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Cooling rate-induced glass-adhesion variations using crystallizing hot-melt adhesives

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Polychlorotrifluoroethylene (PCTFE) and PCTFE copolymeric films are being used in the electronic packaging industry as insulating dielectric layers between microwave circuits. Because these films are semicrystalline and, in this application, are being used as hot-melt adhesives, the cooling rate is an important processing variable, affecting the crystallinity of the PCTFE films which, in turn, affect many properties including dielectric characteristics and mechanical properties. In this study, the crystallinity of PCTFE and PCTFE copolymeric films as a function of cooling rate was characterized by wide-angle X-ray scattering. As expected, the degree of crystallinity decreased as the cooling rate increased. Analysis of mechanical properties as a function of cooling rate by tensile testing showed that the mechanical behaviour of the films became more ductile with faster cooling rates. Because the cooling rate has also been shown to significantly affect adhesion in previous studies, the effect of cooling rate on the bond strength between PCTFE and a glass substrate was analysed. Peel testing was performed on PCTFE/glass laminates revealing that the adhesive bond strength increased as the cooling rate was increased. Thus, optimum adhesion is achieved with faster cooling rates. This was attributed to the higher fracture energy and greater ductility of the adhesive.

1. Introduction

Polychlorotrifluoroethylene (PCTFE) and PCTFE copolymeric films are increasingly being used in the electronic packaging industry in specialized high-speed electronic devices as thin film dielectrics due to their low dielectric constant and dielectric loss [1]. In these applications, these films are processed as hot-melt adhesives using heat and pressure to laminate groups of microwave frequency circuit boards together. The adhesive needs to adhere effectively to both exposed dielectric and conductor regions. The lamination cycle is similar to that for thermoset dielectric processing. The laminated interface is also often subjected to thermal cycling conditions during field testing and use. For semicrystalline thermoplastic dielectrics, the effects of cooling rate and further annealing may play a large role in defining the adhesive's mechanical and electrical properties and, ultimately, the performance of the device.

It is well known that cooling rate affects crystallinity which, in turn, affects mechanical properties, important properties for these applications [2, 3]. In addition, there have been several recent efforts to evaluate process and design issues relating to copper/fluorocarbon polymer interfaces [4, 5]. However, these efforts have generally focused on how the level of crystallinity affects the dielectric characteristics. There have been few efforts to determine how changes in the cooling rate affect the adhesion of the formed interface as well as the level and type of crystalline morphology forming at the interface [6]. Both effects are important to the performance of the device. Thus, very little is known about the relationship between cooling rate and resulting bond strength. This relationship needs to be better understood to identify where both optimum electrical properties and mechanical adhesion are achieved. In this way, adhesion can be controlled through monitored processing, leading to more consistent device performance.

These observations led to our interest in determining how the cooling rate affects the level of crystallization and relating how processing affects the adhesion of a bonded joint. In the present paper, we report the main results of characterization and functional adhesion experiments conducted on commercial PCTFE and PCTFE copolymeric films. Glass was chosen as the substrate material. Obviously, glass is not the ideal microwave circuit board laminate material. However,

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this research is a model study to establish trends in the effects of cooling rate. Such trends would be applicable to other substrate materials as well. The films and adhesion samples were processed using industrially realistic dynamic cooling conditions.

2. Experimental procedure

2.1. Materials

Commercially available films of PCTFE, its copolymers and terpolymers, sold as Aclar® by AlliedSignal, were used in these studies. The films used were RX160 (15 μm thick homopolymer), 22C (51 μm thick copolymer of PCTFE with 3%–4% VF_2) and 33C (51 μm thick terpolymer of PCTFE with 1% VF_2 and 0.8% TFE).

The glass transition temperature, T_g, was taken as the peak in the tan δ versus temperature curves obtained from the Dynamic Mechanical Analyser (DMA). T_g values were 85–90 °C for the homopolymer and the terpolymer and 75 °C for the copolymer. M_n values for RX160 (homopolymer), 22C (the copolymer) and 33C (the terpolymer) were 120, 140 and 112 kg mole^{-1}, respectively, and the polydispersity indices were 2.08, 2.14, and 2.17. These were measured using hot GPC 2–5 dichlorobenzotrifluoride at 145 °C.

2.2. Sample preparation

Wide-angle X-ray scattering (WAXS) samples were processed in a LINKAM THMS 600 hot stage equipped with a LINKAM TP91 unit for controlled heating and cooling. Homopolymer samples were heated to 250 °C and held for 30 min to eliminate the effects of melt history, while copolymer and terpolymer samples were heated to 230 °C and held for 30 min. These samples were subsequently cooled at the rates of 1, 10, 20, and 30 °C min^{-1} to 70 °C. Separate, much larger samples for tensile testing and peel testing were processed using a Carver Laboratory Hot Press at the temperatures specified above for the hot-stage sample preparation and at a low pressure of approximately 1×10^5 Pa. These samples were subsequently cooled at three different rates; slow, intermediate, and fast rates. The slow rate was obtained by leaving the samples in the hot press as it cooled down from the specified elevated temperatures after being held for 30 min. The intermediate rate was obtained by placing the samples in an oven at 125 °C immediately after the 30 min at elevated temperature. The fast rate was obtained by allowing the samples to cool in room-temperature air on a laboratory bench surface. By tracking the temperature of the samples processed under these conditions with a thermocouple, estimates of the average overall cooling rates were determined. These readings for each condition are shown in Figs 1–3 yielding the following results: slow, 2.1 °C min^{-1}; intermediate, 21.5 °C min^{-1}; fast, 33.3 °C min^{-1}.

WAXS was performed using a Scintag XDS 2000 unit consisting of a θ–2θ diffractometer. Continuous 2θ scans in reflection were conducted between 10° and 22° at a rate of 1° min^{-1}. For each sample, two scans were obtained – one for the substrate-crystallized side and one for the free-crystallized side. The substrate-crystallized side was identified as the side of the film melted and crystallized next to the glass coverslip, while the free-crystallized side was identified as the side melted and crystallized in air (i.e. no substrate) in the hot stage.

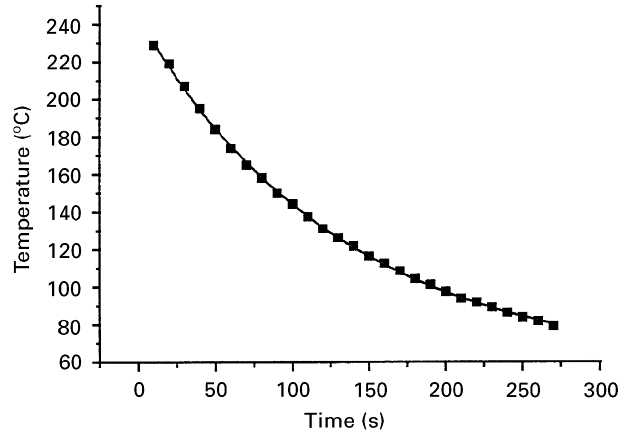

Figure 1 Cooling readings for samples cooled in air (fast-cooled). (——) Fit.

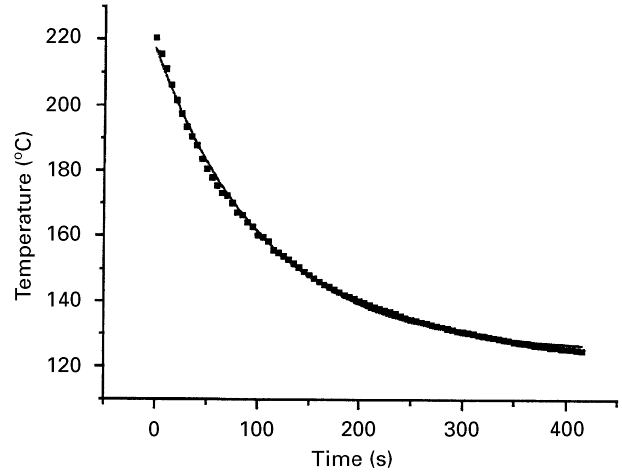

Figure 2 Cooling readings for samples cooled in the oven at 125 °C (intermediate-cooled). (——) Fit.

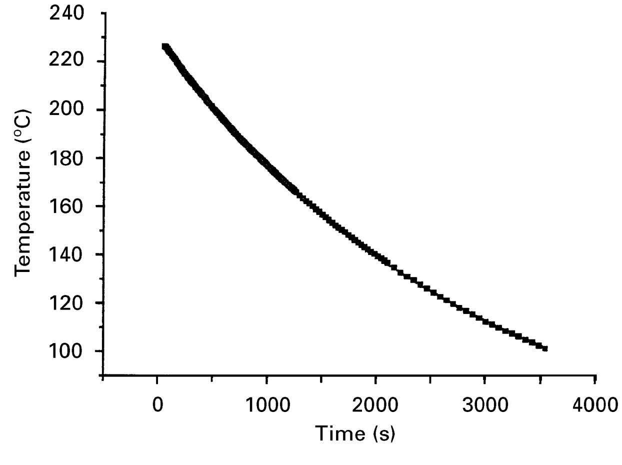

Figure 3 Cooling readings for samples cooled in the hot press (slow-cooled). (——) Fit.

Tensile tests were performed using a Polymer Laboratories miniature materials tester on dogbone-shaped specimens cut from the as-received films and films processed at the slow and fast cooling rate using a Dewes Gumbes die. Because the as-received films were oriented as a result of the manufacturing processing, dogbone specimens of these films were cut in the machine direction (i.e. the direction of drawing) and in the transverse direction. A constant deformation rate of 1 mm min^{-1} was used for each test for comparison purposes. Because the as-received homopolymer film was very thin (15 μm), smaller loads were generated, requiring the use of a more sensitive 20 N load beam for mechanical analysis of this film. For the processed homopolymer samples, three layers of the as-received film were melt-processed together in order to match better the thickness of the copolymer and terpolymer films. For the copolymer and terpolymer films, having thicknesses of 51 μm, a 200 N load beam was used. Both load beams were calibrated prior to testing. A minimum of seven samples at each condition was tested.

To evaluate the effect of cooling rate on adhesion, peel testing was conducted using a laboratory built, load-controlled apparatus which is schematically illustrated in Fig. 4. A fixed peel angle of 45° was chosen. The peel rate was determined by the loads hung from the moment arm. Three different loads were used, 14.8, 16.8 and 19.6 g. A linear voltage differential transducer (LVDT), attached to the moment arm, measured the distance that the moment arm moved as a function of time. The output from the LVDT was a voltage signal which ranged between -5 and $+5$ V. The output was collected on a data workstation. Before applying the loads, the end of the film strip was debonded and placed in the clamp and the sample was fixed to the angle plate by clamping each end of the glass. The turnbuckle was rotated until the LVDT read -5 V, initiating the test. The test was completed at $+5$ V. The generated output was in the form of voltage versus time and was collected 20 times per second. These data were then used to determine the crack growth rate, da/dt, of the debonded film strip. The strain energy release rate, G, was determined by the three loads used to debond the film strip from the glass substrate.

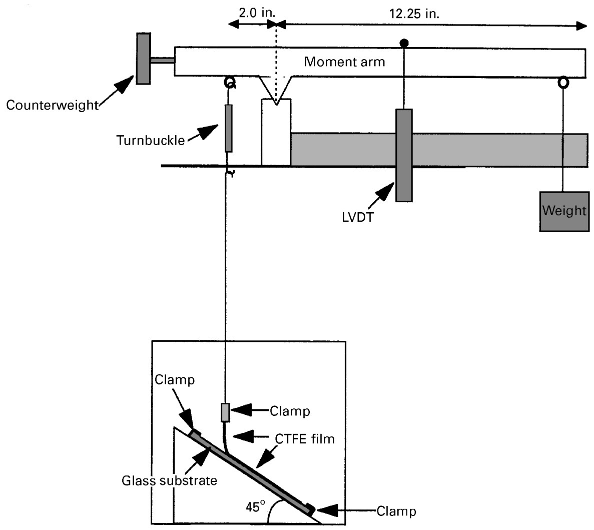

Figure 4 Schematic diagram of the 45° peel tester.

3. Results

3.1. Crystallinity

The degree of crystallinity present in the three films processed at the various cooling rates specified above was determined by WAXS. In addition, a comparison was made between the substrate-crystallized side and the free-crystallized side in terms of the amount of crystallinity present in these two sides. All diffraction plots were analysed using a modified version of the profile fitting program "SHADOW" using modified Lorentzians to describe the amorphous and crystalline peaks [7, 8]. The percentage crystallinity or the crystalline index (CI) was calculated from the equation

$$\text{Crystalline index} = \frac{A_c}{A_c + A_a} \times 100 \qquad (1)$$

in which A_c is the total area of the crystalline peaks and A_a is the area of the amorphous halo. An average of the CI of the free-crystallized scan and the substrate-crystallized scan was taken. The apparent crystallite size (ACS) at each crystalline peak was also determined with this program using the Scherrer equation

$$\text{ACS} = \frac{0.9\,\lambda}{B\cos\theta} \qquad (2)$$

in which λ is the wavelength (0.154 nm), B is the full-width at half-maximum of the peak at 2θ, and θ is the scattering angle [9]. In this analysis, an instrumental broadening of 0.09° was used.

Typical WAXS plots of the free-crystallized side of the homopolymer, copolymer, and terpolymer cooled at 1 °C min^{-1} are shown in Fig 5. As shown, each film has three crystalline peaks. The two large peaks occur at a 2θ between 16.1° and 16.2° (1 0 1) and between 16.4° and 16.5° (1 0 2), respectively, while the small peak occurs at a 2θ between 17.1° and 17.2° (1 0 3) [8].

Table I lists the average CI and the average ACS for each processed sample based on the analysis described above. As expected, slower cooling rates lead to higher crystallinities and larger crystallites. One exception is the homopolymer which when cooled at 1 °C min^{-1}, shows an average crystallinity of 58% whereas when cooled at 10 °C min^{-1}, it shows an average crystallinity of 64%. In addition, at 20 °C min^{-1} it shows an average crystallinity of 61%, still greater than that at 1 °C min^{-1}. Thus, it seems likely that the value at 1 °C min^{-1} is in error and should be greater than 64%. Except for this one discrepancy, the copolymer has the lowest crystallinity and the smallest crystallite size at each cooling rate among the three films. The crystallinities of the homopolymer and terpolymer are closer. These observed differences in crystallinity of the three films can be attributed to the increasing amount of VF_2 (0%–1%–3%) present in these films. These crystallinity results have important implications on the adhesion results as discussed later.

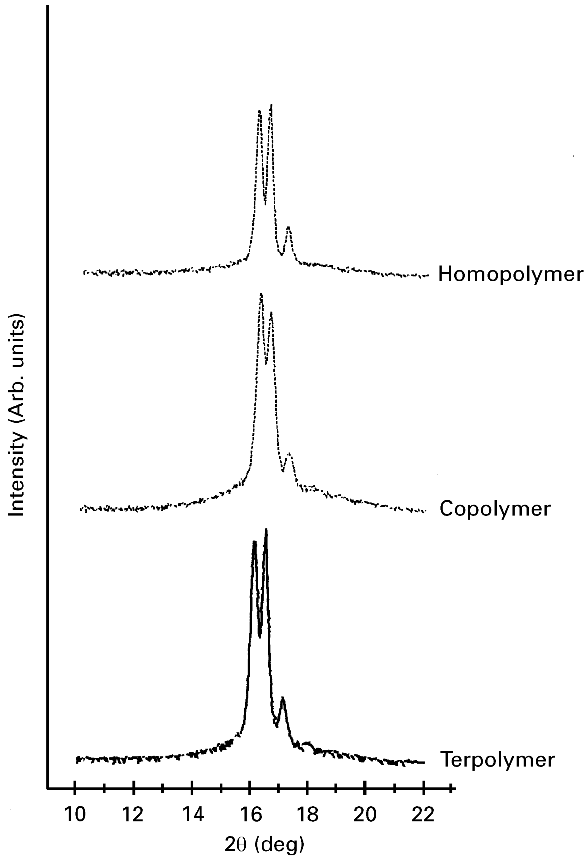

Figure 5 WAXS plot of the three PCTFE films cooled at 1 °C min^{-1}.

3.2. Mechanical properties

Tensile testing was performed to determine the effect of cooling rate on the mechanical behaviour of the films. The as-received films and films cooled at slow and fast rates were tested. The mechanical property evaluation included the Young's modulus, *E*, yield strength, σ_Y, fracture strength, σ_F, and the percentage fracture strain, $\%\varepsilon_F$. The yield strength was taken as the initial maximum stress where yielding was evident. The fracture strength and the fracture strain were taken at the peak loading when tearing began. Table II lists the average and standard deviation of these mechanical properties for each film. The as-received films are noted by "as" and by a "t" for the transverse direction and a "m" for the machine direction.

As expected, at the slow cooling rate, these films exhibited more brittle behaviour due to their higher crystallinities. This more brittle behaviour is evident by the higher moduli and lower fracture strains. The homopolymer and terpolymer have higher moduli and lower fracture strains than the copolymer, with the homopolymer having the highest modulus and lowest fracture strain. Although the copolymer has the highest fracture strain, it is still low (i.e. $< 10\%$), characteristic of embrittlement significantly different than the as-received film. For the yield strength and fracture strength, the expected trends (i.e. as crystallinity increases, σ_Y and σ_F increase) are not observed. In fact, the yield strength and fracture strength of the copolymer are higher than the homopolymer and are the same as that of the terpolymer. However, this is probably due to the greater susceptibility of the homopolymer and terpolymer to flaws because they are more brittle.

As the cooling rate increased, the films exhibited more ductile behaviour due to their lower crystallinity as shown by WAXS. However, the fracture strains of the homopolymer and terpolymer are still low (i.e. $< 10\%$) as opposed to that of the copolymer which is 22.5%. The moduli of the three films are generally lower than those of the slow-cooled samples, as expected. The same trend is still observed, i.e. the homopolymer having the highest and the copolymer having the lowest modulus. For the yield and fracture strengths, the homopolymer and terpolymer have higher σ_Y and σ_F values than the copolymer, which is opposite to the trend observed with the slow-cooled samples. This is to be expected because they are more crystalline than the copolymer. The slow-cooled samples exhibited an opposite trend, most likely due to the greater susceptibility of the very brittle films to flaws either in the material itself, or along the edges of the dogbone samples from cutting them in the die.

The mechanical properties of the as-received films are radically different from those of the processed samples. It is clear from Table II that the as-received films are much more ductile. Both the transverse and

TABLE I Crystallinity results for the processed PCTFE films

Film	Cooling rate (°C min^{-1})	CI (%)	ACS (1 0 1) (nm)	ACS (1 0 2) (nm)	ACS (1 0 3) (nm)
Homopolymer	1	58	55.9	60.4	77.8
	10	64	43.3	39.2	59.5
	20	61	45.5	38.3	51.5
	30	39	42.0	40.8	52.6
Copolymer	1	64	44.8	44.5	63.3
	10	43	38.5	33.0	58.1
	20	40	38.3	33.3	56.2
	30	38	32.1	31.9	47.4
Terpolymer	1	70	55.7	57.3	66.4
	10	55	46.0	42.0	67.4
	20	52	44.4	39.4	57.7
	30	43	41.1	40.5	59.1

TABLE II Mechanical properties of the PCTFE films

Film	Cooling condition	E (GPa)	σ_Y (MPa)	σ_F (MPa)	$\%\varepsilon_F$
Homopolymer	Fast	0.8 ± 0.02	37.8 ± 1.0	36.1 ± 1.9	7.0 ± 0.9
	Slow	0.9 ± 0.05	30.8 ± 1.8	30.8 ± 1.8	3.9 ± 0.3
	As-t	0.7 ± 0.02	30.5 ± 1.1	24.0 ± 1.9	86.2 ± 10.2
	As-m	1.0 ± 0.06	33.5 ± 1.3	47.3 ± 1.6	66.2 ± 3.7
Copolymer	Fast	0.6 ± 0.03	33.6 ± 1.2	29.8 ± 2.2	22.5 ± 4.7
	Slow	0.7 ± 0.02	36.0 ± 1.4	36.0 ± 1.4	6.8 ± 0.6
	As-t	0.6 ± 0.04	26.1 ± 1.2	28.4 ± 2.2	212.3 ± 27.9
	As-m	0.7 ± 0.05	26.5 ± 2.4	37.6 ± 3.6	124.9 ± 14.6
Terpolymer	Fast	0.7 ± 0.03	37.5 ± 1.2	36.0 ± 2.2	8.4 ± 0.6
	Slow	0.8 ± 0.04	33.02 ± 1.8	33.02 ± 1.8	4.4 ± 0.4
	As-t	0.8 ± 0.07	38.9 ± 2.6	27.6 ± 1.6	86.3 ± 15.6
	As-m	0.9 ± 0.04	41.3 ± 1.6	38.1 ± 1.5	103.2 ± 15.0

machine directions have substantially higher fracture strains than the processed films and undergo significant necking prior to fracture. There are also significant differences between the mechanical behaviour of the machine and transverse directions. These differences are attributable to preferred orientation of the polymer chains in the film. For the homopolymer, the machine direction shows a higher modulus, yield strength, and fracture strength and a lower fracture strain. For the copolymer and terpolymer, the machine direction has slightly higher modulus and moderately higher fracture strength than the transverse direction. A comparison of the yield strengths between the machine and transverse directions found that the yield strength variation is statistically insignificant. In addition, for the copolymer, the fracture strain of the machine direction is significantly lower than the transverse direction, while for the terpolymer, the fracture strain is essentially the same.

3.3. Adhesion

A measure of adhesion is the strain energy release rate, G, which is the fracture energy or work of detachment of the film from the glass substrate. 45° peel testing was used to obtain G for the copolymer film/glass joints cooled at the intermediate and fast rates. G is commonly calculated by using the following equation

$$G = \left(\frac{P}{w}\right)(1 - \cos\Theta) \tag{3}$$

where P is the peel force, w is the width of the film strip which is 1.91 cm (0.75 in.), and Θ is the peel angle which, in this case, is 45°. Again, the peel force was controlled by the weights hung from the moment arm and was determined by the following equation

$$P = \left(\frac{12.25\ \text{in.}}{2.0\ \text{in.}}\right)\left(\text{weight} \times 9.81\frac{\text{m}}{\text{s}^2}\right) \tag{4}$$

The ratio 12.25 in./2.0 in. is due to the moment arm in the peel tester (see Fig. 4). Because three different weights were used in order to establish a trend, three peel forces, and, thus, three constant strain energy release rates, were generated. As previously explained, the output of these peel tests is in the form of voltage versus time, the voltage being directly linked to the distance that the LVDT moves during a test. A typical graph of this output is shown in Fig. 6. To obtain the crack growth rate, i.e. the rate that the film strip is debonding from the substrate, the slope of this line (V s^{-1}) was determined using a least squares linear regression. This slope was then converted to the units of mm s^{-1} by using the conversion of $0.21\ \text{mm V}^{-1}$ which was experimentally determined. Finally, this slope was converted to the crack growth rate, $\mathrm{d}a/\mathrm{d}t$, by using the following equation

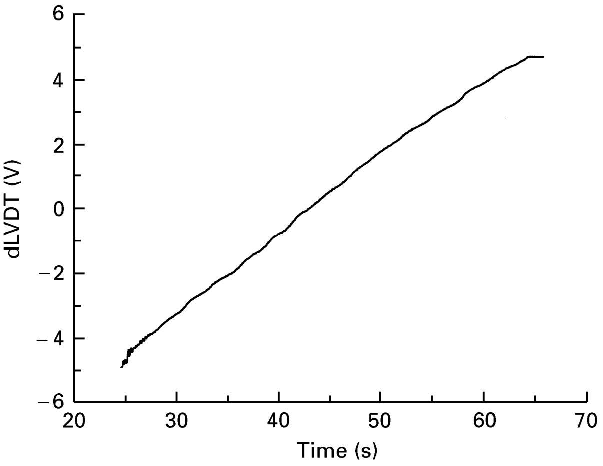

Figure 6 Typical output from the 45° peel tests.

$$\frac{\mathrm{d}a}{\mathrm{d}t} = \left(\frac{\mathrm{dLVDT}}{\mathrm{d}t}\right)\left(\frac{1}{1 - \cos\ 45^{\circ}}\right) \tag{5}$$

where $\mathrm{dLVDT}/\mathrm{d}t$ is the slope of the output in mm s^{-1}. This equation was derived based on geometric considerations.

The strain energy release rate and crack growth rate results for the copolymer cooled at the fast and intermediate rates are listed in Table III. G for the slow-cooled copolymer film samples was essentially zero, because the residual stresses were so high that they spontaneously debonded prior to testing. As expected, the crack growth rate increases with applied weight

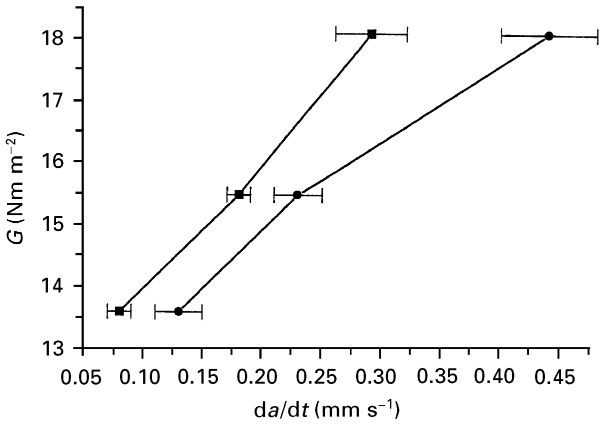

Figure 7 45° peel results for the copolymer cooled at (●) intermediate and (■) fast cooling rates.

loading for both cooling rates. This increase was linear, as shown in Fig. 7. As the cooling rate increased, the crack growth rate decreased for each of the three loads used. Hence, for the same load, the PCTFE film strip peeled off the glass substrate at a slower rate for the fast-cooled samples than for the intermediate-cooled samples. Therefore, the adhesion at the faster cooling rate is stronger. This effect is demonstrated in more conventional terms with the strain energy release rate, G: for the same G value, the faster cooling rate has a lower crack growth rate. Because the peel force, P, is directly related to G by Equation 3, the same can be said about P.

4. Discussion

The results of the 45° peel testing in Table III and Fig. 7 clearly show that the cooling rate influences the adhesion between the PCTFE copolymer and glass. As the cooling rate increased, the crack growth rate decreased for each of the three loads used. Therefore, the adhesion at the faster cooling rate is stronger.

Our results are consistent with those of previous studies in the literature. Nakao [6], Evans and Packham [10], Bialski *et al.*, [11] and Tordella [12] found that as the cooling rate increased, the bond strength, whether it be shear, peel, or tensile, of various polymers bonded to various substrates increased. Although in this study the effect of cooling rate on the crack growth rate for a constant P was measured, the net result is still the same. That is, higher strain energy release rates are obtained for interfaces formed using faster cooling rates.

The original studies identified several factors that contribute to the improved adhesion with increasing cooling rate. The most prominent factors are a decrease in the degree of crystallinity, a transition from brittle to more ductile mechanical behaviour, the formation of a transcrystalline morphology, and the inhibition of molecular weight segregation or weak boundary layer. It is likely that this high surface energy glass substrate would produce some level of transcrystallinity. We are continuing to evaluate the effects of transcrystallinity during these non-equilibrium cooling efforts. The other factors also remain as possible mechanisms.

A reduction in crystallinity with increased cooling rate and its subsequent effects on the mechanical properties of the adhesive are widely accepted to be the cause of the improved adhesion. Nakao [6] concluded that the decrease in modulus with increased cooling rate is responsible for the improved adhesion of polyethylene bonded to aluminium with increased cooling rate. However, he offered no explanation beyond ruling out the weak boundary layer theory. Evans and Packham [10] reported that the increased ductility with quenching more than compensates for a lower modulus and yield stress in their study of polyethylene bonded to steel and copper substrates. They stated that the net effect is a tougher polymer, as evinced by a higher tear or fracture strength for the quenched samples, indicative of greater fracture energy. Thus, they suggested that the higher fracture energy improved the adhesion rather than the lower modulus.

In this study, some of these changes in mechanical properties of the copolymer with increasing cooling rate also occurred. At the slow cooling rate, the copolymer film is stiff and brittle. In addition, it has greater residual stresses from the higher contraction forces due to the higher crystallinity. Although this competes with the greater time available to relieve these residual stresses, the former has the overriding influence because the slow-cooled copolymer films debonded prior to testing. The slow-cooled homopolymer and terpolymer films, which have high crystallinity, also debonded prior to testing. The high residual stresses due to the high crystallinity caused the peel forces to exceed G_c, the critical strain energy release rate, along the edges of the film strip.

On the other hand, the fast-cooled copolymer film, having lower crystallinity than the slow-cooled film, had lower residual stresses and, therefore, did not experience debonding prior to testing. In addition, it

TABLE III 45° peel test results for the copolymer

Cooling rate	Weight (kg)	P (N)	G (Nm m^{-2})	dLVDT/dt (mm s^{-1})	da/dt (mm s^{-1})
Fast	0.0148	0.8894	13.6	0.02	0.08 ± 0.01
	0.0168	1.0094	15.5	0.05	0.18 ± 0.01
	0.0196	1.1778	18.1	0.09	0.29 ± 0.03
Intermediate	0.0148	0.8894	13.6	0.04	0.13 ± 0.02
	0.0168	1.0094	15.5	0.07	0.23 ± 0.02
	0.0196	1.1778	18.1	0.13	0.44 ± 0.04

has a three-fold increase in the fracture strain and a slightly lower modulus than the slow-cooled film. However, the yield and fracture strengths are essentially the same as those of the slow-cooled film. Although the fracture strength did not increase with cooling rate as in the study above, the fast-cooled copolymer film has a greater fracture energy, as evinced by the considerable increase in the area under its stress–strain curves. Thus, the fast-cooled copolymer film has greater ductility, a higher fracture energy, and lower residual stresses due to less crystallinity. Although tensile testing was not performed on the copolymer film cooled at the intermediate rate, it is expected that the mechanical properties would lie between those of the slow and fast-cooled films.

It should be noted again that the homopolymer and terpolymer films cooled at the fast cooling rate still had considerable amounts of pre-stress due to high residual stresses which caused debonding prior to testing. This is attributed to the fact that these films still have high crystallinities at this cooling rate, higher than the crystallinity of the copolymer film.

These observed differences in adhesion and mechanical properties of the three films, the homopolymer, the terpolymer and the copolymer, can be attributed to the increasing amount of VF_2 (0%–1%–3%) present in these films. The presence of additional VF_2 diluent in the copolymer suppresses some level of additional crystallization, which leads to more ductile adhesive material behaviour. Thus, the copolymer remains bonded in a stressed condition where the other films delaminated from excessive crystallization. As the cooling rate decreased, the residual stresses in the film rose and led to increasing crack growth rates when comparing constant strain energy release rates.

The other possible explanation for the observed trend in adhesion with cooling rate is the molecular segregation or weak boundary layer concept. This theory involves the expulsion of low molecular weight polymer and oligomers to the interface during crystallization. This process is favoured by slow cooling rates because there is more time to allow this segregation to occur. This factor was not studied in this investigation. To help confirm whether a weak boundary layer formed, it must be determined if there is polymer left on the surface of the glass which would indicate that the failure was not at the interface. A surface characterization technique, such as X-ray photoelectron spectroscopy (XPS), may be used for this. However, if there is polymer on the glass surface, it may merely indicate cohesive failure in the bulk of the adhesive. Although none was visible to the naked eye for the 45° peel testing, there still may be some polymer on the surface. To determine whether it is cohesive failure in a weak boundary layer or in the bulk, the molecular weight of the polymer on the surface would need to be determined by molecular weight techniques such as GPC or melt viscosity. However, the weak boundary layer theory seems unlikely in this case, because the adhesion between the PCTFE copolymer and glass is poor regardless of the cooling rate, as indicated by the low G values.

Therefore, the improved adhesion with faster cooling rates is attributed to the greater ductility and fracture energy of the adhesive using faster cooling rates. This has important implications on processing in that manufacturers using PCTFE in an adhesive joint as in electronic packaging, can use faster cooling rates to achieve better adhesion. This improved adhesion would improve the as-laminated adhesion of the joint and device performance. The effect on the durability of the joint is not known, because this depends upon environmental conditions after lamination.

5. Conclusions

The adhesive strength between PCTFE films and a glass substrate has been shown to be influenced by the cooling rate used during processing. Faster cooling rates yield stronger adhesion between the PCTFE copolymer and glass. This improved adhesion with quenching is attributed to the greater ductility and higher fracture energy of the adhesive as shown by tensile testing. At slow cooling rates, the PCTFE films exhibit more brittle mechanical behaviour due to higher crystallinity and larger crystallites, with the homopolymer and terpolymer being more brittle than the copolymer, while at the fastest cooling rate, the homopolymer and terpolymer are still relatively brittle while the copolymer is more ductile. This behaviour is attributed to different amounts of VF_2 in the films.

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