

Interlayer Delamination and Adhesion of Coextruded Films

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ABSTRACT: Efforts to evaluate interlayer adhesion of coextruded films are often hampered by the inability to initiate delamination. On the other hand, interlayer delamination was often noticed at cut or trimmed edges of coextruded films. In this study, a test method was developed by first initiating delamination by uniaxial stretching and then measuring interlayer adhesion by peel test. Delamination was initiated by uniaxial stretching under controlled conditions for samples with double-neck geometry. The double-neck geometry was designed to create a specimen for the subsequent 180° peel test. Peel force was used to quantify interlayer adhesion of coextruded films based on polycarbonate

and its copolymers. With this two-step technique, coextruded films with peel force as high as 5300 N/m or 30 lb./in. were quantified. In addition, effects of copolymer composition and coextrusion processing condition on interlayer adhesion of these coextruded films were clearly demonstrated. A great deal of variation of interlayer adhesion across film surface was also revealed. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3901–3909, 2004

Key words: adhesion; coextrusion; films; delamination; peel force

INTRODUCTION

In the past four decades, multilayer coextrusion of polymer films has emerged and developed into an important, profitable, and value-added polymer processing technology.¹ In principle, each layer in the multilayer film provides a specific functionality that is essential to particular end applications, such as moisture or oxygen barrier for packaging and color and esthetics for surface decoration. Advances in process modeling and engineering design have made it possible to produce multilayer coextruded films from two to 11 layers,² and occasionally hundreds of layers.³

Interlayer adhesion is a major concern for the use of multilayer coextruded films.¹ Indeed, interlayer delamination often occurs for these coextruded films. To address both issues, it is necessary to be able to test and quantify interlayer adhesion. Although a host of adhesion test methods are available for multilayer structures, most of the test methods are not applicable to coextruded polymer films.⁴ For multilayer thin (μm scale) coatings in microelectronics and paint applications, it is common to perform button pull or tape peel tests on a virgin or x-scribed/cross-hatched surface area. Sometimes an indentation/scratch test is also applied.⁵ Interlayer adhesion can then be qualified by the degree of surface damage of the coatings as a

result of pull, peel, or indentation/scratch. However, these test methods are difficult to apply to coextruded polymer films, in which individual layers are usually much thicker (tens to hundreds of μm scale) and more ductile (relative to thin coatings).

It is perceivable that the double-cantilever test, originally developed to access interfacial adhesion between polymers, can be adapted to measure interlayer adhesion of coextruded films.⁶ In this method, a wedge (often a sharp razor blade) is driven slowly from an initial interfacial opening placed during sample preparation, and fracture toughness of the interface can be measured. However, if interfacial adhesion is strong, it is difficult to drive the wedge from the initial opening along the interface—crack propagation tends to deviate from the interface and enter adjacent polymer layers. In addition, sample geometry needs to be modified to account for different stiffness of the adjacent polymers.⁶ Furthermore, for coextruded films with a strong interlayer adhesion, it is not always possible to initiate an opening so that the wedge can be inserted.

A direct peel test is the most pertinent method to test interlayer adhesion of coextruded films.⁷ However, efforts to perform a peel test on coextruded films were often hindered by the lack of the ability to initiate delamination, especially for coextruded films with strong interlayer adhesion. For example, we have tried several techniques, as listed in Figure 1, to initiate delamination for a variety of coextruded films based on polycarbonate (PC) and its copolymers. It was noticed that it became very dif-

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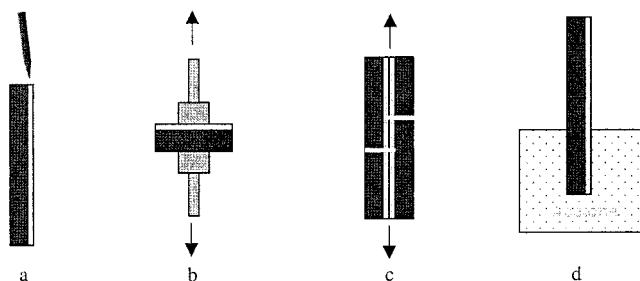


Figure 1 Different techniques commonly used to initiate delamination for coextruded films: (a) razor wedging, (b) button pull, (c) symmetric lap shear, and (d) solvent soak.

difficult to initiate delamination by mechanical means [Fig. 1(a)–(c)] for coextruded films with interlayer adhesion at a peel force greater than 1750 N/m (~ 10 lb./in.) as measured by 180° peel test in this work. In the solvent soak experiment [Fig. 1(d)], a piece of coextruded film was partially immersed in acetone. After a few hours, the layers were separated in the immersed region. However, the individual layers were severely swollen, and it was impossible to perform further peel tests with the same sample. Others have also used the solvent soak technique and experienced similar problems.⁸

It is noticed that real-life failure of coextruded films is often initiated from edges, where the films must have been cut/trimmed in certain ways. With such predelaminated edges, it is sometimes possible to start peel tests to measure interlayer adhesion. It is quite surprising to note that oftentimes measured peel force, at locations away from the cut/trimmed edges, can be much higher than 1750 N/m. In this regard, the cutting/trimming can be considered as a unique mechanical process to introduce delamination. Although cutting/trimming is a very complex mechanical process, fundamentally it is a process that involves a high degree of plastic deformation and fracture.⁹ Therefore, it is postulated that by replacing complex cutting/trimming with a simple and well-controlled uniaxial stretching, it may also be possible to initiate delamination as well.

In this study, a simple uniaxial stretching technique was developed to promote initial delamination of coextruded films based on polycarbonate and its copolymers. As a result, it became possible to perform an interlayer adhesion test on the partially predelaminated film samples. Based on this technique, a high level of interlayer adhesion at a peel force as high as 5300 N/m (~ 30 lb./in.) was quantified. With this technique, effects of polymer composition, coextrusion processing, and manufacturing variations on interlayer adhesion were elucidated. The same technique was recently applied to characterize interlayer adhesion for coextruded films after being planarly and biaxially stretched, in an effort to understand the effect

of thermoforming on interlayer adhesion of coextruded films.¹⁰

EXPERIMENTAL

Film coextrusion

Coextruded films used in this study were made with a single manifold die (1220 mm wide), manufactured by GE Plastic Structured Products (Mt Vernon, IN). The coextruded films have a two-layer structure with a total thickness of 0.762 mm. The individual layers in these films are polycarbonate (PC) and polycarbonate-based copolymers (c-PC), with thicknesses of 0.508 and 0.254 mm, respectively. Both polymers are amorphous with glass-transition temperatures (T_g 's) in the vicinity of 150°C and molecular weights (MW) of about 55,000 g/mol, based on gel permeation chromatography (GPC) measurement (polystyrene standard). The polymers are immiscible, yet compatible, so that interlayer adhesion can be achieved during the coextrusion process. Adjusting c-PC composition and coextrusion conditions can alter the level of interlayer adhesion for these films, as shown later.

Adhesion test

A uniaxial stretching experiment was performed with an Instron apparatus (Model 1331; Instron, Canton, MA). The instrument was equipped with a hot air environment chamber where temperature can be well controlled. For a typical stretching experiment, a sample strip (dimensions 25.4 \times 205 mm) was cut and dried at 110°C for 4 h and then clamped between sample grips enclosed in the hot air environment chamber. The sample was conditioned at 135°C for 5 min to reach equilibrium. No attempts were made to measure the actual temperature of the sample after the conditioning. The sample was then uniaxially stretched with a grip speed of 100 mm/min.

The peel test was performed with the same instrument at ambient conditions. The specimen for the peel test was obtained directly from the previous uniaxial stretching experiment (see later for details). For a typical peel experiment, a 180° peel geometry was used for coextruded films, given that both the PC and c-PC layers are quite flexible. All peel tests were performed with a grip speed of 25.4 mm/min. Force versus displacement data were collected during the peel test.

Optical and electron microscopy

A Zeiss optical microscope (Zeiss, Oberkochen, Germany) was used to collect optical images of delaminated surfaces and interfaces of coextruded films. Both reflection and transmission modes were used. In addition, the interfacial region of the coextruded films

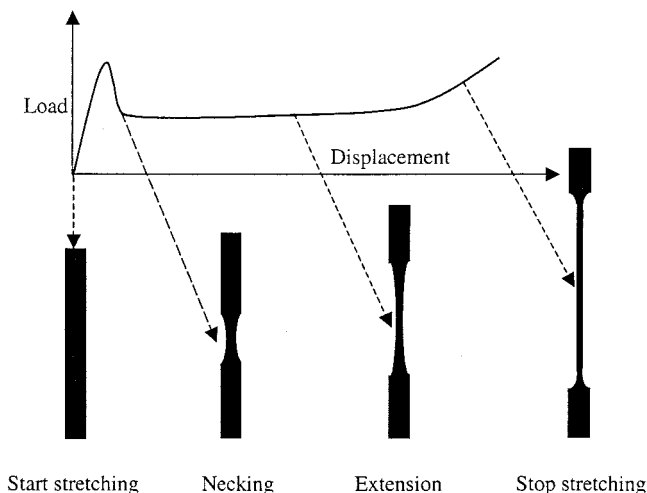


Figure 2 Schematic load–displacement curve and a representation of stretched film during different stages of the uniaxial stretching experiment.

was also investigated by transmission electron microscopy (TEM) by a Philips (The Netherlands) CM100 transmission electron microscope. All TEM samples were microtomed into thin sections with a thickness < 100 nm. The thin sections were stained by ruthenium tetroxide (RuO₄) for 2 min to enhance the contrast between PC and c-PC phases.

RESULTS AND DISCUSSION

Initiation of delamination by uniaxial stretching

Figure 2 depicts schematics with detailed observations of the uniaxial stretching experiment. As a strip of coextruded film was stretched, a neck formed at the moment of yielding (local maximum) in the middle of the strip. The boundaries of the neck then extended toward both ends and eventually stopped by sample

grips at the end of the stretching experiment. The stretched region of the film sample could be easily delaminated with a razor blade. However, the delamination did not propagate across the boundary of the neck. (The significance of the necking will be discussed later.) It was confirmed that indeed a simple uniaxial stretching under the above-mentioned conditions was able to initiate delamination for the coextruded films used in this study. Therefore, by using uniaxial stretching as a means to initiate delamination, it is possible to perform interlayer adhesion measurement for the coextruded films.

Peel test for coextruded films

Based on the above observation, a two-step method was developed to quantify interlayer adhesion. The details of this method are shown in Figure 3. First, a double neck (50 mm long) was placed in the middle of a sample strip with a dimension of 25.4 × 205 mm (width × length) [Fig. 3(a)]. The double-neck feature ensures that deformation during uniaxial stretching is confined within this region. Other types of neck geometries were also investigated (e.g., a slit or a circular opening in the middle of the strip). However, the double-neck geometry gave the best control on neck propagation. The sample was stretched at a temperature of 135°C and a grip speed of 100 mm/min [Fig. 3(b)]. Other temperatures and grip speeds were also used, and the above conditions were found to be the optimum for all samples used in this study. The extent of stretching has to be well controlled so that, at the end of the stretching, the boundaries of the neck stop close to the shoulder of the original double neck [Fig. 3(b)]. In this work, 50 mm was found to be the optimal amount of displacement for the stretching. The stretched region was then cut in the middle [Fig. 3(b)] and the two halves became the specimens for the peel

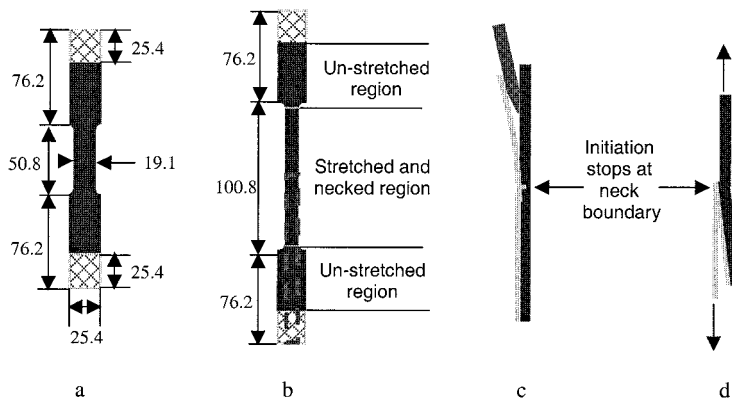


Figure 3 Procedure of adhesion test for coextruded films: (a) a double-necked film sample, (b) stretch at 135°C at 100 mm/min speed for 50 mm displacement, (c) initiation of delamination with a razor blade from cut end, and (d) 180° peel test at 25.4 mm/min.

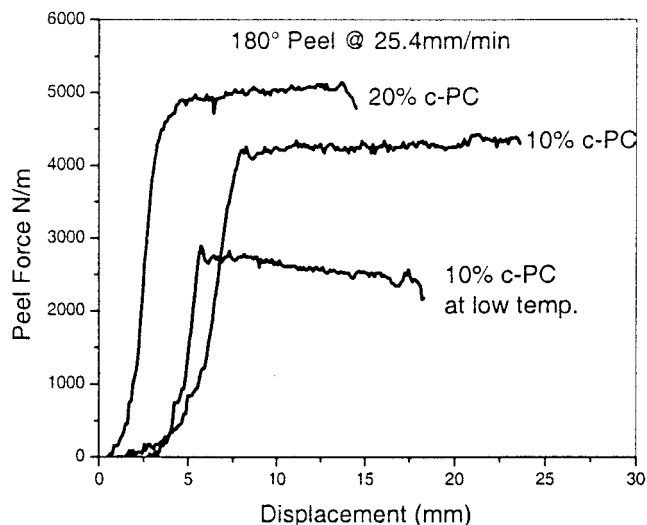


Figure 4 Peel curves for three coextruded films: 20%PC and 10%PC in c-PC composition processed under the same coextrusion condition and another film with 10%PC processed under a low temperature condition.

test. For a peel test specimen, delamination was introduced with a razor blade from the cut end in the stretched region [Fig. 3(c)] and propagated to the middle, where necking stopped during uniaxial stretching. Finally, the partially predelaminated specimen was tested with a 180° peel geometry [Fig. 3(d)].

Figure 4 shows peel curves for three coextruded films to display the effect of c-PC composition and processing on interlayer adhesion of the coextruded films. For a typical peel curve in Figure 4, the peel force began with a small value and increased quickly because of bending and tightening of the c-PC and/or the PC layer and eventually reached a plateau, reported as (steady-state) peel force in this study. The data in Figure 4 suggest that the film with 20%PC in c-PC composition has a higher peel force than that of the film with 10%PC in c-PC composition (5000 versus 4200 N/m). This is expected, given that the copolymer with 20%PC is somewhat more compatible with PC than that with 10%PC. In addition, it is evident that

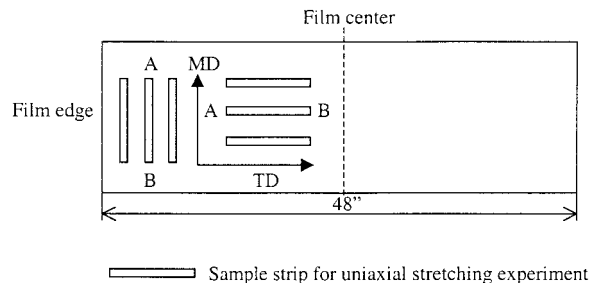


Figure 5 Definition of locations A and B for peel force data listed in Table I.

there is a big difference in peel force between films produced at a low processing temperature with the same c-PC composition (4200 versus ~ 2500 N/m). Clearly, quantification of interlayer adhesion for these films allows one to understand the effect of polymer composition and coextrusion processing. Note that the peel forces in Figure 4 are all >1750 N/m (~ 10 lb./in.); this level of interlayer adhesion is not often reported in the literature because of the inability to initially delaminate with other techniques.

Table I summarizes peel force data collected at different locations (A and B) along the machine direction (MD) and transverse direction (TD) of the coextruded films made with different manufacturing lines (C and D). Definitions for locations A and B in both the MD and TD are shown in Figure 5. From Table I and Figure 5, it is obvious that there is a great deal of variation in interlayer adhesion across surfaces of the coextruded films. The variation exists from run to run within the same manufacturing line (Table I, films C1–C5) and from line to line for the same coextruded films (Table I, C films versus D1 film). The data in Table I also show that, as expected, interlayer adhesion varies mostly along the TD [Table I, TD(A) versus TD(B)]. The observed variations have been related to the details of the coextrusion process, including single- versus multimanifold die, heating profile of the dies, process line speed, and so forth.

TABLE I
Peel Force (N/m) Variation Between Run to Run and Line to Line for Coextruded Films Used in This Study^a

Coextruded film	Manufacturing line	MD (A + B)	TD(A)	TD(B)
C1	C	890 ± 196	1608 ± 36	1424 ± 18
C2	C	534 ± 125	534 ± 18	1246 ± 18
C3	C	3382 ± 71	na	na
C4	C	712 ± 142	890 ± 89	1424 ± 36
C5	C	2136 ± 142	1780 ± 107	1958 ± 142
D1	D	3560 ± 249	3738 ± 142	2492 ± 160

^a Each data point is based on five measurements.

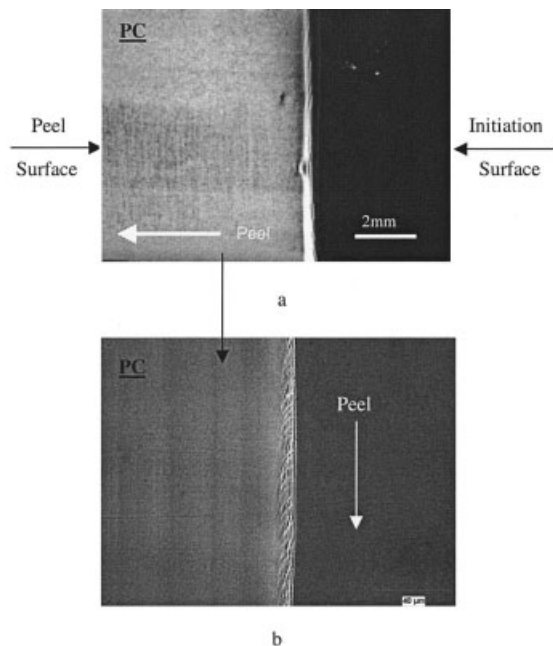


Figure 6 Failure analysis of PC surface after delamination of coextruded films. Surface reflection (a) reveals a smooth surface after stretching and “rough” surface with fine “lines” after peel with a sharp neck boundary between them. Cross-sectional transmission view (b) reveals subsurface shear bands in peel surface.

Failure analysis

Visually, the surface as a result of the peel test (peel surface) looks very different from that as a result of stretching (initiation surface). Such a difference is captured by an optical image as shown in Figure 6(a). Only off-specular reflection was collected in this image; therefore, the dark area means a smooth (initiation) surface and the gray area means a rough (peel) surface. A sharp boundary due to necking is visible in the middle of Figure 6(a). Closer examination of the peel surface revealed many fine lines that are perpendicular to the peel direction [gray surface in Fig. 6(a)]. From cross section optical microscopy [Fig. 6(b)], it is clear that these lines are not on-surface but rather subsurface, at roughly 45° with respect to the peel direction. These subsurface lines are believed to be shear bands.¹¹ The presence of these shear bands as a result of peel is an indication of strong interlayer adhesion. On the contrary, the initiation surface shows no detectable subsurface features (image not shown).

Cross section optical microscopy in Figure 7(a) reveals a detailed microscopic process of stretching and peel test—from the stretched region (narrower because of necking) to the tip of peel (c-PC layer is pulled apart from PC layer), with a neck boundary in the middle. The necked region is highly birefringent with visible shear bands. On the other hand, the unnecked region remains in its initial state, with

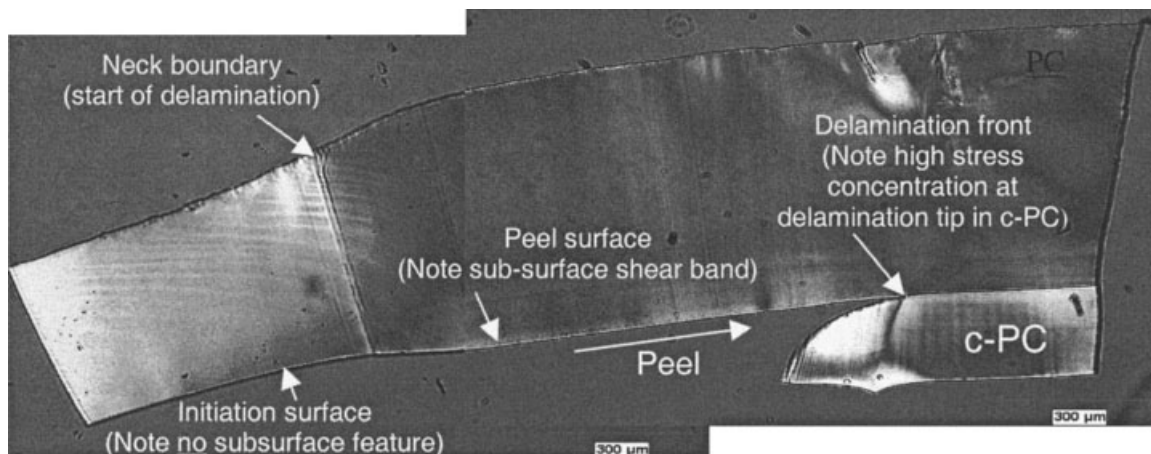
no sign of permanent deformation. This suggests that deformation during uniaxial stretching is indeed confined within the original double-neck region and has no impact on the unnecked region. Therefore, peel force generated from the unnecked region is a true representation of interlayer adhesion of coextruded film. At the tip of the delamination, the c-PC layer was highly stressed, as indicated by high birefringence ascribed to bending and stretching during the peel test process.

It is clear from Figure 7(a) that, before delamination, the interface between c-PC and PC layers is straight, with no sign of interfacial mixing or interfacial instability often encountered during coextrusion.¹² After delamination, there is no sign of c-PC layer on the delaminated PC surface. To confirm this observation, a TEM experiment was performed at the tip of the peel front [Fig. 7(b)]. Figure 7(b) clearly shows no remnant of a PC or c-PC layer on the delaminated surface of c-PC or PC. Therefore, it can be concluded that interlayer delamination of the coextruded films is a clean interfacial breakup, and the peel force is a true measure of interlayer adhesion, with no contribution from interfacial mixing or interfacial instability.

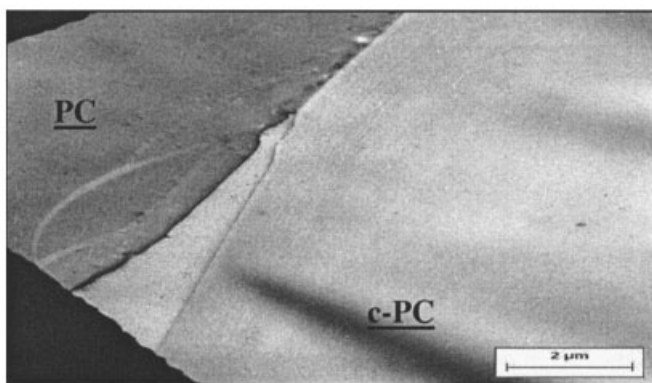
From a molecular standpoint, the origin of adhesion for the coextruded film is interdiffusion of c-PC and PC molecular chains during coextrusion to form an interphase with certain thickness. Therefore, both resin composition and coextrusion processing are important factors affecting the level of interlayer adhesion. Resin compositions (PC%, MW, degree of branching, etc.) and processing parameters (melt temperature, line speed/feed rate, die design, etc.) affect diffusion thermodynamics and/or kinetics: both are critical to achieve sufficient interlayer adhesion. For example, a higher melt temperature, slow line speed, lower MW (sufficiently larger than entanglement MW), and a higher PC% in c-PC would result in a stronger interlayer adhesion. The effect of shear-induced orientation is believed to be marginal because the coextrusion processing is performed at low shear rates and high melt temperatures, where molecular orientation is expected to be relaxed quickly during melt processing.¹³

Neck-induced delamination

We can now speculate the cause of initial delamination or dramatic loss of adhesion that occurred during uniaxial stretching. After the uniaxial stretching or necking, film thickness was reduced and polymer chains were preferentially oriented to the stretching direction. Both events can adversely affect interlayer adhesion. The interphase has to reduce its thickness in proportion with the total film thickness upon necking, and reduced interphase leads to a lower interfacial adhesion.¹² Molecular orientation along the stretching



a



b

Figure 7 Microscopic view of delamination and peel test: (a) an optical image of delamination and peel test and (b) a TEM image at the tip of delamination show a clean interfacial breakage for the coextruded films.

direction reduces polymer chains' load-bearing capability across the interphase and, as a result, reduces interlayer adhesion.

However, the above speculations were not confirmed by experiments. For example, for the coextruded film with 20%PC in co-PC composition, after uniaxial stretching film thickness in the necked region decreased from 0.760 to 0.533 mm (30% thickness reduction); yet the peel force decreased from 5250 to 340 N/m (94% peel force reduction). On the other hand, a real-life failure of a thermoformed part from the same coextruded film with a thickness of 0.254 mm (66% thickness reduction) had a peel force of 1750 N/m (66% peel force reduction). In addition, coextruded films have shown different levels of interlayer adhesion at different thicknesses after planar and biaxial stretching.¹⁰ Therefore, it is believed that the initiation of delamination is not attributed to thickness reduction but to the nature of stretching. Specifically, the formation of neck dur-

ing uniaxial stretching is the cause for the drastic loss of interlayer adhesion.

As shown in Figure 2, necking occurred during uniaxial stretching of the coextruded films used in this study, as evidenced by a local maximum on a load-displacement curve.¹⁴ For a thermoplastic polymer, necking is usually followed by a cold-draw process and some degree of strain hardening before sample breakup (Fig. 2). It is important to point out that as cold draw proceeds, the neck boundary moves from the necked region to the unnecked region—the necked region does not undergo any further deformation until neck propagation stops and strain hardening begins. Interestingly, observations of stretch-induced delamination in this work are consistent with the necking process. As shown in Figure 8, it is possible to delaminate the coextruded film as long as necking developed during uniaxial stretching. In addition, the low level of interlayer adhesion in the necked region (340 N/m) is not dependent on the degree of cold

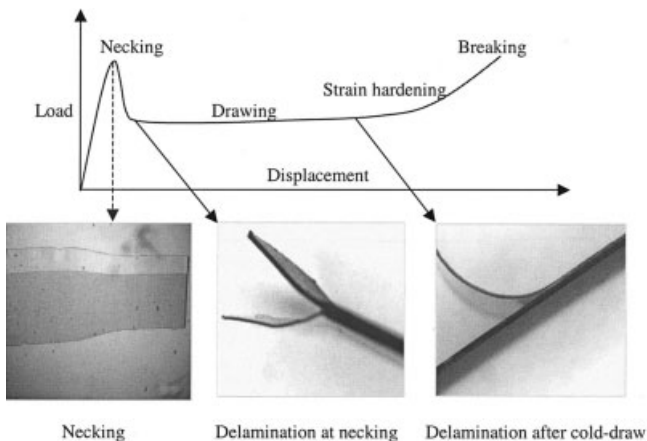


Figure 8 Neck-induced delamination for the coextruded films. Delamination occurs as long as necking takes place during uniaxial stretching.

draw. Therefore, it is speculated that, upon necking, the interlayer adhesion between c-PC and PC layers is destroyed.

Figure 9(a) displays room temperature stress–strain curves for c-PC, PC, and a coextruded film based on the respective c-PC and PC layers. It is clear that these materials have different yield stress, yield strain, and cold-draw stress. Figure 9(b)–(d) plot yield stress, yield strain, and cold-draw stress as a function of temperature. The coextruded film behaves intermediate with respect to individual composing layers. Increasing the stretching temperature reduced yield stress and cold-draw stress as well as yield strain as a result of softening of the polymers at high temperatures. c-PC has a higher yield stress and cold-draw stress at room temperature and a somewhat lower T_g value than those of PC. As a result, crossover points were observed for both yield stress and cold-draw stress in Figure 9(b) and (d).

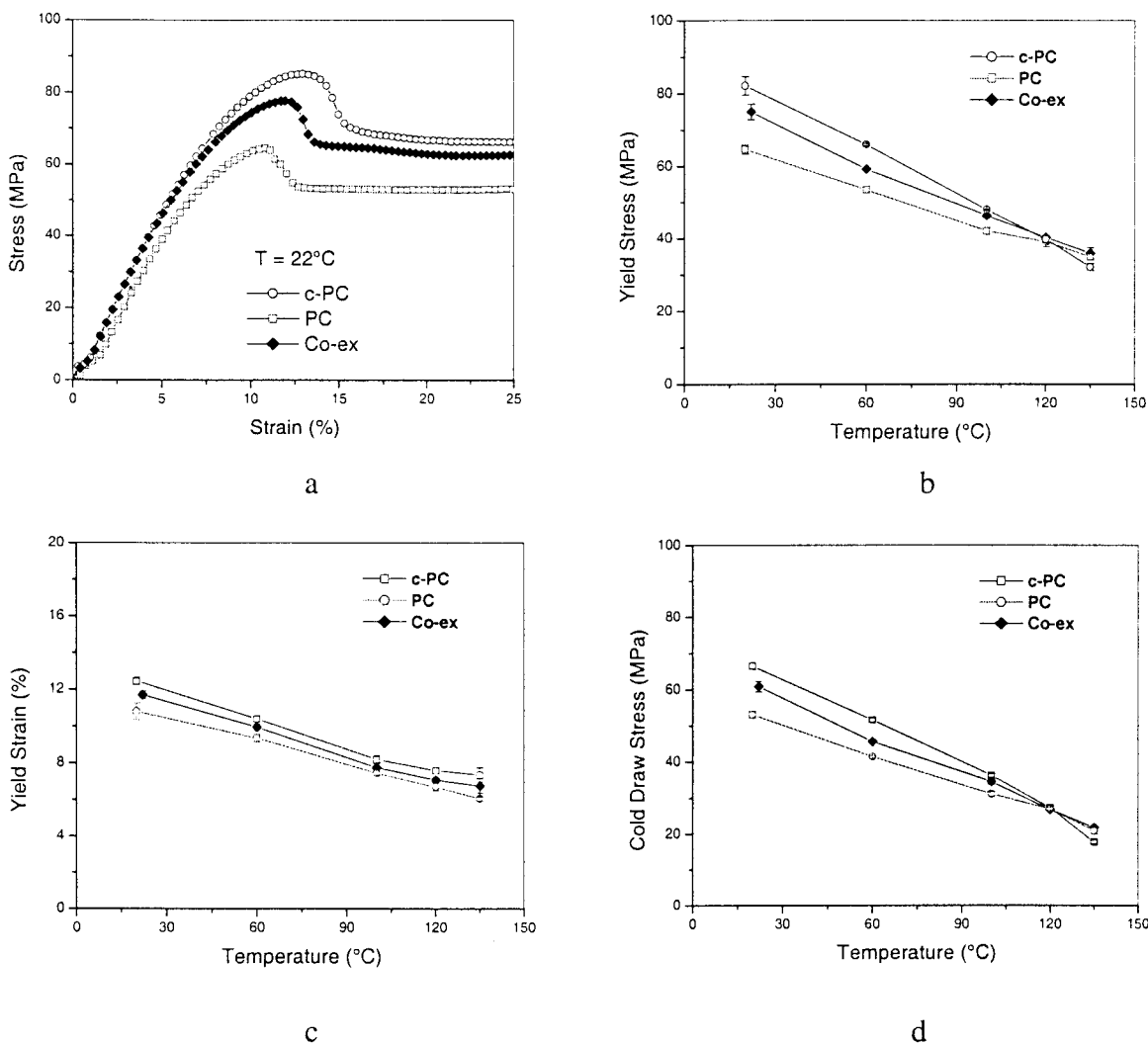


Figure 9 Stress–displacement behavior of c-PC, PC, and coextruded film of c-PC/PC at room temperature (a) and yield stress (b), elongation at yield (c), and cold draw stress (d) as a function of stretching temperature.

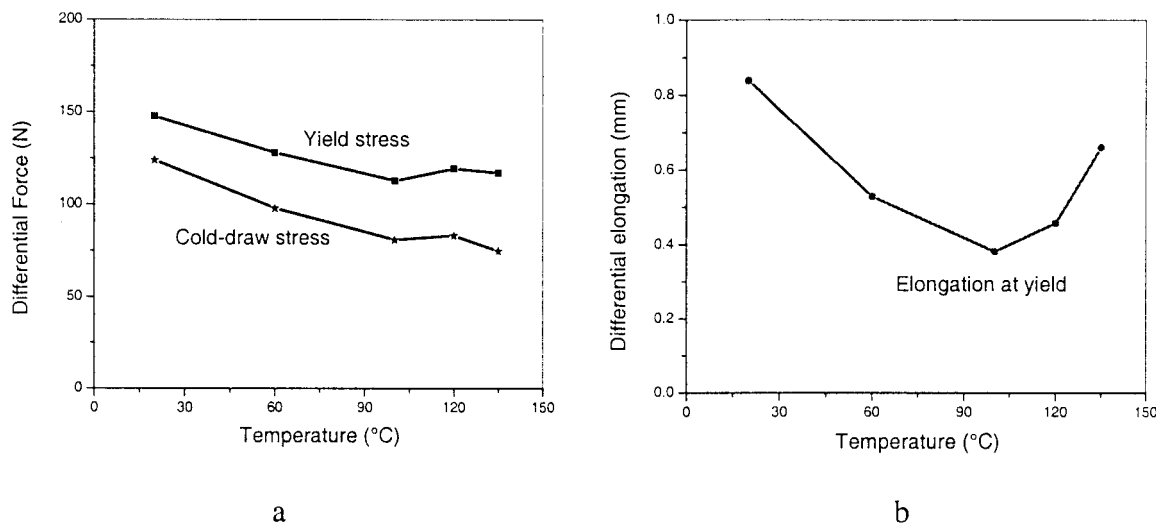


Figure 10 Calculated differential force and differential elongation of coextruded c-PC/PC film during uniaxial stretching experiment at different temperatures.

It is clear from Figure 9(b)–(d) that, when the coextruded films yielded or necked, the deformation of individual layers experience different force and elongation. Based on Figure 9(b)–(d), it is possible to estimate differential force and differential elongation for the coextruded films upon necking. Figure 10(a) and (b) present such calculated differential force and differential elongation for a specimen of $50 \times 12.5 \times 0.762$ mm (length \times width \times thickness), typical for the uniaxial stretching experiment. Note that at all temperatures the differential force and differential elongation are nonzero values. It is therefore conjectured that upon necking the nonzero differential force and/or differential elongation created interfacial shear stress and/or interfacial displacement, which ultimately caused interlayer delamination.

Lap shear experiments were performed at room temperature with a symmetric lap shear geometry [Fig. 2(c)], and no c-PC and PC interlayer delamination was observed for the lap shear sample under a tensile stress much larger than the differential stress in Figure 10(a). Therefore, interfacial displacement is believed to be the major cause of neck-induced delamination. Essentially, upon yielding or necking, the c-PC and PC layers slip, relative to each other layer, to accommodate their difference in elongation at yield. Such a local interfacial displacement causes interfacial breakup.

According to the above speculation and Figure 10(b), uniaxial stretching at any temperature between room temperature and T_g could delaminate the coextruded film as long as necking occurs during uniaxial stretching. This was indeed confirmed by experiments in this study. However, the elongation low temperature was very limited, given that the coextruded films tend to break prematurely, with little use for the pur-

pose of predelamination for the peel test. Therefore, it is still preferable to perform uniaxial stretching at relative high temperature to initiate delamination. It is worth pointing out that peel force data for the same coextruded film samples were almost identical, regardless of the temperature at which uniaxial stretching experiment was performed.

CONCLUSIONS

A novel uniaxial stretching technique was discovered and used to introduce initial delamination for coextruded films with strong interlayer adhesion. It was demonstrated that necking during the uniaxial stretching caused an instantaneous delamination for the coextruded films. Based on these findings, double-neck sample geometry was designed to control the necking process, and the initial delamination was followed by a direct peel test to quantify interlayer adhesion of the coextruded films. Because the uniaxial stretching was confined within the necked region and interlayer adhesion was measured from the unnecked region, there is no effect of predelamination on peel force measurement.

Coextruded films with interlayer adhesion (peel force) as high as 5300 N/m were measured in this study. It was also demonstrated that the interlayer adhesion of the coextruded films used in this study is strongly influenced by polymer composition and coextrusion processing. In addition, there is a great deal of variation from run to run in the same manufacturing line and from line to line for the same coextruded films. With the help of the test method developed in this work, it was possible to understand and quantify these effects.

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