

Structure and Properties of Multilayered PET/PC Composites

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Summary: With the aid of layer multiplying coextrusion techniques, polymer composites comprising up to thousand of uniform and alternating layers polyethylene terephthalate (PET) and polycarbonate (PC) were produced. Morphology and micromechanical deformation processes in these composites were investigated by means of transmission electron microscopy (TEM) and atomic force microscopy (AFM). In particular, the effect of thickness of individual layers on the large strain deformation micromechanisms was analyzed. On decreasing the thickness of individual polymer layers, a transition in deformation mechanism from two-component behaviour (i.e. the localization of shear bands in individual layer) to one-component-like behaviour (with the shear bands passing unhindered through different layers) was observed at the layer thickness of ca. 1 μm . On further decreasing the layer thickness below 100 nm, the composites exhibited homogeneous plastic deformation (i.e. no localization of deformation). In contrast to pure PET, even after long annealing, the composites showed tough behaviour during tensile loading.

Keywords: deformation mechanism; electron microscopy; multilayered composites; nanostructure

Introduction

Ultra-thin polymer films find several practical applications. Therefore, various methods have been developed to manufacture such films. An attractive way of synergistically combining the properties of two or more polymers in ultra-thin film assemblies is provided by multilayer coextrusion.^[1] This strategy comprises the *forced assembly* of the polymers in different layered architectures^[1–7] and has an advantage that the layered composites consisting of continuous alternating polymer layers with thick-

ness ranging from several microns down to several nanometers can be produced.^[2] These systems combine not only the useful properties of the constituent polymers but also provide model systems for the study of crystallization of polymers under physically confined environment.^[7–10]

In the recent years, new microlayered and nanolayered components have been produced with hundreds or even thousands of alternating layers.^[2] As a result, new insight has been developed in the area of rubber toughening of amorphous thermoplastics and reinforced layered structures. From the micromechanical point of view, different models have been developed to explain toughness enhancement as a result of co-operative crazing and shear banding.^[11] Baer and co-workers have developed analytical models for microlayered systems that inter-diffuse and concurrently crystallise.^[12] Recently, via finite elements

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simulations and constitutive modelling the micromechanical behaviour of the multilayered composites comprising a ductile and a brittle polymer have been studied.^[13,14] These studies have described the co-operative action of the deformation structures of the polymers involved in the multilayer assembly as well as volume fraction dependence on the deformation mechanism. It has been demonstrated that these composites possess attractive mechanical optical and barrier properties.^[2,12,13,15–18]

The multilayered polymer films comprising polyethylene terephthalate (PET) and polycarbonate (PC) offer an ideal system for the study of impact of physical confinement on the crystallization behaviour of the crystallisable PET component. This potential has been utilized by carrying out comprehensive studies using ultra-small angle X-ray scattering (U-SAXS), microhardness indentation and different microscopic techniques.^[3,7,8,17–19] It was found that the crystallization of the PET in the laminates is strongly suppressed if the thickness of the PET layer is less than 1 μm .^[3,8,20] In preceding studies, the deformation micromechanisms of some of the PET/PC multilayered samples were investigated.^[17,18] Homogeneous yielding of PET and PC layers was observed by transmission electron microscopy TEM.^[17] Motivated by our preceding studies, we investigated the influence of layer thickness of the individual layers on the micromechanisms of deformation in the PET/PC multilayered composites, which will be the object of this paper.

Experimental Part

Materials

The starting materials used for preparing multilayered composites were polycarbonate (PC: Dow Calibre) and polyethylene terephthalate (PET: M&G Cleartuff), both having molar mass of about 30,000 g/mole.

The layered composites of the samples were produced at Case Western Reserve University (CWRU) using the well estab-

lished coextrusion procedures.^[1,2] Given volume of each polymer was fed into a single screw extruder maintained at a temperature of 290 °C in order to extrude a film of each polymer. The films coming out of each extruder were put one above another and then passed through a dye. The film coming out of the first die had two layers. The resulting film was cut vertically and again passed through a second dye in the same manner as for the first dye element. By using n such dye elements or multipliers, one can produce n^{2+1} layered composites.^[2] The samples described in this work have PET/PC compositions by volumes of 10/90, 30/70 and 50/50.

Microscopic Techniques

Transmission Electron Microscopy (TEM: JEM 4000FX, JEOL, Japan) and Atomic Force Microscopy (AFM: MultiMode Atomic Force Microscope, Digital Instruments, Santa Barbara, USA) were used to visualize the structural details of the composites. Ultra-thin sections (ca. 80 nm thick) along the extrusion direction (see scheme in Figure 1) were ultramicrotomed from a piece of bulk specimen using a diamond knife at room temperature. Prior to the TEM studies, the ultra-thin sections were treated with Ruthenium tetroxide (RuO_4) vapor for several hours at room temperature in order to selectively stain the less dense PC component of the composites. Tapping mode AFM was performed on the ultramicrotomed block formed after the sectioning for TEM studies. The microfabricated silicon cantilevers used for AFM imaging had a resonant frequency of approximately 300 kHz and spring con-

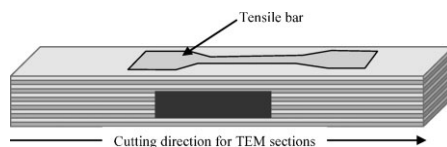


Figure 1.

Scheme showing the ways of preparing TEM sections and tensile specimens for mechanical properties characterization.

stant of about 15 N/min. The radius of curvature of the AFM probes was approximately 10 nm.

Cryo-fracture surface of the specimens broken in tensile tests were analyzed by scanning electron microscope (SEM, Jeol JSM 6300, Japan). The fracture surfaces were sputter-coated with approximately 10 nm gold layer before the SEM examinations.

Mechanical and Micromechanical Testing

Tensile tests were performed using a universal tensile machine (Zwick, Ulm, Germany) at room temperature (23 °C) at a cross-head speed of 50 mm/min. Tensile specimens punched out of the extruded sheets (see Figure 1) with their long axis along the extrusion direction were 80 mm long. The specimens were measured using traversal displacement of the cross-heads.

For the study of strain induced structural changes (i.e., the micromechanical properties) of the composites, semi-thin sections (ca. 800 nm thick) were cut using glass knives parallel to the extrusion direction of each specimen (see Figure 1) at room temperature. Thereafter the sections were strained in a special tensile desk. The strained films were fixed in the strained state and directly studied with a transmission electron microscope (TEM; JEM 4000FX, JEOL Japan) operating at an acceleration voltage of 400 kV. Those studies were conducted at Max Planck Institute (MPI) for Microstructure Physics, Halle.

Results and Discussion

Structural Characterization of Multilayered Composites

For the structural characterization of the multilayered composites, differential scanning calorimetry (DSC) and microscopic techniques were utilized. In parallel studies on the same systems by Balta Calleja et al., X-ray scattering and microindentation hardness techniques were used.^[3,7,8,20] In a recent study, for the comparative analysis

of morphology of those samples, atomic force microscopy (AFM) and Ultra-small Angle X-ray Scattering (U-SAXS) were utilized.^[7] In this work, we further explore the morphology and structure of the composites using TEM and AFM. Figure 2 shows the micrographs of some of the sample films having approximately 1 mm thickness.

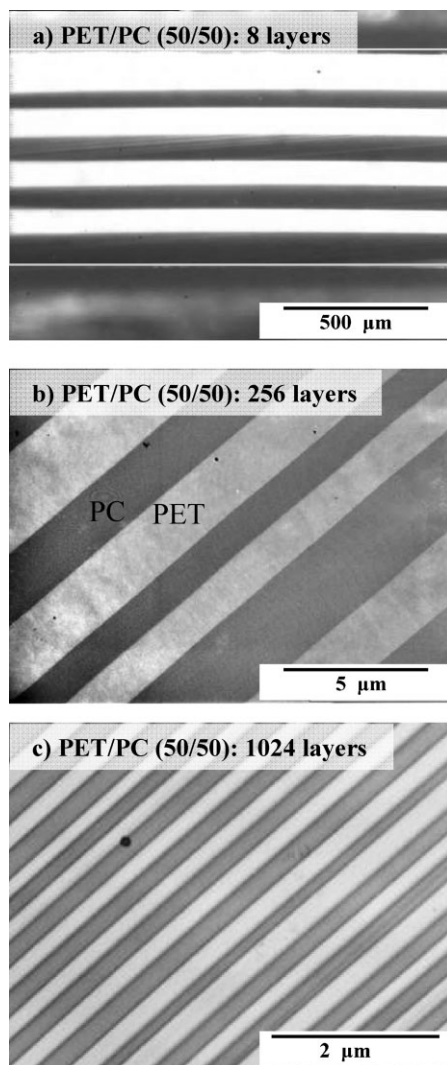


Figure 2. Optical (a) and TEM (b,c) micrographs of some of the multilayered composite films having thickness of approximately 1 mm.

Each film had a PET/PC composition of 50/50. In every image, the PET phase appears brighter than the PC phase. Figure 2a is an optical micrograph of an 8 layered sample while Figure 2b and 2c are the TEM micrographs of 256 layered and 1024 layered samples, respectively. In the micrographs presented in Figure 2, one can clearly notice that the composites comprise the uniform and continuous sheets of two polymers arranged in an alternating fashion. Furthermore, confirming the inferences of our earlier studies on different systems, the thickness of each layer is close to one set during processing.

Phase contrast tapping mode AFM which allows the straightforward imaging of polymer nanostructures based on local variation in mechanical properties,^[21,22] was employed to examine the morphology of the ultramicrotomed surface of the multilayered composite film. It is known that both PC and PET (at the amorphous state) belong to the class of rigid thermoplastics. These differ significantly in the mechanical properties such as stiffness, hardness and even on the extent of ductility. Therefore, AFM phase imaging allows the successful microscopic characterization of the composites. Typical result is presented in Figure 3, which revealed that

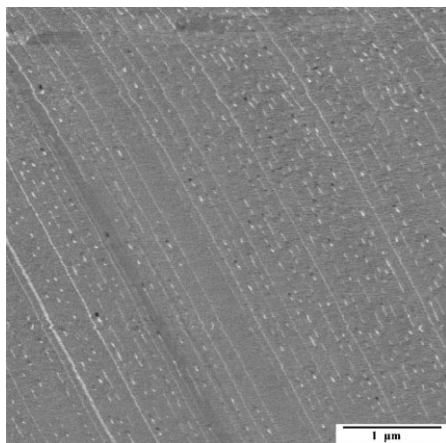


Figure 3.

AFM phase micrograph showing the morphology of a 4,096 layered PET/PC (10/90) composite; PET phase appears bright in the image.

the composites having the PET laminate thickness as small as 10 nm could be successfully fabricated via coextrusion technique. This minimum thickness of the laminate that could be assembled in the composite is very close to the gyration radius (R_g) of the PET molecule.^[23] Approaching the dimension of R_g , the PET layers break into elongated droplets forming the discontinuous structures characteristic of the typical polymer blend. Nevertheless, the segregation of the domains is in the nanometer range.

When quenched from the melt, both PC and PET are frozen in to the amorphous state. PC is usually an amorphous polymer, but PET phase can undergo crystallization giving rise to semicrystalline texture upon annealing from the solid state (or from the melt). The formation of the spherulitic super-structure is strongly suppressed due to the physical constraint imposed by the neighbouring PC layers. Therefore, such a system provides ideal cases for the study of physical phenomena such as confined crystallization, kinetics of molecular diffusion etc. The effect of physical confinement on the crystallization phenomena and deformation micromechanics was reported elsewhere.^[3,8–10,18–20]

Mechanical Properties and Analysis of Fracture Surfaces

The macroscopic mechanical behaviour of the multilayered composites was determined by carrying out uniaxial tensile tests on the samples differing in total number of the layers. The PET/PC composition by volume was set to 50/50.

Macroscopically, all the samples, including the pure homopolymer films, deform by formation of well defined neck that propagate throughout the tensile bar until the specimen breaks. Figure 4 shows, for example, the tensile specimens of a sample annealed at 135 °C for 72 hours and subjected to tensile testing. Note that the optical translucent of the sample arises from the crystallization of PET phase in the composite. In the deformed region, the sample again reveals the optical clarity

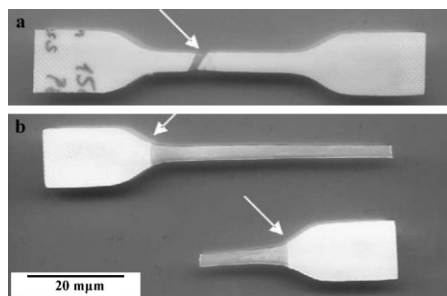


Figure 4.

Optical photographs of the tensile specimens of an annealed PET/PC (50/50) composite having: a) specimen right after the formation of neck; b) a specimen after the fracture; the arrows show the regions where the necking zones terminate.

indicating the complete destruction of the crystalline phase of the PET.^[24]

Figure 5a presents the tensile stress-strain curves of the multilayered PET/PC (50/50) composites which have identical film thickness of 1 mm each and differ in the total number of the layers. Each sample shows the stress maximum and undergoes cold drawing following the necking of the sample. The yield stress of each sample is approximately 60 MPa which falls by about 20%, after which the process of cold drawing onsets.

The elongation at break (ϵ_B) for pure and neat PC and PET lies in the range of 100% and 400%, respectively. The value of ϵ_B for all the composites, irrespective of the layer thickness (or the number of layers present in the films), is approximately 150%. This value is significantly lower than that one would expect assuming the additivity of the strain at break of the two components. It means that assembling extremely tough component (such as PET) together with a less tough component (such as PC), the deformability of the former will be suppressed. It was found that other mechanical parameters such as Young's modulus, yield stress and stress at break of the composites were approximately the average of the neat components.^[25]

A dramatic effect of the multilayer assembly of the polymers on the mechan-

ical deformation behaviour appears when the samples are annealed for a long time. The representative results obtained from tensile testing of the annealed samples are presented in Figure 5b. On annealing the samples at 135 °C under vacuum (at which the PET phase crystallizes^[3,8] while the PC is well below its T_g) for 72 hours leads to a embrittlement of the PET layers. The yield point in the annealed samples is surprisingly higher (about 90 MPa) than that of the neat samples (approximately 60 MPa). The drop in the strain at break for pure PET as a consequence of annealing is the most dramatic observation.

The annealing under these conditions represents simultaneously the physical ageing of polycarbonate. In fact, as expected, the yield stress of the PC is nominally increased while making it a less ductile material. On the other hand, the multilayered composites were found to show macroscopically ductile behaviour (see Figure 4b). Nevertheless, the strain at break remains almost unaltered for the composites. Similar trend in the mechanical properties was obtained for the composites having asymmetric compositions as well.

In summary, the multilayer assembly of PC and PET endows otherwise embrittled polymers (such as PET after thermal annealing) with high toughness if assembled in combination with tough polymers (such as PC). Nevertheless, under quasi-static tensile loading conditions, opposed to some of the previous studies investigating other kinds of multilayered composites,^[5,26] the effect of decreasing layer thickness on the enhancement of macroscopic mechanical properties was not observed.

An investigation into fracture surface morphology of multilayered films reveals a significant difference in the micromechanical properties. Figure 6 compares the typical SEM micrographs of two multilayered films differing in the thickness of individual layers: one ca. 100 μm thick layers and the other with ca. 1 μm thick layers. The specimens were the fracture surfaces obtained after tensile testing. In

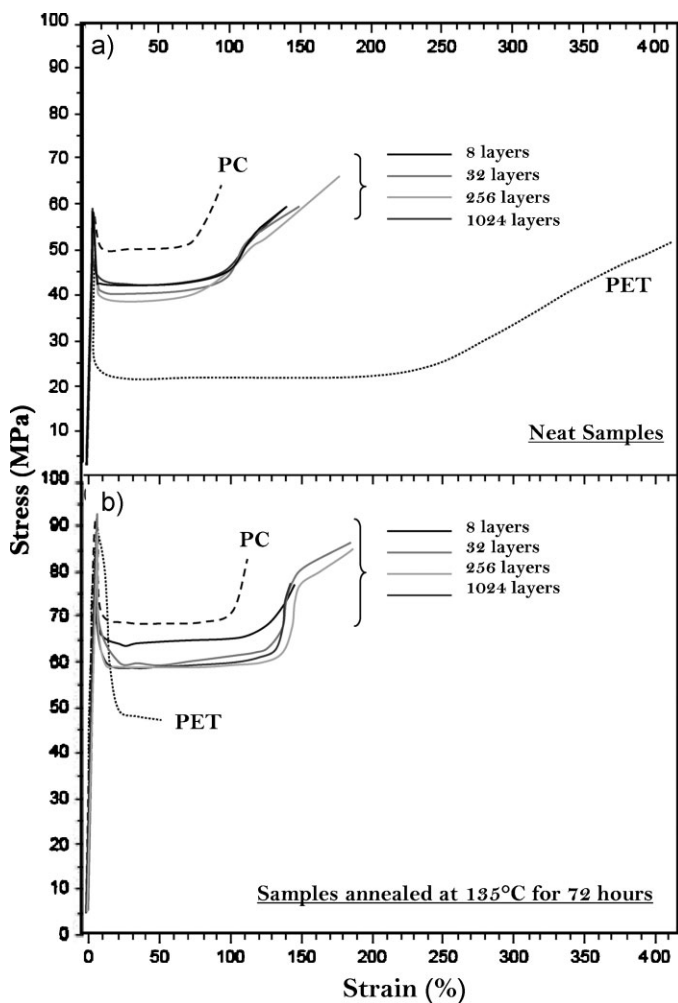


Figure 5.

Tensile stress-strain curves of thick multilayered PET/PC (50/50) films comprising various numbers of layers; note a dramatic decrease in strain at break for PET but not for the composites.

the specimen comprising 100 μm thick laminates, the individual layers exhibiting characteristics of two different polymers (i.e., PET and PC) are clearly visible (see Figure 6a). Based on the SEM observation of tensile fracture surfaces of pure homopolymers, it can be concluded that the rougher areas in Figure 6a correspond to the PET layers while the smoother ones the PC layers. The observed fracture surface morphologies suggest that PET is more susceptible to intensive plastic deformation and forms larger number of deformation zones than PC. The fracture surface

morphology of the composite changes dramatically when the thickness of each layer is decreased to approximately 1 μm (see Fig 6b). The individual and distinct deformation of each polymer component observed in the 8 layered samples (see Figure 6a) is not manifested in the 256 layered samples, where the thickness of each polymer layer is approximately 1 μm (see Figure 6b). In the latter case, the film behaved in the same manner as it would have consisted of the single polymer, i.e., the identity of each polymer layer as single component vanished in this composite.

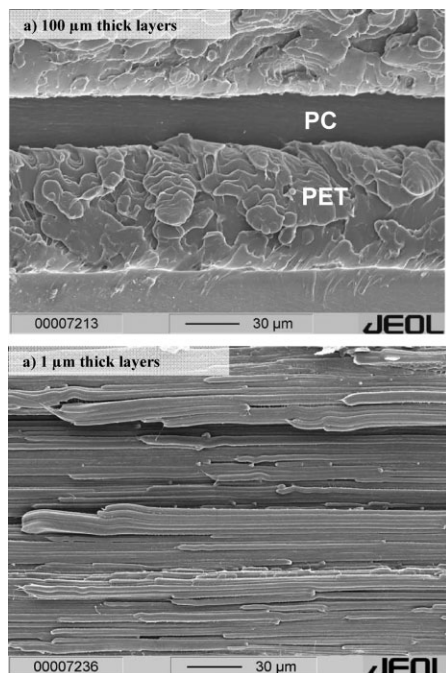


Figure 6. Representative SEM micrographs of 8 layered (a) and 256 layered (b) multilayered PET/PC (50/50) samples having variable layer thickness as indicated.

Investigation of Micromechanical Properties by TEM

The detailed studies on the micromechanical behaviour of the composites were conducted with the aid of relatively high voltage transmission electron microscopy (TEM, 400 kV). The stretched semi-thin sections were directly transferred to the specimen holder of the TEM. Before we present the results, it would be worth to mention some important notes about the contrast mechanisms.

The contrast in the stretched sections without staining during TEM investigations arises mainly from two facts: strain induced thickness contrast and contrast induced by electron beam damage of the sample components.^[27] In the first case, the more strained regions appear brighter (by virtue of lesser thickness of those areas) than the less strained regions. In the second case, the higher the irradiation damage, the brighter will appear the specimen area.

Additionally, in multi-component polymeric systems, the deformation of individual components will be recognized by comparing with the deformation structures of the corresponding homopolymers. In the present work, we have taken all the above mentioned possibilities into account to analyse the deformation structures of the multilayered composites.

The analysis of the deformation of the individual components (i.e., PET and PC) revealed that PET deforms by the formation of shear bands (i.e., the deformation zones inclined at an angle of 45° relative to the principal strain direction) and homogeneous craze-like zones (i.e., the deformation zones running perpendicular to the strain direction) while PC deforms more homogeneously. Thus, by taking the deformation structures of the homopolymers as reference, one can easily identify the deformation structures of the corresponding polymers in the multilayered composites.

Figure 7 shows the initial stage of deformation of 8 layered PET/PC (50/50) film whereby four layers were removed during the specimen preparation. The PET layers undergo strong shear yielding initiating homogeneous deformation zones in the adjacent PC layers. In both the layers, shear bands and craze-like deformation zones are noticed. It should be noted, however, that the PET layers have much stronger tendency to form shear bands during the tensile deformation. The intensive plastic deformation of PET layers with the formation of multiple shear bands is correlated with much rougher fracture surface morphology of PET layers (compare with Figure 6a).

At high deformation, strong plastic flow of both the layers was observed. Similar results were obtained for the composites having individual layer thickness down up to 10 µm. The composites with asymmetric PET/PC compositions also followed the same trend.

The deformation behaviour of the composites was found to change drastically when the thickness of each polymer layer is

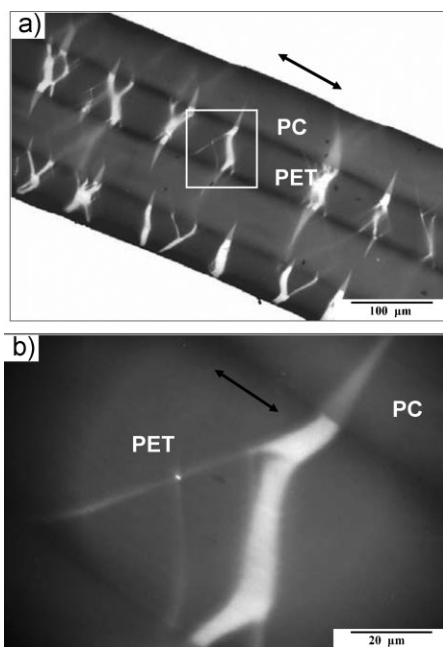


Figure 7.

TEM micrographs of deformed semi-thin section of 8 layered PET/PC (50/50) sample showing shear bands in PET phase which initiate the homogeneous deformation zones in adjacent PC layers; the area indicated by a rectangle in (a) is magnified in (b); the arrows indicate the deformation direction.

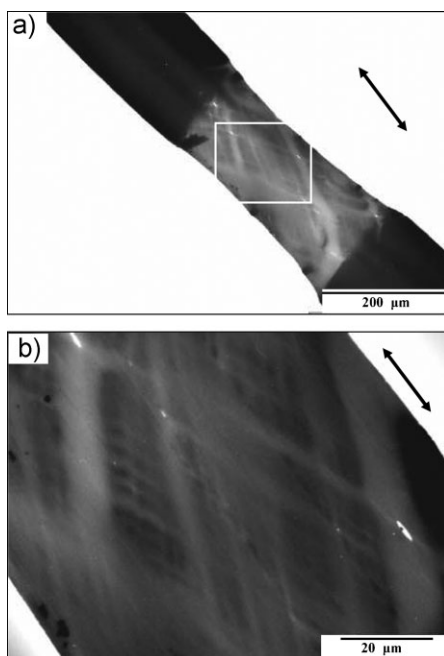


Figure 8.

TEM micrographs of deformed semi-thin section of 1024 layered PET/PC (50/50) sample showing shear bands running through the whole film thickness; the area indicated by a rectangle in (a) is magnified in (b); the arrows indicate the deformation direction.

reduced to about 1 μm . Figure 8 shows, for instance, the deformation structures formed by stretching the PET/PC (50/50) composite comprising 200 nm thick polymer layers. The deformation bands running across the whole film thickness at an angle of 45° relative to the principal strain direction are evident in Figure 8. Now, the shear bands have not been localized in a single polymer layer but have become inseparable from one polymer to the other, i.e., the film comprising two different polymers behaves as if it were a single polymer (*one-component-like behaviour*) provided that the layer thickness $\leq 1 \mu\text{m}$. Conversely, the films exhibit the deformation mechanisms of the individual polymers (*two-component behaviour*) when the layer thickness $> 1 \mu\text{m}$.

This situation also defines the geometrical criterion for the formation of localized deformation zones in single polymer

layer. Based on our results, it can be concluded that the minimum thickness of the sample susceptible to macroscopic shear band formation is approximately 1 μm . In the same line, for a crazable material like polystyrene a critical thickness of approximately 30 nm was found below which the specimen yields homogeneously.^[28,29] The transition in the deformation mechanism from *two-component behaviour* to the *one-component-like* one is also correlated with the confinement effect in PET crystallization, which is strongly hindered if the layer thickness is below 1 μm .^[3]

In a preceding paper, we described the deformation behaviour of the PET/PC (50/50) composites having the layer thickness of about 130 nm.^[18] We further extended the study to an extremely asymmetric sample having PET/PC composition of 10/90 volume and PET and PC layer thickness

of approximately 10 and 100 nm, respectively (results not presented here). It was found in those cases, astonishingly, that both the layers deformed in homogeneous manner without formation of any localized zones supporting the conclusions drawn in our previous works.^[17]

Conclusion

In this work, we investigated the morphology and the deformation behaviour of layered polymer composites based on polycarbonate (PC) and polyethylene terephthalate (PET) produced by multi-layered coextrusion technology (via so called *forced assembly* route). The composites having uniform PET and PC laminate thickness of several microns down to several nanometers could be successfully produced in which the interfacial region had adequate adhesion between the polymers.

A significant shift in the micromechanical deformation behaviour occurred on changing the sample dimension from macroscale to micro- and nanoscale. It was found that the sample films having the polymer laminate thickness of $\leq 1 \mu\text{m}$ exhibited the shear zones passing across the thickness of the whole extruded film (*one-component-like behaviour*). Above $1 \mu\text{m}$, the individual polymers preserved their inherent deformation properties and hence endowing the composites with *two-component behaviour*. On further decreasing the thickness of the layers below 100 nm, the composites showed homogeneous plastic deformation (i.e., no localization of deformation zones).

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