DOI: 10.1002/masy.200650104

Nanostructured Composites with Layered Morphology: Structure and Properties

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Summary: Using different microscopic techniques, we investigate the morphology and the micro-deformation processes in two entirely different classes of polymer based composites: natural biocomposites and synthetic polymer composites. The emphasis has been put on the comparison of the micromechanical properties of those composite materials. In the natural layered composites exemplified by human cortical bone, analogous to the synthetic glassy polymers, craze-like deformation zones were formed. A strong dependence of deformation mechanisms (such as transition from formation of single crazes to multiple crazing behaviour) on the layer dimension was observed in the layered composites made up of different amorphous polymers.

Keywords: electron microscopy; lamellae; multilayers; nanostructured polymers; polymer blends

Introduction

The optimisation of mechanical properties is one of the main goals of contemporary physical polymer science. For most of the applications of heterogeneous polymers, one is interested to increase their toughness without sacrificing strength and stiffness [1]. Generally, this is achieved by incorporating a small amount of rubber into the glassy polymer matrix. In these modifications, which involve the initiation of various local energy absorbing processes in the material, an increase in toughness is usually achieved by compromise of transparency of polymeric materials. On the other hand, it has been known for long time that there exist polymeric composite materials in the nature which possess properties suited for specific loading conditions. In fact, no artificial materials possess so optimum property profile as the natural ones [2–4]. Therefore, an alternative approach of developing tailored polymeric materials is to learn from the nature and reconstruct the polymer architectures on different length scales.

Nowadays, the micro- and nanostructured biomaterials such as bones, fibres produced by different insects, mollusc shells etc. have been attracting research interests of materials scientists due to the promise that advanced functional materials can be designed based on the unique architecture of these natural composites. In nature, these materials are produced by self-assembly phenomena on the micro- and nanoscopic level.

An excellent example of natural polymers possessing promising mechanical properties is offered by several tropical plants such as coconut and date palms. These plants have feather-type leaves (so called blades), in which the petiole or leaf stem reveals specially woven composites structure. The perfectly cross-woven network of cellulose fibres endows the leafs with strength and flexibility. As a result, the leaves remain intact even under extreme environmental conditions thereby ensuring

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different physiological process taking place in unhindered manner. Fig. 1a shows a photograph of naturally woven fibres of cellulose in a coconut leaf stem. Each fibre is composed of a bundle of oriented fibrils.

It is noteworthy that similar laminate-like structures, but on much smaller length scales (thickness in the range of several nanometers), are produced by α-modification of isotactic polypropylene (iPP) where the lamellae (or layered nanostructures) are arranged in a so called cross-hatched architecture [5,6], see Fig. 1b. Owing to this microscopic morphology, iPP possesses a much higher stiffness, strength and excellent toughness compared to atactic polypropylene.

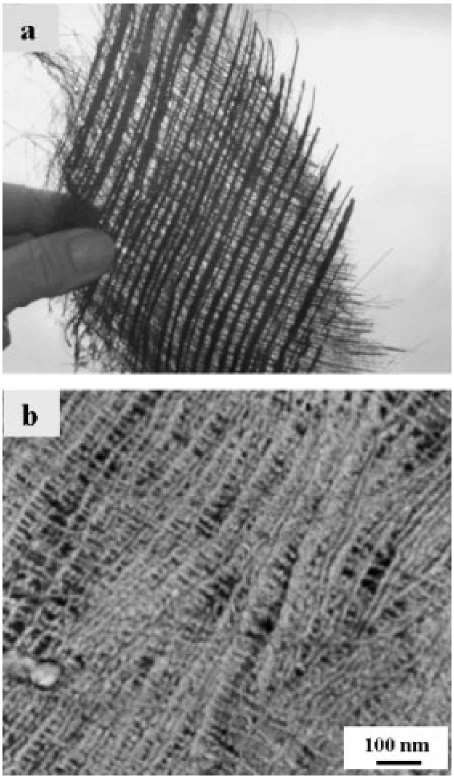

Figure 1.
Comparison of natural and man-made fibrous web: a) Photograph of cellulose fibre web after the natural degradation of the tissue between the venation network; and b) Atomic force micrograph (phase image) of iPP film showing the characteristic cross-hatched structure.

To search for a new generation of advanced materials, the conventional solutions available to mankind have nearly been exhausted. So the material scientists have turned to biomimetic (or biology-inspired) structures with the goal of developing new synthetic products. For instance, inspired by the composite structures produced by nature, polymer scientists are trying to reconstruct artificially the biomimetic morphologies [7–9]. Recently, totally recyclable monocomposites based on polypropylene (PP) homopolymer have been developed which possess the properties far better than the classical PP formulations [10,11]. These composites are evolving as replacements of automobile parts in new generation cars meeting the environmental criteria suggested by the European Union (EU).

The materials in nature have been found to possess the internal structures adapted for some specific purposes. Following the art of nature to produce composites of various architectures, polymer scientists are attempting to develop composite materials having optimum mechanical performances. Layered polymer nanocomposites are good examples of such materials. In this work, we will review some of the successes of this strategy with special emphasis on correlation between structure and mechanical properties of the composites.

Materials and Methods

Three different sets of materials were studied in this work.

Bionanocomposites

This category includes nacre and human cortical bone. For our investigation we used nacre of the Blue Mussel (*Mytilus edulis*) from the Baltic Sea (Darß, Germany). Fracture surfaces were sputter-coated with an approx. 12 nm thick gold layer (EDWARDS SPUTTER COATER) and studied by means of a scanning electron microscopy (SEM, JEOL-JSM 6300). Samples of human cortical bone (Femur) were supplied by Dr J. Brandt, Department of Orthopaedics, Martin Luther University Halle-Wittenberg. Semithin sections (approx. 300 nm thick) were prepared using an RMC ultramicrotome equipped with a diamond knife. For morphological characterisation, the sections were spread onto regular copper grids and investigated using a JEOL JEM 4010 FX high voltage electron microscope. For the deformation studies, the semithin sections were attached to rectangular copper meshes (ATHENE) that were previously coated with collodium. A MINIMAT miniaturised materials tester was used to deform samples under light optical observation. For the visualisation of the morphology of the deformed material, a PHILIPS ESEM-30 FEG environmental SEM was used.

Multilayered Composites

Multilayered polymer composites prepared by special coextrusion technique were used. The composites based on polystyrene (PS) and polymethyl-methacrylate (PMMA) was supplied by Prof. H. E. H. Meijer (Eindhoven University of Technology, Eindhoven) and those based on polyethylene terephthalate (PET) and polycarbonate (PC) was provided by Prof. E. Baer (Case Western Reserve University, Cleveland, Ohio). For the study of deformation structures of the samples, ca. 500 nm thick sections of each sample was ultramicrotomed which were later strained using a special stretching device and investigated by means of high voltage transmission electron microscope (JEOL 1000 kV, HVEM).

Block Copolymer/Polystyrene Blends

Blends of a polystyrene-polybutadiene block copolymer (BCP) and general purpose polystyrene (GPPS) was supplied by Dr. K. Knoll (BASF Aktiengesellschaft, Ludwigshafen). The blends with appropriate compositions were produced by extrusion moulding. The specimens for deformation studies were prepared in the same way as the multilayered composites. Prior to the electron microscopic examination by means of HVEM, the sections were treated with osmium tetroxide (OsO_4) vapour to selectively stain the double bond containing polybutadiene phase.

Results and Discussion

Morphology and Properties of Bionanocomposites

Through the course of evolution of living beings on earth, the nature has synthesised countless number of composite materials which are characterised by incredible structural perfection and wonderful matches of properties suited for specific physiological functions of individual organism. For instance, there are layered composites everywhere in nature - both in animal and plant kingdoms. The wall of living cell, the rings of a tree, eye lens of mammals are a few a few examples. In this paper, we will introduce two composite materials bio-synthesised by nature: nacre and human bone.

Although nacre from the shell of abalone snail (commonly known as 'see ear') is the most popular example cited in the literature, the material itself seems to follow the same general construction plan also in other nacre products, as there are mussel shells and pearls.

The shells of mussels as well as those of the abalone snails are protective shields of these animals. The shell begins to grow already in the larval stage of the animal. The shell-less creature would not survive if left free in natural environment. Thus, for these soft invertebrates the shell is a protection against unwanted physical force.

To keep it protected from the physical injuries and from the attack of the predators, the body is covered by a specially designed apparatus having excellent mechanical properties. The outstanding mechanical stability of the shell results from the specially designed architecture, i.e., a composite arrangement consisting of thousands of alternating hard/soft layers. Fig. 2b depicts the SEM micrograph of nacre from the shell of the Blue Mussel.

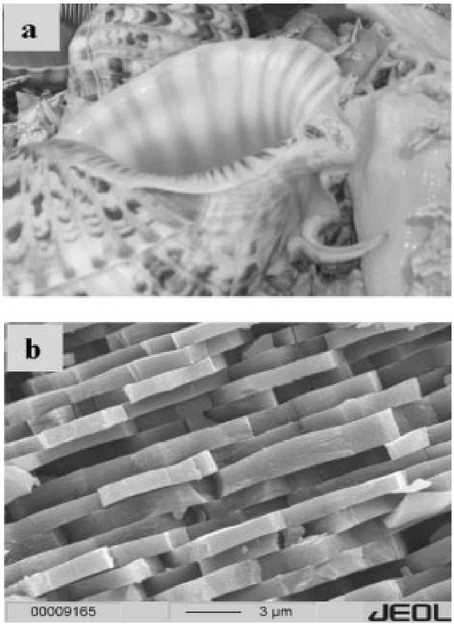

Figure 2.
a) Optical micrograph of a mussel shell and b) SEM micrographs showing the internal structural details of nacre from *Mytilus edulis* (Blue Mussel).

The stiff layers approximately 1.5 microns in thickness are made up mainly of calcium carbonate. One can notice that the layers are organised in such a perfect manner that over a macroscopic dimension of the sample no defects can be identified.

The abalone and mussel shells demonstrate that the living organisms are capable of synthesising high-strength and high-toughness mineralised tissues via biomolecular control of mineral crystals type combined with an organic adhesive layer. In the shell, the flat platelets of calcium carbonates ($CaCO_3$: the orthorhombic aragonite polymorph) are stacked like bricks glued together by a thin film of proteins and polysaccharides [2,12,13]. The biocomposite consists of 95% inorganic mineral and 5% organic polymer, the two being held together by means of electrostatic force of attraction. The organic glue is strong enough to hold layers of tiles firmly together, but weak enough to permit the layers to slip apart absorbing the energy of a heavy blow in the process. In fact the abalone shell is much stronger than the conventional man-made ceramic materials. The biomineralisation processes can turn the brittle materials such as calcium carbonates into a high durability organic/inorganic laminates [2]. The layering of alternating hard/soft elements makes it a really tough composite material.

Whereas these layers in mussels and abalone shells form plate-like, only slightly curved objects, pearls are formed by concentric layering. The construction principle on the microscopic level is, however, very much the same. There is another effect that can be explained by the very regular periodic arrangement of approx. 1 μm thick layers: the beautiful optical appearance that is making pearls so attractive. Amazingly, a very similar optical effect is found for layered polymer systems where the two components have a comparable layer thickness of approx. 1 μm.

With respect to the promising mechanical properties, the bones of vertebrates offer another excellent example of bionanocomposite. Human cortical bone, for instance, comprises hard-soft composite arrangement on the nanoscopic scale giving bone material the excellent balance of stiffness and toughness that is needed to maintain structural integrity of the skeleton. Bone tissue can be regarded as a perfect composite material developed through the course of evolution.

Nanoscopic platelets of hydroxy apatite mineral are embedded in a fibrous matrix of organic polymer, the collagen (see Fig. 3b). In other words, bone tissue itself could be described as a material made of composite nanofibres of different orientation. Bundles of such fibres of the same orientation are alternated with bundles of different orientation, forming lamellar structures very similar to plywood (see Fig. 3a). The typical thickness of the lamellae is some microns. Again, a layered system is at hand if one considers the microscopic level of the bone architecture: Within cylindrical building blocks (osteons) concentric rings of lamellae can be distinguished around central canals that are responsible for the transport

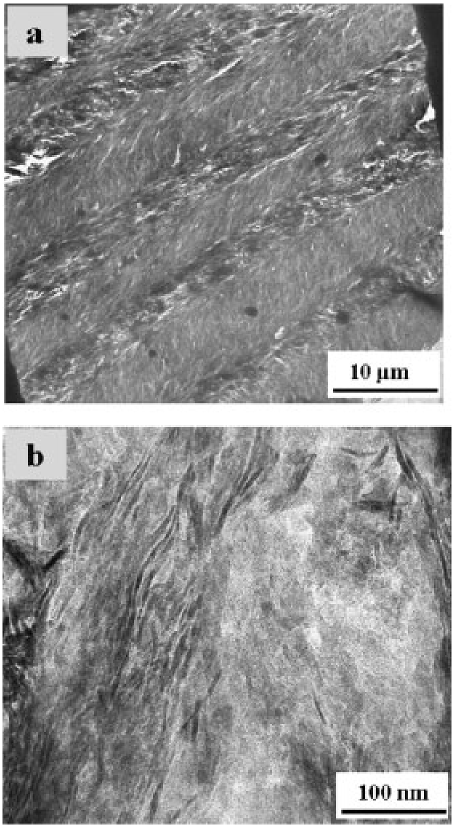

Figure 3.
TEM micrographs showing the morphology of human cortical bone; a) overview showing the lamellar arrangement of alternating layers (so called 'twisted plywood' structure) and b) details with platelets of hydroxy apatite mineral (dark areas) separated by collagen (white areas) fibrils (details to follow in [14]).

of nutrients. It is this hierarchical organisation of nano- and micro-sized structures that gives bone its unique mechanical properties. As in the case of mussel and abalone shells, the organic polymer matrix enables a slippage of platelets of calciferous tissues guarantying the mechanical stability and flexibility of the composite material.

Fig. 4 shows ESEM micrographs of thin sections of cortical bone subjected to tensile deformation. It is of particular interest to understand the processes that occur during mechanical loading, deformation and fracture. Detailed micromechanical analysis of bone reveals that the mineralised collagen fibrils might act as bridging elements between the edges of a crack [14]. A closer look at the tip of a micro-crack (Fig. 4a) that is formed in cortical bone under tensile load reveals the existence of fibrils bridging this micro-crack (Fig. 4b). The crack itself is growing perpendicular to the direction of the applied stress. In other words, the micromechanical mechanism here can be denoted as a localised, craze-like deformation process comparable to the crazing phenomenon observed in a number of amorphous and semicrystalline polymers and composites [1] (see next sections). In the case of mineralised tissue, dissipation of mechanical energy can take place during localised plastic deformation involving deflection, stretching and separation of mineralised collagen nanofibres. Additionally, the fibrils stabilise the crack helping to keep mechanical integrity.

Coextruded Multilayered Composites

The study of physical properties of nanostructured materials is a very active research field of contemporary materials science and it has stimulated in the recent years a great deal of interaction among physicists, chemists, biologists and engineers. The design of nanostructured functional materials with specific physical properties is one of the important objective of modern materials science and engineering. Being stimulated by the fact that the living beings in nature have synthesised some very sturdy materials with surprising mechanical properties through millions of years of evolution and natural selection, the materials scientists have turned their attention to develop new synthetic materials that mimic the fundamental structure and properties of natural biocomposites. The development of layered composites of metal laminates [15] and of polymers [9] are the attempts towards designing biomimetic functional composites.

Coextruison is one way in which two or more polymers can be physically combined for the purpose of achieving the polymer composites possessing improved mechanical, electrical and barrier properties [9]. Via this technique, polymer composites

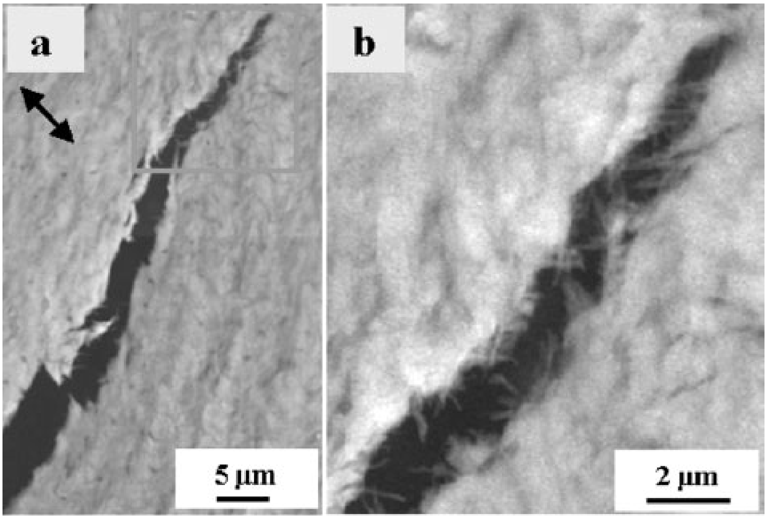

Figure 4.
ESEM micrographs showing the strain-induced structural changes in thin sections of a cortical bone; the tip of micro-crack in (a) is magnified in (b).

containing thousands of alternating laminates of different polymers can be produced in which the thickness of individual layers goes down to several nanometers [9,16–18].

Nanolayer processing via multilayer coextrusion facilitates the creation of new hierarchical systems. Although this route is far away from the unique behaviour of the living cells, in which the complex biosynthesis and nanoprocessing take place concurrently, this is highly flexible tool for the fabrication of unique architectures of otherwise incompatible polymers [19] such as PS and PMMA. The electron micrographs of multilayered PMMA/PS (Fig. 5a) and PET/PC (Fig. 5b) composites presented show the nearly uniform and continuous layers of the constituent homopolymers which may extend up to the extruded tape length.

Both the polyesters PC and PET are compatible to each other. Therefore the adhesion between the polymers is good enough to ensure the integrity of the layers. In contrast, even for the strongly incompatible polymers such as PS and PMMA, the alternating layers keep mechanical integrity surprisingly well in the multilayered

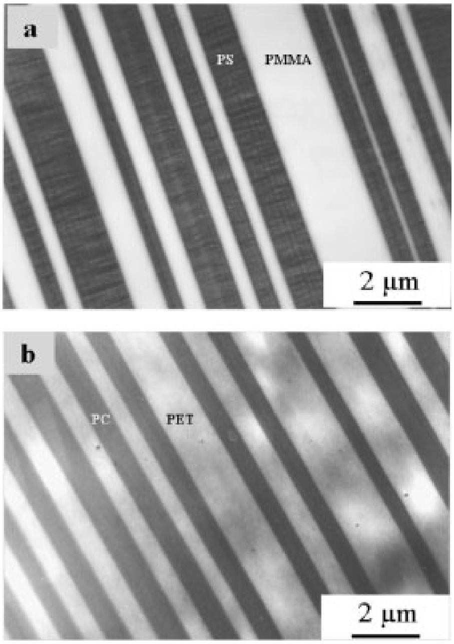

Figure 5.
TEM micrographs showing the layered morphology of multilayered composites (256 layers): a) PS/PMMA composite; PS appears dark due to staining by Ruthenium Tetroxide (RuO_4); and b) PET/PC composite; RuO_4 staining makes PC appear dark.

composites. Particularly, the adhesion between the layers was found to improve with the decreasing thickness of individual polymers thereby enhancing the mechanical performance of the composites [20].

It has been shown that the layered composites comprising up to 8 thousand continuous layers (with layer thicknesses in the range of a few nanometers) can be successfully prepared by coextrusion technique. Further, more than two polymers can be used and there is no limitation in the relative composition of the polymers [18]. The interface between the layers of two highly incompatible polymers can even strengthened by incorporating a tie layer as compatibilizer in the composites [9,18].

The architecture comprising the alternating layers different polymers provides synergistic combination of mechanical properties [18]. In the following, we demonstrate the positive effect of microlayering on the toughness of heterogeneous polymer taking PS/PMMA composites as an example. Both PS and PMMA are well known for their brittle behaviour. Under tensile loading conditions, localised deformation zones in the form of single, isolated craze are observed in the neat polymers [21]. These crazes are usually long and thin; and grow quickly to macroscopic cracks. This may lead to the catastrophic fracture before the deformation zones could be spread throughout the specimen, thus the brittle behaviour.

Fig. 6 shows the deformation structures observed in PS/PMMA composite tapes consisting of 64 (Fig. 6a) and 4096 layers (Fig. 6b). The decrease in layer thickness with increase in total number of layers in a tape is obvious in the micrographs. In the 64 layered sample (Fig. 6a), the crazes run in the PS layers with their tips terminated in the adjacent PMMA layers. Owing to lower yield stress of polystyrene (ca. 55 MPa) compared to that of PMMA (ca. 75 MPa) the crazes are initiated in the former which extend to the neighbouring PMMA layers at the location of stress concentration (i.e., craze tip). The feasibility of the stress transfer marked by the movement of craze tip from PS layers to the PMMA ones and the absence of delamination are the signs of sufficient adhesion between the layers.

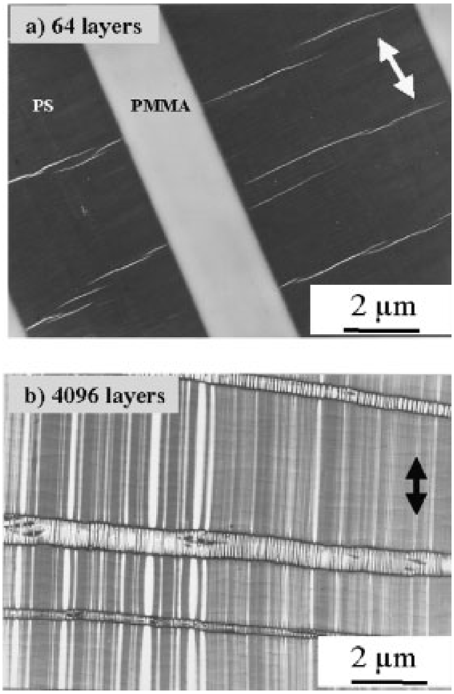

Figure 6.
TEM micrographs showing deformation structures in multilayered PS/PMMA composites: a) 64 layers sample; and b) 4096 layers sample; deformation direction is shown by an arrow; PS phase appears dark due to staining by RuO_4.

Looking closely at the internal details of the crazes, it can be found that the layers still keep the properties of individual neat polymers – formation of fibrillated crazes by PS layer and the homogeneous crazes by PMMA layers irrespective of thickness of the individual layers. Fig. 6b examine the situation when the thickness of the layers is in the range of 100 nanometers (microlayers). Now, the crazes are no more localised in a single layer but spread unhindered though many layers. As a result, the crazes reach the lengths of several hundred microns. For 4096 layered sample, not only the length of the crazes but also the number of crazes per unit volume was increased leading to larger volume of yielded material. In summary, on combining the otherwise brittle polymers into a single composite comprising thousands of individual layers, the micromechanism changes from single crazing to multiple-crazing, a more energy absorbing process. As a result, the microlayered sample reveal much higher toughness than the bulk materials [18,20].

Block Copolymer/Homopolymer Blends

In block copolymers, the local segregation of the different homopolymer chains yields molecular-scale aggregates. Recent progress in synthetic chemistry has unveiled unprecedented opportunities to prepare tailored block copolymers at reasonable cost [22,23]. Since the development of living anionic polymerisation in mid-fifties, the block copolymers have been at the focus of continuous research. Today, development of these polymers has reached such a dimension that tons of nanostructures can be produced from a single reactor.

Polymer blends based on polystyrene-polybutadiene-polystyrene (SBS) block copolymer and polystyrene (PS) homopolymer have been the object of our recent studies [24]. It was demonstrated that, by modifying molecular and processing variables, the morphology and mechanical properties of such blends can be significantly controlled. Under the influence of strong shear-force (such as during injection moulding or extrusion processing), the mixing behaviour of the blends can be drastically changed leading to the morphologies which are far from equilibrium but are more interesting for practical application.

Fig. 7 shows TEM micrographs of deformation structures in a mixture comprising a lamellar SBS block copolymer and 80 wt.-% general purpose polystyrene (GPPS). By processing the mixer via extrusion moulding, the layered composites having analogous architecture as the multilayered composites can be produced. However, it should be noted that the continuity as well as the uniformity of the layers cannot be controlled as precisely as in the microlayered tapes.

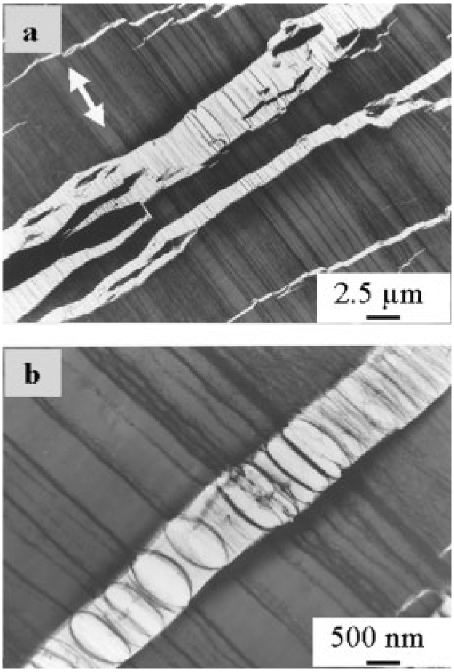

Figure 7.
TEM micrographs of different magnifications showing the craze-like deformation zones in SBS block copolymer/GPPS blend (20/80); deformation direction is shown by an arrow; polybutadiene-rich phase appears dark due to staining by Oso$_4$.

White stripes running perpendicular to the layer orientation direction (which is also the extrusion direction and later the deformation direction) are the crazes which appear brighter (Fig. 7a) than the surrounding due to the micro-voids and the reduced local thickness caused by deformation.

Along the extrusion direction one can see the dark lines formed by block copolymer lamellae which are coupled to the adjacent PS layers (lighter layers) by means of physical cross-links called entanglements. On stretching the semithin section (ca. 500 nm thickness), a large number of crazes are formed (multiple crazing) similar to multilayered composites. The glassy polystyrene layers form dense fibrils of drawn materials parallel to the deformation direction. Each PS layer shows a sort of 'necking' in the crazes where a bundle of fine fibrils appear (see Fig. 7b). The thickness of each fibril lies in the range of about 10–20 nm as in the bulk polystyrene homopolymer [21].

The thin SBS material (20...100 nm) sandwiched between the glassy layers, which are bound intact to the glassy layers, can deform to much higher extent and possibly initiate formation of larger voids. As a result, lens-like deformation zones are formed along the craze (see Fig. 7b). No need to say, the crazes, which absorb energy during deformation, endow the brittle PS with high toughness while keeping the transparency of the products.

Reducing the thickness of polystyrene layers to the size of the craze fibrils (10–20 nm) observed in the microlayers induces a dramatic effect on the mechanical properties of polymers. By doing so we approach practically the distance between the knots in entanglement network of the glassy polymer. This situation appears on coupling the glassy PS chains with polybutadiene (PB) chains to form a lamellar block copolymer. Under these circumstances, the glassy polymer lamellae can plastically flow up to the limit of theoretical value (stretching ratio of about 4) without the hindrance of liquid-like adjacent PB layers [25,26]. The deformation mechanism has been described as ‘thin layer yielding’ and discussed in detail elsewhere [25].

Fig. 8 shows for example the TEM micrograph of such an SBS block copolymer. A small amount of high impact polystyrene (HIPS) was purposefully added to use the particles as markers for the local deformation of the sample. The deformation test was conducted as in the case of SBS/GPPS blend. One can see that the sample deforms almost homogeneously without forming locally confined deformation zones. The HIPS particle appear as elongated lenses which are otherwise spherical particles with characteristic ‘salami’ morphology. The local deformation of the block copolymer amounts up to several hundred percent, which can be easily estimated by the elongation of HIPS which also induces void formation and appear white (see Fig. 8a).

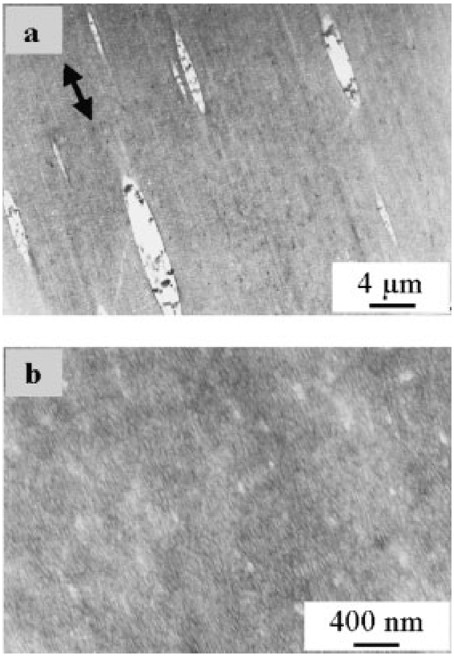

Figure 8.
TEM micrographs of different magnifications showing deformation of a lamellar SBS block copolymer where the PS lamellae, approximately 20 nm thick, are chemically bound to liquid-like PB lamellae, deformation direction is shown by an arrow; PB phase appears dark due to staining by OsO_4.

Concluding Remarks

In an attempt to understand the properties of natural biocomposites and to look for synthetic analogues possessing tailored mechanical properties, an overview of some of the existing methods to prepare biomimetic polymer combinations has been given. The micromechanical properties of these combinations, which are responsible for mechanical performance of the resulting product, are discussed in particular. It has been demonstrated that the reconstruction of the composites following the routes of nature may help to design advanced polymeric materials having optimum property profile, although it is a long way towards to development of perfect polymer composites. It has been shown that the multilayered composites possess very interesting properties and even the entirely different classes of layered composites (such as bone and synthetic multilayer) may deform via similar micromechanisms if the dimension of heterogeneity is comparable.

Acknowledgements: The research was supported by German Science Foundation (DFG Projects SFB 418 and 'Transferinitiative: Optimierung von Steifigkeit/Festigkeit/Zähigkeit von Polymer-werkstoffen'). We are grateful to Dr. J. Brandt (Halle), Prof. H. E. H. Meijer (Eindhoven), Prof. E. Baer (Cleveland) and Dr. K. Knoll (BASF, Ludwigshafen) for providing materials. Our sincere thanks also go to Dr. E. Ivankova, Ms. F. Wulf, Mr. W. Lebek and Dr. R. Godehardt for their assistance during some of the electron microscopic studies.

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