Japan) at an applied frequency of 5 kHz, a plasma power of 28 W and an Ar pressure of 0.04 torr. Near-u.v. light induced surface graft copolymerization of the Ar plasma pretreated PTFE films with AAc, NaSS and DMAA was carried out according to the procedures reported earlier[17].

Surface characterization

The polymer films after graft copolymerization were characterized by angle-resolved X-ray photoelectron spectroscopy (x.p.s.). X.p.s. measurements were made on a VG ESCALAB MKII spectrometer with a Mg Kα X-ray source (1253.6 eV photons) at a constant retard ratio of 40. The polymer films were mounted on the standard sample studs by means of double-sided adhesive tapes. The core-level signals were obtained at a number of photoelectron take-off angles (α, with respect to sample surface), ranging from 20 to 75°. The X-ray source was run at a reduced power of

120 W (12 kV and 10 mA). The pressure in the analysis chamber was maintained at 10^{-8} mbar or lower during each measurement. All binding energies (BEs) were referenced to the C1s neutral carbon peak at 284.6 eV. In peak synthesis, the linewidth (full width at half maximum or FWHM) for the Gaussian peaks was maintained constant for all components in a particular spectrum. Surface elemental stoichiometries were determined from peak–area ratios, after correcting with the experimentally determined sensitivity factors, and were accurate to within 5%. The elemental sensitivity factors were determined using stable binary compounds of well-established stoichiometries.

Adhesion strength measurements

Adhesive-free adhesion was achieved by lapping together two graft copolymerized polymer strips in the presence of 4 μl of deionized water and under a constant load of 10.5 N at 25°C. The contact area of the films was kept at 0.5 cm × 0.5 cm, unless otherwise specified. The adhesion strengths were determined by measuring the lap shear force with the Miniature Materials Tester from Rheometric Scientific, UK. All measurements were carried out at a crosshead speed of 0.1 cm min^{-1}, and as a function of the lapping time. For each lap shear strength reported, at least three sample measurements were averaged.

RESULTS AND DISCUSSION

The concentration of the surface graft, defined as the number of repeating units of the graft chain per repeating unit of the substrate chain, is determined in each case from the x.p.s. derived surface compositions, similar to the method reported earlier[18,19].

Low density polyethylene (LDPE) films

The concentration of the surface grafted AAc polymer is determined by comparing the area of the $\overline{COOH}$ component at the binding energy (BE) of 288.7 eV in the C1s core-level spectrum and that of the main neutral C1s peak at 284.6 eV, taking into account of the fact that each AAc monomer unit also contributes two carbon atoms to the latter peak component. The concentrations of the surface grafted NaSS, DMAA and DMAPS polymers, on the other hand, are calculated directly from the sensitivity factors—corrected S2p and C1s (for NaSS) or N1s and C1s (for DMAA and DMAPS) core-level spectral area ratios, taking into account of the carbon stoichiometries of the graft and the substrate chains in each case. *Table 1* summarizes the concentration of the surface graft, as determined at two x.p.s. photoelectron take-off angles (αs) of 20 and 75°, for the ozone pretreated LDPE films after graft copolymerization in 10 wt% aqueous AAc, NaSS, DMAA and DMAPS monomer solutions. In each case, the angular dependent x.p.s. data readily reveal a significantly lower graft-to-substrate chain ratio at the outermost surface of the LDPE film compared to that in the sub-surface layer. The angular-dependent x.p.s. results thus suggest that the hydrophilic

Table 1 The concentrations of the surface graft (moles of graft per mole of substrate), measured at two αs, on ozone pretreated LDPE films after the thermally induced graft copolymerization in 10 wt% AAc, NaSS, DMAA and DMAPS monomer solutions

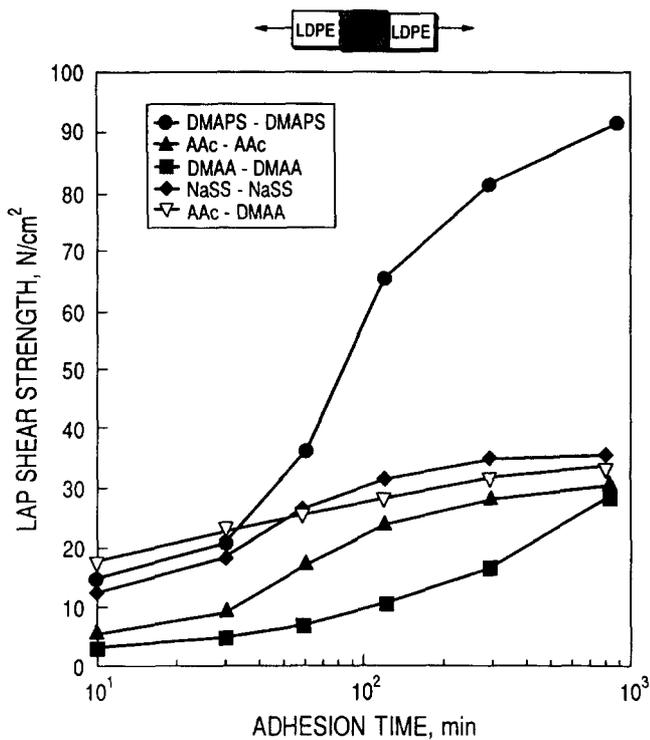|	[AAc]	[NaSS]	[DMAA]	[DMAPS]
$\alpha = 20°$	0.68	0.16	1.36	6.36
$\alpha = 75°$	2.14	0.82	8.69	9.05

Figure 1 Lap shear adhesive-free adhesion strength as a function of adhesion (drying) time between two surface-modified LDPE films from surface graft copolymerization

polymer graft must have become submerged beneath a thin surface layer, which has a higher substrate-to-graft chain ratio than the sub-surface layer, to form a stratified surface microstructure. This stratified surface microstructure has been reported in a number of earlier studies involving the

graft copolymerization of hydrophilic monomers on hydrophobic substrates[17-21].

The lap shear adhesion strengths between two identically modified LDPE films from graft copolymerization with AAc, NaSS, DMAA and DMAPS were measured after a fixed period of drying (adhesion) time, as shown in *Figure 1*. The respective graft concentrations correspond to those reported in *Table 1*. In all cases, the lap shear adhesion strengths increase steadily with adhesion time. With sufficient drying time, the adhesion force between the films becomes so strong that the lap shear strengths for all film pairs reach the tensile yield strength of the pristine LDPE film used. Substrate yielding in this case occurs when the shear force experienced by the 0.5 cm $\times$ 0.5 cm junction exceeds 30 N cm^{-2}. At this point, the LDPE film undergoes a substantial elongation before failure occurs at the lapped junction. Thus, with proper drying of the lapped junction, the LDPE film with surface grafted AAc, NaSS, DMAA and DMAPS polymers are capable of achieving an adhesion strength approaching or greater than the tensile yield strength of the pristine LDPE film ($\sim$30 N cm^{-2}), when an adhesion area of 0.5 cm $\times$ 0.5 cm was used. In fact, the DMAPS graft copolymerized films adhere to one another so strongly that the lapped adhesion area for this particular junction was reduced to 0.5 cm $\times$ 0.1 cm in *Figure 1* in order to obtain the ultimate adhesion strength of this junction in the absence of any substrate yielding. Thus, for the present DMAPS graft copolymerized LDPE films, an 'adhesive-free' lap shear adhesion strength above 90 N cm^{-2} can be readily achieved.

The stratified surface microstructure associated with the graft copolymerized surface in the dehydrated (dried) state and its relation to the observed 'adhesive-free' adhesion between two polymer surfaces are depicted schematically in *Figure 2*. Rehydration of the stratified
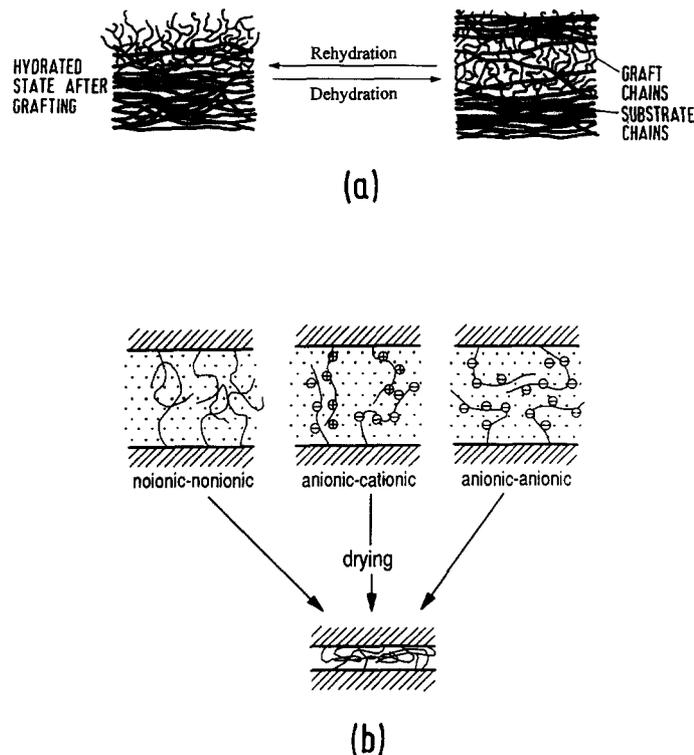

Figure 2 Schematic diagrams of (a) the stratified surface microstructure after graft copolymerization and (b) the hydrated or wetted interface during the 'adhesive-free' adhesion process

surface microstructure readily results in the resurfacing of the grafted hydrophilic chains (*Figure 2a*)[19]. As the water-soluble chains are tethered to the substrate surface, they do not dissolve into the aqueous medium in the re-hydrated state, but become swollen in the presence of water. The adhesion process can be defined in terms of microscopic interactions at an interface and is related to the sum of all the intermolecular interactions at the interface[22,23]. After the intimate contact is established between the two polymer surfaces, segments of the grafted chains diffuse across the interface and the adhesion is related to the extent of interdiffusion and chain interpenetration across the inter-face. The chain diffusion and entanglement are made possible by the aqueous environment at the interface. With the decreasing water content at the interface during drying, the interfacial viscosity of the graft phase increases, resulting in a reduction in mass transfer but an increase in shear strength and frictional force. Finally, the water evaporates and the diffused chains contract and become strongly entangled with one another[24,25]. The process is shown schematically in *Figure 2b*.

In the case of DMAPS graft copolymerized film, the adhesion strength is further enhanced by the interchain and intrachain electrostatic (Coulombic) interaction arising from the amphoteric nature (i.e. containing both the $-CN^+-$ and $-SO_3^-$ species) of the grafted chains. Furthermore, as the electrostatic interaction is less dependent on chain diffusion and entanglement, as well as the presence of water at the interface, respectable lap shear adhesion strength developed immediately after the two DMAPS graft copolymerized films are brought into contact. The latter phenomenon is further confirmed in the case of the 'hetero-junction' formed between AAc and a DMAPS graft copolymerized film (*Figure 1*). Although the electrostatic interaction may contribute to the development of adhesion strength especially in the initial stage, chain diffusion and entanglement become of increasing importance with adhesion time. As a result, the overall final adhesion strength is still governed by the surface graft concentration and, in the case of films with chemically different graft chains, the miscibility between the graft chains. The last two factors may help to account, partially, for the lower final adhesion strength observed between the AAc–DMAA pair than that of the DMAPS–DMAPS pair.

Poly(carbonate) (PC) films

As in the case of LDPE, the ozone pretreated PC films are susceptible to further surface modification via thermally induced graft copolymerization with AAc, DMAA, NaSS and DMAPS. The x.p.s. C1s core-level spectrum of the pristine PC film, with $(C_6H_4-C(CH_3)_2-C_6H_4-O-COO)$ repeating structural units, can be resolved into three main components with BEs at about 284.6, 286.2 and 290.4 eV, arising from the neutral backbond carbons, carbon single bonded to oxygen (–C–O), and the PC functional group (–OCOO–), respectively[26]. The concentration of the surface grafted AAc polymer is again determined from the appearance of a distinct high BE-component at about 288.6 eV, attributed to the carboxyl group, and taking into account of the fact that each AAc unit also contributes two carbon atoms to the neutral carbon peak component. The concentrations of the surface grafted NaSS, DMAA and DMAPS polymers are determined as before from the S2p and C1s (for NaSS) or N1s and C1s (for DMAA and DMAPS) core-level spectral area ratios, taking into account

Table 2 The concentrations of the surface graft (moles of graft per mole of substrate), measured at two αs, on ozone pretreated PC films after the thermally induced graft copolymerization in 10 wt% AAc, NaSS, DMAA and DMAPS monomer solutions

	[AAc]	[NaSS]	[DMAA]	[DMAPS]
$\alpha = 20°$	5.62	0.47	2.53	7.23
$\alpha = 75°$	10.15	0.50	7.80	9.65

the carbon stoichiometries of the graft and the substrate chains in each case.

Table 2 summarizes the concentration of the surface graft, as determined at αs of 20 and 75°, for the ozone pretreated PC films after graft copolymerization in 10 wt% aqueous AAc, NaSS, DMAA and DMAPS monomer solutions. The extensive graft coverages in the case of AAc, DMAA and DMAPS graft copolymerized films have also resulted in the disappearance of most of the carbonate component (–OCOO–) signal in the C1s core-level spectra. On the basis of the distinct angular-dependent surface compositions, the graft structure or morphology of the modified PC surface can also be described by a stratified surface microstructure. This microstructure must have resulted from the migration and counter-migration of the substrate and the grafted chains. This process is probably made possible, at least in part, by the lowering of the glass transition temperature of the substrate due to modifications in the surface region by ozone treatment, thermal effect during grafting, and finally graft copolymerization. The reorientation of polar groups into the more hydrophobic bulk phase has also been known to reduce the overall free energy of the system[20,27].

The lap shear adhesion forces at break between two identically modified PC films from graft copolymerization with AAc, NaSS, DMAA and DMAPS were measured after a given adhesion (drying) time (*Figure 3*). The adhesion strength increases monotonically with adhesion time in each case. In the case of DMAPS graft copolymerized film, the electrostatic interactions arising from the amphoteric nature of the grafted chain readily give rise to adhesion strength exceeding the tensile yield strength of the substrate. Substrate yielding in this case was initiated when the shear force experienced by the 5 cm × 5 cm lapped junction reached about 76 N cm^{-2}. Electrostatic interactions also give rise to a respectable lap shear adhesion strength even when the junction is wet. Similar phenomena are also observed in the case of lap shear adhesion strength of the hetero-junction formed between an AAc and a DMAPS graft copolymerized film, as shown in *Figure 3*. The lapped area for the last two assemblies was reduced to 0.5 cm × 0.1 cm to avoid the yielding of the substrate before the adhesion failure. It should be emphasized that electrostatic interaction alone is insufficient for high adhesion strength. The point is further supported by the fact that the adhesion strengths for the corresponding hetero-junction formed between the NaSS and the DMAA graft copolymerized films were only comparable to those observed between the NaSS graft copolymerized films in *Figure 3*, due to the low concentration of the surface grafted NaSS polymer.

Emeraldine (EM) base films of poly(aniline)

Due to the reactive nature of the conjugated polymer surface, the pristine EM base films of poly(aniline) are readily susceptible to thermally induced graft copolymerization with AAc, NaSS, DMAPS and acrylamide (AAm). The concentrations of the surface graft can be readily
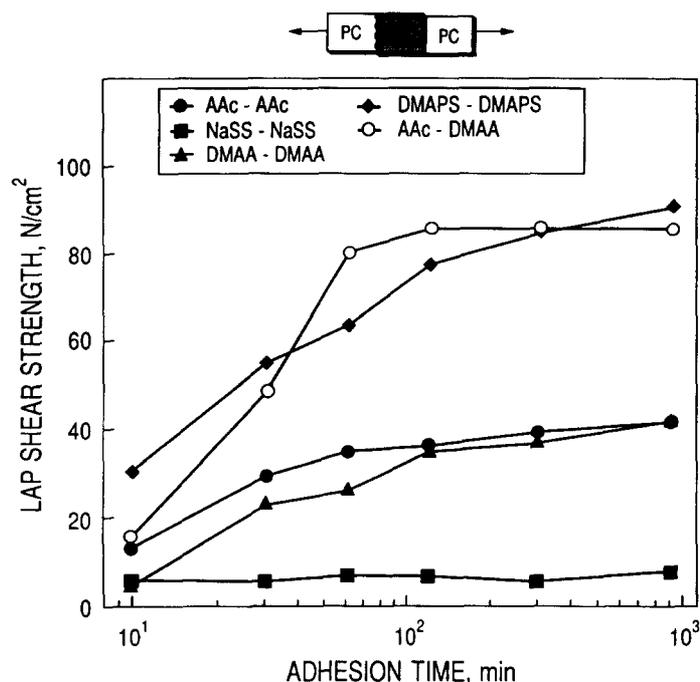
Figure 3 Lap shear adhesive-free adhesion strength as a function of adhesion (drying) time between two surface-modified PC films from surface graft copolymerization

determined from the x.p.s. derived [COOH]/[N], [S]/[N], [S]/[neutral N] and [H$_2$NC = O]/[N of EM] ratios, respectively[28,29]. The positively charged nitrogen of the surface grafted DMAPS polymer (N1s BE = 401.5 eV) can be quantitatively differentiated from the neutral imine (N1s BE = 398.2 eV) and amine nitrogen (N1s BE = 399.4 eV) of EM base in the properly curve-fitted N1s core-level spectrum[29]. The amide functional group of AAm has a C1s component BE at about 287.8 eV and contributes one nitrogen atom to the overall N1s spectrum[28]. *Table 3* summarizes the concentrations of the surface graft, as determined at αs of 20 and 75°, for the EM base films after graft copolymerization in 10 wt% aqueous AAc, NaSS, AAm and DMAPS monomer solutions. The angular-dependent surface compositions in this case readily suggest that a higher graft-to-substrate chain ratio is present at the outermost surface (α = 20°), rather than in the sub-surface region, of the EM base films. This result differs from the stratified surface microstructure of the thermoplastics film after the surface grafting of a hydrophilic polymer. Nevertheless, this result is consistent with the reduced substrate chain mobility arising from the lightly crosslinked nature[13] of the EM base film.

The lap shear adhesion strengths between two identically modified EM base films from graft copolymerization with AAc, NaSS, AAm and DMAPS are plotted against the adhesion (drying) time in *Figure 4*. With the exception of the NaSS graft copolymerized films, which have relatively
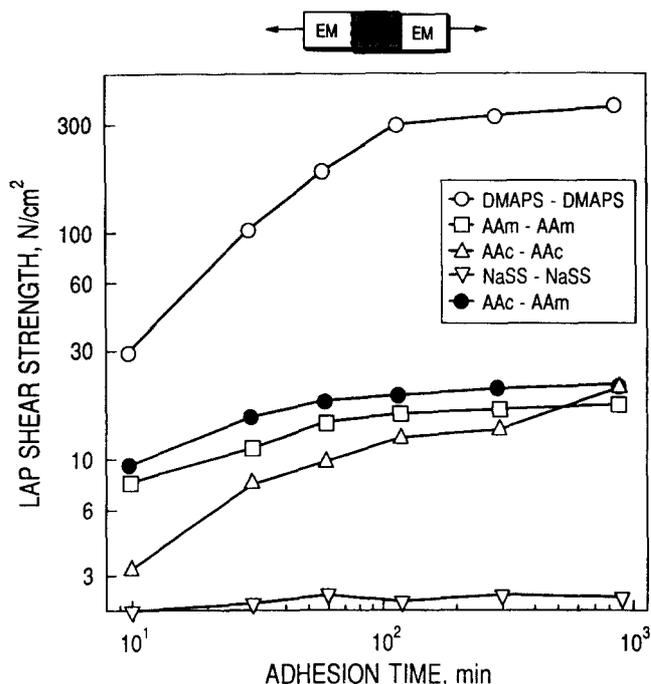

Figure 4 Lap shear adhesive-free adhesion strength as a function of adhesion (drying) time between surface-modified EM base films from surface graft copolymerization

low graft concentration, the adhesion strengths increase monotonically with adhesion time in the other three cases. In the case of the DMAPS graft copolymerized EM films with 300 min of adhesion time and a reduced lapping area of 0.5 cm × 0.1 cm, an adhesion strength of about 340 N cm^{-2} was observed. The lap shear adhesion strengths of the AAc and AAm graft copolymerized EM base films are far below that observed between the two DMAPS graft copolymerized films. The unusually high adhesion strength observed in the latter assembly must have resulted from a combined effects of high surface graft concentration and the presence of

Table 3 The concentrations of the surface graft (moles of graft per mole of substrate), measured at two αs, on pristine EM base films after the thermally induced graft copolymerization in 10 wt% AAc, NaSS, DMAA and DMAPS monomer solutions

	[AAc]	[NaSS]	[AAm]	[DMAPS]
α = 20°	3.0	0.39	2.85	*[a]
α = 75°	2.35	0.22	1.40	*

[a]Complete surface coverage by DMAPS polymer, no EM base chain was detected at the probing depth of the x.p.s. technique

strong electrostatic interaction arising from the amphoteric nature of the DMAPS units. The presence of the electrostatic interaction again readily gives rise to a respectable adhesion strength even for the 'wet' junction. The latter effect is also observed in the case of the hetero-junction formed between an AAc and an AAm graft copolymerized EM film. The fact that the final adhesion strength of this hetero-junction is not substantially enhanced by electrostatic interaction over those of the corresponding homo-junction further supports the earlier conclusion that electrostatic interaction alone is insufficient for achieving high adhesion strength.

Adhesive-free adhesion between emeraldine and conventional polymer films

In exploring the practical applications of an electroactive polymer film, it is important to study its adhesion to other conventional polymer films. The PTFE film was first selected among all the conventional polymers because of its importance as a dielectric polymer and also because of its physical and chemical inertness.

Our earlier studies[17,18] have shown that the Ar plasma pretreated PTFE films are readily susceptible to further surface modification via near-u.v. light induced graft copolymerization with various hydrophilic monomers. In all cases, the graft yield increases with increasing plasma pretreatment time. *Table 4* summarizes the x.p.s. derived concentrations of surface grafted AAc and DMAA polymer on PTFE films with 10 and 40 s of plasma pretreatment time. The surface concentrations of the grafted AAc and DMAA polymers are determined first from the [COOH]/[F] and [N]/[F] ratios, respectively, and then taking into account also the fact that there are four fluorine atoms per repeating unit of the PTFE chain. The angular-dependent x.p.s. results again suggest the presence of 'surface restructuring' to minimize the surface free energy after graft copolymerization. A significantly higher substrate-to-graft chain ratio in the top surface layer than in the sub-surface layer is always obtained for the PTFE surface with a substantial amount of grafted hydrophilic chains. The phenomenon of adhesive-free adhesion between two surface-modified PTFE films from surface graft copolymerization has been reported earlier[30].

Figure 5 summarizes the adhesive-free adhesion results of the AAc, AAm and DMAPS graft copolymerized EM base films with the AAc and DMAA graft copolymerized PTFE films. The adhesion strength of the AAc or AAm graft copolymerized EM base film with the AAc graft copolymerized PTFE film is higher than that of the corresponding EM base film pair. The result can be attributed to the more intimate contact between the 'stiff', lightly crosslinked EM base film and the 'flexible' PTFE film, as well as a higher AAc polymer concentration on the PTFE surface. Due to the high adhesion strength for the EM–PTFE assembly, the lapped adhesion area was reduced to only 0.5 cm × 0.1 cm
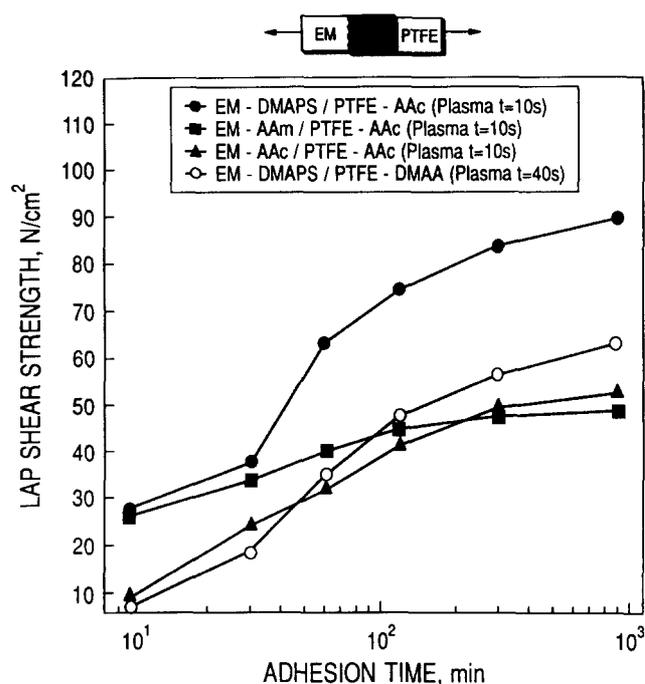

Figure 5 Lap shear adhesive-free adhesion strength as a function of adhesion (drying) time between two surface graft copolymerized EM base and PTFE films from surface graft copolymerization
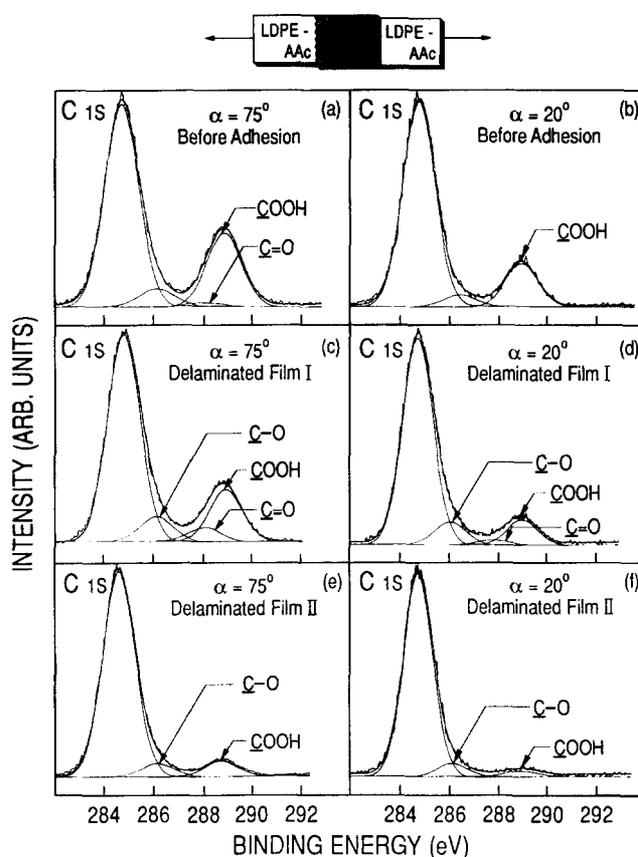
Table 4 The concentrations of the surface graft (moles of graft per mole of substrate), measured at two αs, on Ar plasma pretreated PTFE films after the near-u.v. light induced graft copolymerization in 10 wt% AAc and DMAA monomer solutions

	Ar plasma pretreated $t = 10$ s		Ar plasma pretreated $t = 40$ s	
	[AAc]	[DMAA]	[AAc]	[DMAA]
$\alpha = 20°$	14.6	0.48	88.0	0.80
$\alpha = 75°$	72.8	0.44	278	3.28

Figure 6 C1s core-level spectra, obtained at αs of 75 and 20°, for the AAc graft copolymerized LDPE film before adhesion, (a) and (b). The corresponding spectra for the two delaminated surfaces after adhesive-free adhesion are shown in (c) to (f)

so that the adhesion strength remained below that of the yield strength of the PTFE film used. Yielding of the PTFE substrate commences when the shear force experienced by the 0.5 cm × 0.5 cm lapped junction exceeds 20 N cm^{-2}. It is also discernible that the electrostatic interaction dominates the observed adhesion strength in the initial stage and the diffusion and entanglement of the grafted chains become predominant in the later stage. The adhesion strength between the DMAPS graft copolymerized EM base film and the AAc graft copolymerized PTFE film, or the DMAP-S(EM)–AAc(PTFE) pair, is always higher than that of the AAc(EM)–AAc(PTFE) or the DMAPS(EM)–DMAA(PTFE) pair. This phenomenon is again attributable to the high concentrations of grafted DMAPS and AAc chains on the EM and PTFE surfaces, respectively, as well as the amphoteric nature of the DMAPS chains.

The failure mode of adhesive-free adhesion

Two AAc graft copolymerized LDPE film were lapped together under load for 900 min. They were then subjected to shear force until the lapped junction failed. *Figure 6a* and *b* shows the x.p.s. C1s core-level spectra, obtained at αs of 75 and 20° respectively, for the AAc graft copolymerized film before adhesion. The corresponding C1s core-level spectra for the two delaminated surfaces are shown in *Figure 6c–f* and are dissimilar in surface composition. One of the delaminated surfaces has a substantially reduced

COOH component intensity, in comparison to the surface before lamination. Similar disparity in composition for the delaminated surfaces is also observed for LDPE films grafted with DMAA, NaSS and DMAPS polymers. It appears that a substantial proportion of the grafted chains has been detached from one substrate surface at failure, due to the strong entanglement of the graft chains at the interface. The failure mode involving a disparity in the fracture of the grafted chains from the two lapped surfaces is also observed for the graft-modified PC films after adhesive-free adhesion failure. The surface compositions of AAc, DMAA and DMAPS graft copolymerized PC films before adhesion are compared with those corresponding to the delaminated surfaces in *Table 5*. A distinct asymmetry in surface compositions between the two delaminated surface is again discernible in each case.

Finally, the failure mode of the hetero-junction involving the DMAPS graft copolymerized EM base film and the AAc graft copolymerized PTFE film was investigated. *Figure 7a* and *b* shows the C1s core-level spectra, obtained at α of 20°, for the delaminated PTFE and EM film surfaces. The corresponding spectra before adhesion are shown as inserts. For the AAc graft copolymerized PTFE film after delamination, there is a sharp reduction in intensity of the COOH component (BE = 288.7 eV) in comparison with that of the PTFE film before adhesion. On the other hand, the intensity of the O–C=O component in the C1s
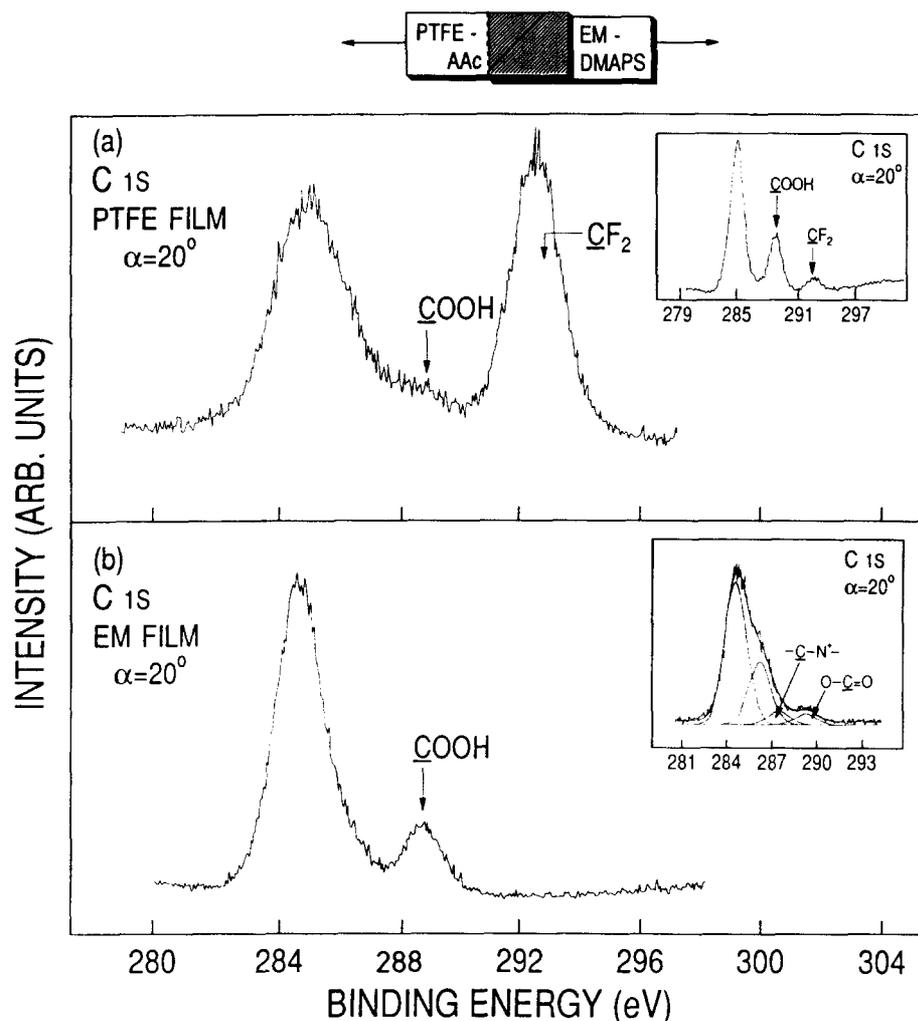

Figure 7 C1s core-level spectra, obtained at αs of 75 and 20°, for the delaminated surfaces of (a) the AAc graft copolymerized PTFE film and (b) the DMAPS graft copolymerized EM base film after the 'adhesive-free' adhesion failure. The corresponding C1s spectra before adhesion are shown as inserts

Table 5 The concentrations of the surface graft (moles of graft per mole of substrate), measured at two αs, for the AAc, DMAA and DMAPS graft copolymerized PC film before and after 900 min of lap adhesion

	AAc polymer on PC		DMAA polymer on PC		DMAPS polymer on PC	
	$\alpha = 75°$	$\alpha = 20°$	$\alpha = 75°$	$\alpha = 20°$	$\alpha = 75°$	$\alpha = 20°$
Film before adhesion	10.15	5.62	7.80	2.53	9.65	7.23
Delaminated surface I	0.40	0.13	1.32	0.97	1.00	0.38
Delaminated surface II	6.07	2.63	3.07	1.70	2.18	0.60

core-level spectrum of the DMAPS graft copolymerized EM base has been significantly enhanced after delamination (*Figure 7b*). The x.p.s. spectra readily suggest that the adhesion failure occurs predominantly at the graft–substrate interface of the PTFE film and a substantial amount of the fractured AAc chains are retained in the DMAPS polymer graft layer on the EM base film surface. These results can again be attributed to the extensive chain entanglement and strong electrostatic interaction among the grafted chains at this lapped junction, arising from high graft concentrations and the amphoteric nature of the DMAPS chains, respectively.

CONCLUSION

The surfaces of LDPE, PC, PTFE and EM base films were modified via graft copolymerization with hydrophilic monomers, such as AAc, NaSS, DMAA and DMAPS. The surface composition and microstructure of the graft modified films were analysed by angle-resolved x.p.s. The graft copolymerized films also exhibit 'adhesive-free' adhesion to each other when lapped together in the presence of water and under load. The adhesion strengths are determined to a large extent by the degree of chain entanglement, which is related to graft concentration, and the degree of electrostatic interaction among the graft chains at the lapped junction. Adhesive-free adhesion strengths in excess of 90 N cm^{-2} can be readily achieved between films with surface grafted amphoteric DMAPS polymer, and between a DMAPS graft copolymerized EM film and an AAc graft copolymerized PTFE film. X.p.s. results of the delaminated surfaces suggest that the failure mode of the graft-induced adhesive-free adhesion involves the fracture of the graft chains at the graft–substrate interface.

REFERENCES

1. Ikada, Y. and Uyama, Y., *Lubricating Polymer Surface*. Technomic, Lancaster, PA, 1993.
2. Penn, L. S. and Wang, H., *Polym. Adv. Technol.*, 1994, **5**, 809.
3. Chan, C. M., Ko, T. M. and Hiraoka, H., *Surface Science Reports*, 1996, **24**, 1.
4. Wu, S., *Polymer Interface and Adhesion*. Marcel Dekker, NY, 1992.
5. Strobel, M., Lyous, C. S. and Mittal, K. L. (ed.), *Plasma Surface Modification of Polymers: Relevance to Adhesion*. VSP, Zeist, The Netherlands, 1995.
6. Mittal, K. L. (ed.), *Polymer Surface Modification: Relevance to Adhesion*. VSP, Zeist, The Netherlands, 1995.
7. Yasuda, H., Marsh, H. C., Brandt, S. and Reilley, C. N., *J. Polym. Sci., Polym. Chem. Ed.*, 1977, **15**, 991.
8. Briggs, D., in *Practical Surface Analysis by Auger and X-ray Photoelectron Electroscopy*, ed. D. Briggs and M. Seah. Wiley, NY, 1983.
9. Golub, M. A., Lopata, E. S. and Finney, L. S., *Langmuir*, 1994, **10**, 3629.
10. Byan, M. E. and Badyal, J. P. S., *Macromolecules*, 1995, **28**, 1377.
11. Sapieha, S., Cerny, J., Klemberg-Sapieha, J. E. and Martinu, L., *J. Adhes.*, 1993, **42**, 91.
12. Ray, A., Asturies, G. E., Kershner, D. L., Ritcher, A. F., MacDiarmid, A. G. and Epstein, A. J., *Synth. Met.*, 1989, **29**, E141.
13. Li, Z. F., Kang, E. T., Neoh, K. G. and Tan, K. L., *Synth. Met.*, in press.
14. Liaw, D. J., Lee, W. F., Whung, Y. C. and Lin, M. C., *J. Appl. Polym. Sci.*, 1985, **30**, 4697.
15. Kang, E. T., Neoh, K. G., Khang, X., Tan, K. L. and Liaw, D. J., *Surf. Interf. Anal.*, 1996, **24**, 51.
16. Kang, E. T., Kato, K., Uyama, Y. and Ikada, Y., *J. Mater. Res.*, 1996, **11**, 1570.
17. Kang, E. T., Tan, K. L., Kato, K., Uyama, Y. and Ikada, Y., *Macromolecules*, 1996, **29**, 6872.
18. Tan, K. L., Woon, L. L., Wong, H. K., Kang, E. T. and Neoh, K. G., *Macromolecules*, 1993, **26**, 2832.
19. Kang, E. T., Neoh, K. G., Tan, K. L., Loh, F. C. and Liaw, D. J., *Polym. Adv. Technol.*, 1994, **5**, 837.
20. Yasuda, H. and Sharma, A. K., *J. Polym. Sci., Polym. Phys. Ed.*, 1981, **19**, 1285.
21. Ratner, B., Weathershy, P. K., Hoffman, A. S., Kelley, M. A. and Acharpem, L. H., *J. Appl. Polym. Sci.*, 1978, **22**, 643.
22. Pritchart, H. W., *Acta Polym.*, 1983, **34**, 112.
23. Voyutskii, S. S., *J. Adhes.*, 1971, **3**, 69.
24. Chen, K. S., Uyama, Y. and Ikada, Y., *J. Adhesion Sci. Technol.*, 1993, **6**, 1023.
25. Chen, K. S., Uyama, Y. and Ikada, Y., *Langmuir,*, 1994, **10**, 1319.
26. Chastain, J. (ed.), *Handbook of X-Ray Photoelectron Spectroscopy*. Perkin-Elmer Corp., Eden Prairie, MN, 1992, p. 217.
27. Ikada, Y., Matsunaga, T. and Susuki, M., *Nippon Kagaku Gakkaishi*, 1981, **19**, 1285.
28. Kang, E. T., Neoh, K. G., Tan, K. L., Uyama, Y., Morikawa, N. and Ikada, Y., *Macromolecules*, 1992, **25**, 1959.
29. Kang, E. T., Tan, K. L., Liaw, D. J. and Chiang, H. H., *J. Mat. Sci.*, 1996, **31**, 1295.
30. Kang, E. T., Neoh, K. G., Chen, W., Tan, K. L., Liaw, D. J. and Huang, C. C., *J. Adhesion Sci. Technol.*, 1996, **10**, 725.