Colloid Polym Sci (2004) 282: 203–208
DOI 10.1007/s00396-003-0906-1

ORIGINAL CONTRIBUTION

Elena M. Ivan'kova
Marina Krumova
Goerg H. Michler
Peter P. Koets

Morphology and toughness of coextruded PS/PMMA multilayers

E.M. Ivan'kova · M. Krumova
G.H. Michler (✉)
Institute of Materials Science,
Martin Luther University Halle Wittenberg,
06099 Halle(Saale), Germany
E-mail: michler@iw.uni-halle.de
Tel.: +49-3461-462745
Fax: +49-3461-462535

P.P. Koets
Department of Materials Technology,
Eindhoven University of Technology,
WH 4.139, PO box 513, 5600 MB
Eindhoven, The Netherlands

Present address: E.M. Ivan'kova
Fracture Physics Department,
Ioffe Physico-Technical Institute RAS,
Politechnicheskaya 26,
194021 St. Petersburg, Russia

Abstract The micromechanical behaviour of multilayered tapes made of two brittle incompatible amorphous polymers PS and PMMA was studied by means of an optical and a High Voltage Electron Microscope (HVEM). Microlayers of PS and PMMA were coextruded with varying number of layers: 64, 512 and 4096 layers. Mechanical properties of the PS/PMMA tapes were also examined. An increase in layer numbers was found to lead to a decrease in layer thickness that, in turn, resulted in: a) formation of thicker and longer crazes and, therefore, increased volume of the material involved in the plastic deformation; b) a noticeable increase in strength and strain at break (i.e. of toughness) of the samples. Enhanced toughness of the multilayered tapes is accounted for by massive cooperating crazing and yielding of both PS and PMMA phases.

Keywords Multilayers · Electron microscopy · Micromechanical behaviour · Crazing · Toughness

Introduction

Polymers are used in a wide range of applications because of their intrinsic properties. During the last few years the properties of thin and ultrathin polymeric films have been intensively studied by a number of authors [1, 2, 3, 4, 5, 6, 7, 8, 9, 10]. It was found that brittle polymers such as PS, PMMA and SAN became ductile when their thickness was reduced below a critical value. A concept of critical thickness was discussed [1, 4, 6, 8] and a strong influence of layer thickness on the toughness of the polymeric material was revealed.

Van der Sanden et al. [1, 4] studied the deformation behaviour of PS/PE multilayers with different layer thicknesses. They observed the onset of a strong increase in strain at break when the PS layer thickness was below 1 μm. This brittle-to-ductile transition was attributed to a stress transfer mechanism operating through interlayer adhesion and allowing for a multiple fracture of each single PS layer. With the help of optical light microscopy, the second brittle-to-ductile transition was found when the thickness of PS layers was approximately 0.05 μm. This was explained by a change in the deformation mechanism from crazing to shear deformation. As a result, high strains (up to 200%) were reached. It was also determined that a decrease in layer thickness leads to an increase in the adhesion between the multilayers.

The same effect was noticed by Baer and co-workers [8, 9, 10, 11, 12, 13, 14, 15, 16] investigating microlayer systems of PC/PMMA and PC/SAN. These two systems also revealed a sharp increase in the ductility and peel strength (i.e. adhesion) with decrease in layer thicknesses. Lin and Yang [6] found super-plastic behaviour of a thin PS film (0.1 μm thick) between two ductile polymer films of PPO when necking was suppressed. All of the authors mentioned above laid emphasis on another very important role of the adhesion between the layers: interfacial strength should be good enough to ensure the stress transfer between the components, but excessively strong adhesion can be detrimental to plasticity and lead to premature fracture of the sample [10].

Recently, a "thin layer yielding" mechanism was proposed by Michler et al. [17] after studying the influence of the layer thickness of PS in more detail by using electron microscopic techniques on styrene-butadiene block copolymers. PS layers were able to be homogeneously drawn up to 300% when their thickness was below a critical value in the range of 20 nm, which was about half the value predicted by van der Sanden. Below the critical thickness, samples deformed uniformly without any strain localisation and crazing.

An overview of the literature data referred to above leads us to the very important conclusion that the toughness of the polymeric materials can be greatly increased by controlling the microstructure. However, in the papers cited, attention was focussed on multilayered systems consisting of alternating macroscopically brittle (such as PS, PMMA, SAN) and ductile (PE, PPO, PC) polymers. Our research was therefore concentrated on the study of the micromechanical behaviour of multilayered tapes made of two brittle polymers. To this end, two incompatible amorphous polymers PS and PMMA were chosen as a model system.

Experimental

The PS was NOVA Breda N5000 with a molecular weight of 200,000 g/mol; the PMMA was Ato-Haas Vo52 (Chicago, IL) with a molecular weight of 110,000 g/mol. Microlayers of PS and PMMA were coextruded using a Multiflux static mixer [18] with a varying number of layers: 64, 512, 4096 layers. The PS/PMMA multilayer tapes had a 50/50 composition.

Semi-thin sections (~1 μm) were cut from the centre of the layered specimen using glass knives at room temperature parallel to the direction of extrusion and perpendicular to the layers. The sections were strained in a special tensile-desk (stress [σ] was applied parallel to the direction of extrusion). After staining in RuO_4 vapour the sections were investigated with the help of an optical light microscope (Leica Makroskop 420; Heerbrugg, Switzerland) and a High Voltage Electron Microscope (HVEM JEOL 1000; Japan) operated at 1000 kV.

The mechanical properties of the multilayer PS/PMMA tapes were also examined. Stress-strain curves were recorded by means of a Minimat microtensile tester (Polymer Laboratories, Ltd., Loughborough, UK) for uniaxial tensile testing. Five specimens from each material (0.5 mm thick; 5 mm wide and 20 mm long) were stretched at room temperature and at a speed of 2 mm/min.

Results and discussion

Figure 1 demonstrates an optical light microscope image of the PS/PMMA multilayered tape with 64 layers. The thickness of the PS layers ranges between 2.3 and 16 μm; and that of the PMMA layers between 1.5 and 14 μm. It can be clearly seen that adhesion between the PS and PMMA layers is rather weak, and that the layers can easily debond during straining. The crack ({*1*} in Fig. 1) propagates along a single interface. Small crazes ({*2*} in Fig. 1) inside the PS layers are observed in this picture.

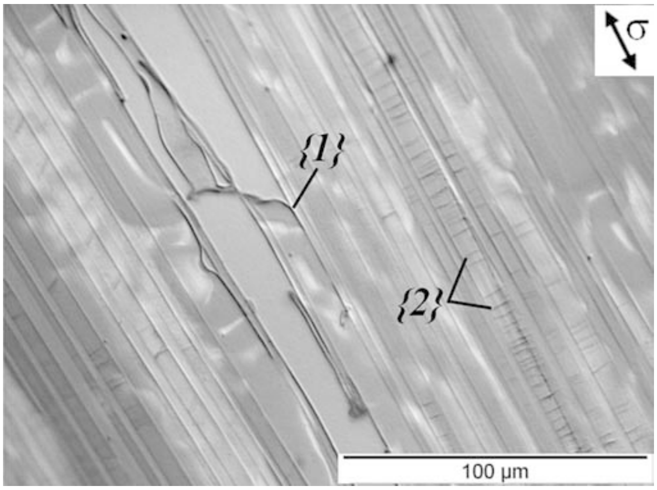

Fig. 1 Optical light micrograph of deformed multilayered sample with 64 layers. The *arrow* indicates tensile direction (i.e. parallel to the direction of extrusion and to the layers)

An HVEM micrograph of the same sample is shown in Fig. 2a. Here the craze structure can be seen in more detail. Due to the selective staining by RuO_4 the PS layers appear dark grey in the electron micrographs while the PMMA layers appear light. The presence of enhanced free space inside the crazes results in their preferential staining by RuO_4. Hence, the crazes look like black lines in the micrographs.

As can be inferred from Fig. 2a, the macroscopic deformation of the specimen comes from the numerous crazes initiated in the PS layers perpendicular to the applied stress. Crazes are a well known feature of thermoplastic polymers. The craze formation process plays an essential role in the fracture of polymers particularly in the case of brittle materials. Crazes are reputed to be a precursor to fracture. It is also stated that crazing acts as a stress relief mechanism hindering macroscopic fracture of the material.

It is seen that almost all the PS crazes tore into neighbouring PMMA layers and then stopped. As known from the literature [19], pure PS and PMMA possess similar values of Young's modulus (about 3000 MPa) but the yield stress of PMMA is higher than that of PS. Therefore, it is assumed that the stress applied to the specimen was not high enough to initiate yielding of the whole PMMA layer. Crazes in the PMMA phase could be only formed at places of higher stress concentration, that means, in front of the PS crazes propagating into the PMMA layers.

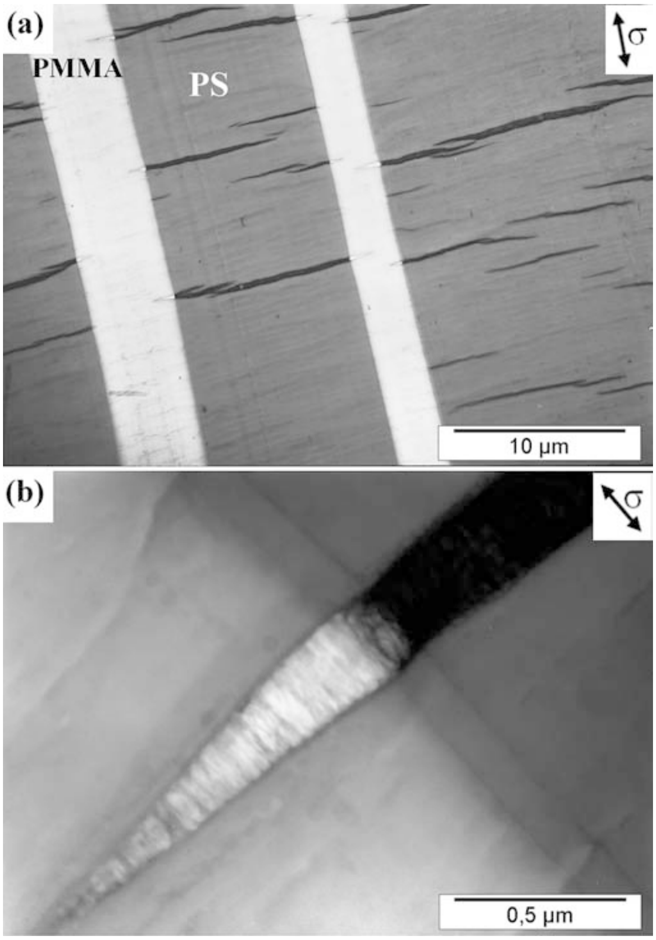

Fig. 2 HVEM micrographs of the deformed sample with 64 layers: (**a**) low magnification; (**b**) high magnification (the *arrow* indicates applied stress direction). Due to the selective staining by RuO_4 the PS layers appear *dark grey* in the electron micrographs while the PMMA layers appear *light*

As pointed out earlier, interlayer adhesion was rather weak in the sample, nevertheless, it seems to have been sufficient to allow stress transfer across the PS/PMMA interface.

Figure 2b shows one of the crazes at a higher magnification. The craze structure consists of numerous fibrils with diameters of about 10 nm running across the whole craze from one craze interface to the other. These main fibrils are interconnected by somewhat thinner, so-called cross-tie fibrils. This kind of internal structure turns crazes into load-bearing areas which cracks are unable to do. Fibrillated crazes are typical of PS. PMMA, in turn, usually demonstrates homogeneous crazes [19], but fibrillated crazes can also be found. The thickness of the craze fibrils were measured: 5–18 nm for PS crazes and 8–20 nm for PMMA crazes—these values are typical of PS and PMMA.

The deformation structure of the PS/PMMA multilayered tape with 512 layers is presented in Fig. 3 (optical light micrograph). It can be clearly seen that the thicknesses of the PS and PMMA layers in this tape are smaller than in the previous one (PS layers are 1–10 μm thick; PMMA layers are 0.5–12 μm thick). Crazes and cracks are able to propagate through several neighbouring PS and PMMA layers. Decreasing the thickness of individual layers leads to an increasing number of crazes. As distinct from the previous sample, crazes in the specimen with 512 layers look quite different. Close examination of an electron micrograph (Fig. 4a) clearly reveals craze arrays in several PS and PMMA layers. A similar effect was observed elsewhere [12] in PC/SAN multilayered samples. Crazing was found to extend across several SAN and PC layers. It is noteworthy that there is also a stopping tendency in the PMMA phase: in thick PMMA layers the PS crazes stop with a wedge-shaped tip; in thin PMMA layers (about a few micrometers) crazes can propagate through the layer although with decreasing thickness. It can be also observed that thick PMMA layers are able to retard crack propagation. The tip of the crack in the thick PMMA layer is rounded (crack tip blunting). This indicates strong energy dissipation in the PMMA layer.

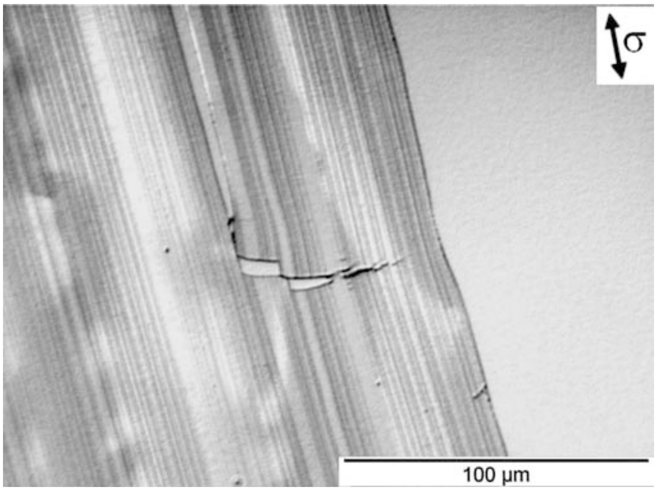

Fig. 3 Optical light micrograph of deformed multilayered sample with 512 layers (the *arrow* indicates applied stress direction)

The formation of craze arrays in the sample with a higher number of microlayers proves interlayer adhesion to be good enough for stress transfer between the layers. However, the adhesion is not very strong, leading to debonding and delamination of the layers at higher local deformation.

In Fig. 4b, the deformation structure of the sample is displayed in more detail. Crazes possessing a fine fibrillated structure both in the PS and PMMA phases closely resemble those of the previous sample with 64 layers (see Fig. 2b). It should be noted that numerous very small fibrillated crazes also appeared in the PMMA layer. This fact suggests that the applied external stress was rather

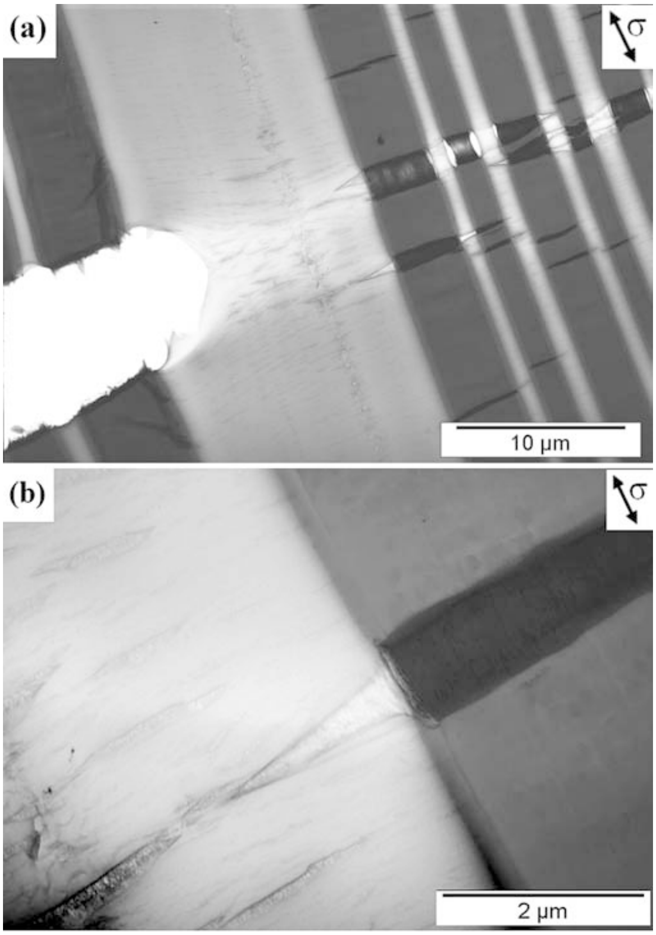

Fig. 4 HVEM micrographs (in lower (**a**) and higher (**b**) magnifications) of the deformed sample with 512 layers. The *arrow* indicates tensile direction

large to provide local yielding of PMMA and generation of multiple crazing. Increased accumulative fraction of the crazed sample (i.e. the total fraction of the sample involved in crazing) supposes enhanced energy absorption under strain conditions.

The sample with the greatest number of microlayers (4096 layers) demonstrates quite distinct deformation structures, as readily observed in the optical light micrographs (Fig. 5). It is obvious that a lot of very long crazes (>200 μm long) appear during straining. The thickness of the individual PS and PMMA layers is much smaller than in both the samples described previously, therefore, the layered structure can be imaged well using only electron microscopy (Fig. 6a). The thickness of the PS layers ranges from 0.06 to 0.7 μm; and the PMMA layers are 0.05 to 1 μm thick. Higher magnification (Fig. 6b) of a relatively thick craze (~2 μm thick) allows observation of a fibrillar structure in the PS phase and a homogeneous structure in the PMMA. The cross-tie fibrils connecting the main fibrils in the PS crazes can

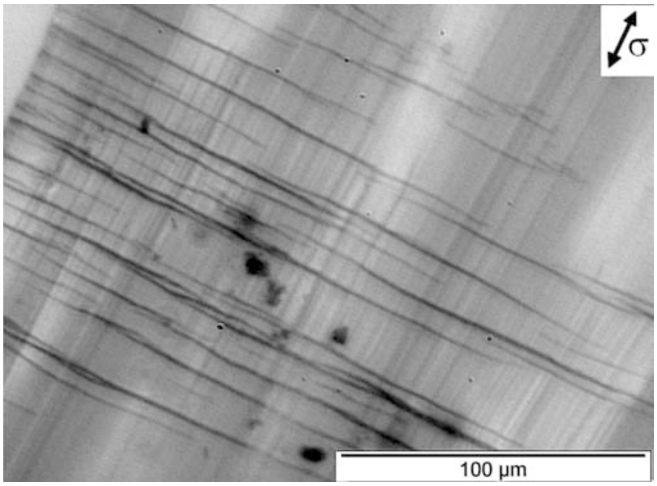

Fig. 5 Optical light micrograph of deformed multilayered sample with 4096 layers

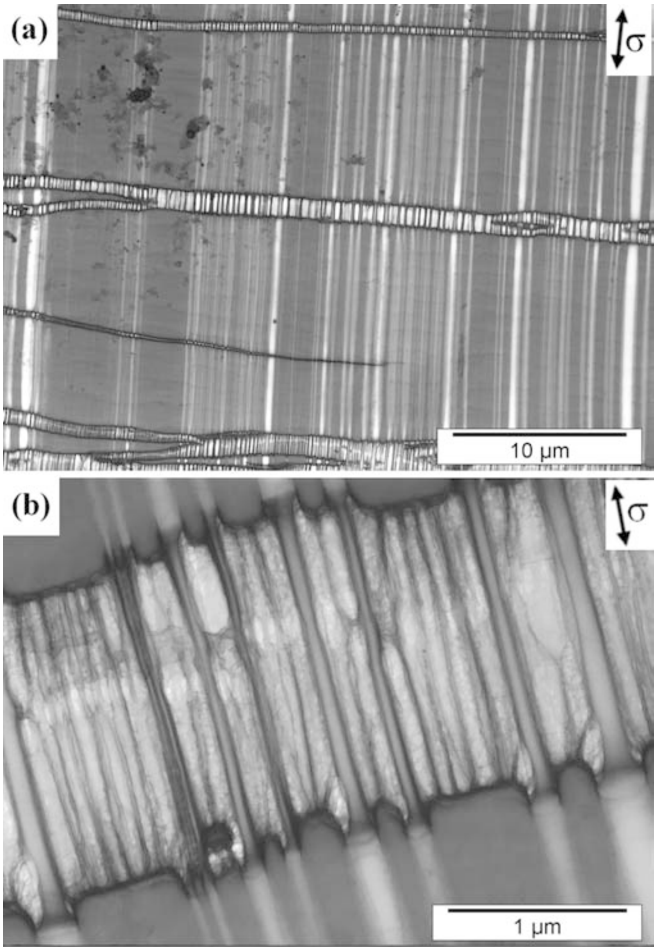

Fig. 6 HVEM micrographs in different magnifications of the deformed sample with 4096 layers. The applied stress is indicated by the *arrow*

Table 1 Main characteristics of the craze structure

		PS/PMMA 64 layers	PS/PMMA 512 layers	PS/PMMA 4096 layers
Thickness of layers, µm	*PS*	2.3–16	1–10	0.06–0.7
	PMMA	2.5–14	0.5–12	0.05–1
Maximum thickness of crazes, µm	*PS*	0.5	1.8	2
	PMMA	0.4	1.2	2
Fibril thickness in crazes, nm	*PS*	5–18		
	PMMA	8–20		
Maximum craze length, µm		17	20	> 200
Craze number density, mm^{-1}		310	880 (PS), 3500 (PMMA)	280

be clearly seen. The cross-tie fibrils are known to increase the load bearing capacity of the crazes. Such strengthening of the crazes results in the prevention of a premature fracture.

Delamination of the multilayers was not found, correlating with earlier findings [8, 9, 10, 11, 12, 13, 14, 15, 16] of increased interfacial strength as the individual layers became thinner. Moreover, cooperative microdeformation of both the PS and PMMA layers is only possible due to sufficient adhesion between the components enabling stress transfer. As it was found earlier [12, 13, 14, 15, 16], multilayered samples consisting of brittle (SAN) and ductile (PC) polymers demonstrated an evident change in the deformation mechanism of SAN layers from crazing to cooperative shearing when the layers were thinner. In contrast, in the case of a combination of two brittle polymers (PS and PMMA) no transformation in the deformation mechanism was registered, i.e. crazing remained the basic mechanism of deformation in both PS and PMMA layers.

On the basis of a great number of micrographs obtained by HVEM, the main characteristics of the craze structure were measured and summarised in a comparative Table 1. An increase in the number of layers (leading to decrease in layer thicknesses) results in the formation of thicker and longer crazes. In the varyingly thick crazes, the internal fibrillar structure (thickness and spacing of fibrils) was found to be unchanged. Though the craze number density drops in the sample with the highest number of layers (4096 layers), the total fraction of the crazed material should increase because crazes become thicker and longer than in the other samples. The question then arises as to why crazes become thicker and longer as the layer thicknesses decreases. The reasons for these effects are as follows: 1) none of the crazes stop in thin PMMA layers. Therefore, propagation of crazes from PS layer to the next PS layer, passing the neighbouring PMMA layers, takes place; 2) long crazes can grow to a larger thickness.

It is well known that one of the possibilities of increasing macroscopic toughness is the initiation of multiple deformation mechanisms in a large part of the material. One of these energy-absorbing deformation mechanisms is multiple crazing. The intense crazing obviously seen in the multilayered samples is responsible for increased ductility and toughness of the material. It is consistent with the previous studies of microlayers which showed that decreasing the layer thickness to nano scale drastically enhances the toughness of these nanolayers.

In order to check these findings, stress-strain curves of all the samples investigated were obtained by means of a Minimat microtensile tester. The curves are plotted in Fig. 7. It can be deduced that an increase in the number of layers and, therefore, a decrease in the thickness of layer is accompanied by an increase in strength and strain at break (and, therefore, of toughness) of the samples. However, the super plastic deformation of ~200% found elsewhere [1] was not achieved. There is good reason to believe that premature rupture of the samples is a result of the distribution of the layer thicknesses inside each sample and, particularly, the presence of rather thick layers which cannot be drawn up to high deformation degrees.

It can be seen from the slope of the stress-strain curves in the elastic region that Young's modulus increases with the number of layers. This fact may be explained by improved adhesion between layers with reduction of the layer thickness.

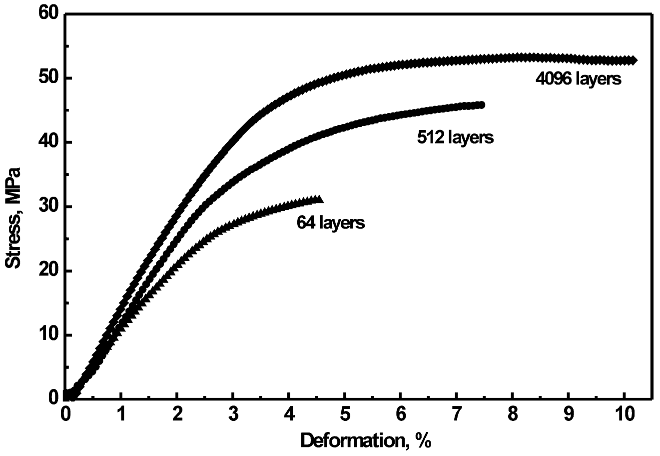

Fig. 7 Stress-strain curves of the multilayered samples studied. Tensile tests were carried out at room temperature and at a speed of 2 mm/min

Table 2 Tensile strength and strain at break of the investigated PS/PMMA multilayers. Values of strength and strain at break for bulk polymers (PS (lit.) and PMMA (lit.)) are given for comparison

	σ_{br}, MPa	ϵ_{br}, %
64 layers	31	4
512 layers	45	7.5
4096 layers	54	10
PS (lit.)	40–50	3
PMMA (lit.)	75–80	2–5

The measured tensile strength (σ_{br}) as well as strain at break (ϵ_{br}) are presented in Table 2. Values of σ_{br} and ϵ_{br} of pure bulk PS and PMMA obtained from the literature [17] are given for comparison. It can be clearly seen that the total deformation at break of the samples with the highest number of layers (4096 layers) is about three times higher than that of the bulk polymers. This finding is in contrast to previous observations [13, 16] of microlayered composites of one brittle and one ductile polymers manifesting mechanical properties intermediate between those of the two components. In our case of two brittle polymers, only the tensile strength does not surpass the literature values. Reduced strength in comparison with values from the literature is accounted for by the lower adhesion between thicker layers, resulting in separation under load and initiation of premature fracture.

As was emphasised above, enhanced toughness and ductility of the multilayered tapes can be achieved when one or both components are capable of the energy absorption under high deformation. The results described above have clearly revealed that the sample consisting of the thinnest layers demonstrated rather high strain before fracture due to massive cooperative crazing and yielding of both PS and PMMA phases.

Conclusions

The following conclusions can be drawn from the present results:

1. Use of the high voltage electron microscope gives us an unique opportunity to investigate the morphology and micromechanical processes of microlayered specimens in more detail.
2. With decreasing layer thickness of brittle microlayers (PS and PMMA), the volume of the material involved in the plastic deformation increases and cooperative yielding of both PS and PMMA layers takes place, though the basic mechanism of deformation (i.e. crazing) remains unchanged.
3. Decrease in layer thickness is accompanied by a noticeable increase in the toughness (increase in strength and strain at break) of the samples. Increased toughness of the multilayered tapes can be accounted for by an interlayer stress transfer mechanism as well as a cooperative crazing mechanism.

Acknowledgements E.M.Ivan'kova is grateful to the Graduiertenkolleg "Polymerwissenschaften" for providing the research scholarship. The comments from Prof. H.E.H. Meijer are greatly acknowledged.

References

1. Van der Sanden MCM, Meijer HEH, Lemstra P (1993) Polymer 34(10):2148
2. Van der Sanden MCM, Meijer HEH, Tervoort TA (1993) Polymer 34(14):2961
3. Van der Sanden MCM, Meijer HEH (1994) Polymer 35(13):2774
4. Van der Sanden MCM, Buijs LGC, de Bie FO, Meijer HEH (1994) Polymer 35(13):2783
5. Dooley J Viscoelastic Flow Effects in Multilayer Polymer Coextrusion. PhD Thesis, Eindhoven University of Technology, Eindhoven, The Netherlands
6. Lin CH, Yang ACM (2000) J Mater Sci 35:4231
7. Kleideiter G, Prucker O, Bock H, Frank CW, Lechner MD, Knoll W (1999) Macromol Symp 145:95
8. Ebeling T, Hiltner A, Baer E (1998) J Appl Polym Sci 68:793
9. Ebeling T, Hiltner A, Baer E (1999) Polymer 40:1525
10. Kerns J, Hsieh A, Hiltner A, Baer E (1999) Macromol Symp 147:15
11. Kerns J, Hsieh A, Hiltner A, Baer E (2000) J Appl Polym Sci 77:1545
12. Ma M, Vijayan K, Hiltner A, Baer E (1990) J Mater Sci 25:2039
13. Ma M, Im J, Hiltner A, Baer E (1990) J Appl Polym Sci 40:669
14. Shin E, Hiltner A, Baer E (1993) J Appl Polym Sci 47:245
15. Shin E, Hiltner A, Baer E (1993) J Appl Polym Sci 47:269
16. Im J, Baer E, Hiltner A (1991) Microlayer Composites. In: Bare E., Moet A (eds) High Performance Polymers: Year Book, Hanser, New York, p.175.
17. Michler GH, Adhikari R, Lebek W, Goerlitz S, Weidisch R, Knoll K (2002) J Appl Polym Sci 85:683
18. Van der Hoeven JC, Wimberger-Friedl R, Meijer HEH (2001) Polymer Eng. Sci 41(1):32
19. Michler GH (1992) Kunststoff-Mikromechanik: Morphologie, Deformations- und Bruchmechanismen. Hanser, Munich