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Influence of nanofillers on the deformation process in layered silicate/polyamide-12 nanocomposites

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Abstract

Polymer nanocomposites based on a synthetic layered silicate and polyamide-12 (PA-12) are prepared by injection molding to study their morphology, and the influence of nanofiller particles on local deformation processes. One of the most striking results from morphological studies by transmission electron microscopy is that although the layered silicates, locally stacked in the PA-12 matrix, are arranged on planes parallel to the injection molding direction, the fine lamellae are oriented with their planes perpendicular to the injection molding direction owing to nucleation at the interface between layered silicate and polymer matrix. The dispersion of layered silicates and the orientation of lamellae are reflected in the complexity of the deformation mechanisms, which in turn determine the ultimate macroscopic properties. From studies of in situ deformation under the high voltage electron microscope, it is concluded that the main deformation mechanism is microvoid formation inside the stacks of layered silicates. According to the orientation of these stacks the applied energy is dissipated by splitting, opening or sliding of separate bundles in the stacks during deformation. The nanofiller particles are load-bearing because surfaces in the microvoids are connected and hinder further growth of the microvoids, thus preventing catastrophic failure. As a consequence, the stiffness/strength/toughness balance has been synergistically improved. Finally, based on the present experimental results, a molecular network in polymer nanocomposites is proposed, that leads to the desired superfunctional characteristics. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Layered silicate; Polyamide-12; Deformation process

1. Introduction

One of the most important features of polymeric materials is the possibility of controlling their macroscopic physical properties by tailored manipulation of their structures at a nanoscopic scale. Because inorganic and organic materials can be combined on a nanometer length scale, inorganic–organic hybrid materials can exhibit an improved stiffness/strength/toughness balance, improved thermal stability as well as self-extinguishing fire-retardant characteristics and selective molecular transport properties, which are unique and different from any other current composites with typical filler amounts of less than 5 wt% [1–5]. Since the reinforcement efficiency of inorganic fillers is strongly related to their aspect ratio (length/thickness), frequently used inorganic filler particles are platelet clay mineral particles consisting of layered silicates, e.g. montmorillonite. Layered silicates are able to undergo cation-exchange reactions [6–8]. The surface of layered silicates, in general, is hydrophilic and this limits their dispersion in organic phases, e.g. in polymer matrices [9–11]. In order to make organophilic layered silicates it is possible to exchange inorganic cations with organic cations, preferably R–NH_3^+ groups where R is usually a long aliphatic residue [1,12,13]. The long organic chains with positively charged ends will be tethered to the surface of negatively charged silicate layers, thus resulting in an increase of the gallery height [1–3,14–17].

Nanocomposites are prepared by mixing the ion-exchanged layered silicate with the monomer (followed by

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polymerization) or by melt mixing the layered silicate with polymer [18–22]. The monomer or polymer can enter the gallery resulting in a further separation of the silicate layers. Depending on the organization of the silicate layers in a polymer matrix, two types of morphology can be achieved in nanocomposites; intercalated or exfoliated. Intercalates are obtained when the polymer is located between the silicate layers but regularly spaced stacks of layered silicates are maintained. Exfoliates are obtained when the silicate layers are homogeneously dispersed throughout the whole polymer matrix.

In general, the presence of modifier particles (rubber/inorganic filler particles) influences directly the crystallization behavior of the polymer matrix [23]. After the introduction of modifier particles, the change of the morphology of polymer matrix is reflected in a variety of deformation mechanisms, which cause in turn remarkable differences in mechanical properties [24,25].

Although intensive research efforts have been devoted to the development of novel synthetic approaches in polymer nanocomposites as well as to the investigation of the physical properties of these materials in recent years, the mechanisms responsible for the improvement of mechanical properties have not been identified. In order to achieve a fundamental understanding of nanolayer reinforcement, there is a great need to define the exact role of nanofiller particles in the matrix and the effect of interfacial interactions between the silicate nanolayers and the polymer matrix during the deformation processes. The aim of the present work is to prepare PA-12 nanocomposites containing intercalated synthetic layered silicates to examine their morphology, and to understand the role of nanofiller particles during the deformation processes.

2. Experimental

2.1. Nanocomposite

As the inorganic component of the nanocomposites a synthetic layered silicate was used, which is formed by heating Na_2SiF_6 with talc. The synthetic layered silicate (SLS) SOMASIF™ ME100 was obtained from CO-OP Ltd, Japan. The negative charge of the layers is compensated by Na^+ ions in the interlayer space. The cation-exchange capacity (CEC) is in a range from 0.7 to 0.8 meq/g. The interlayer spacing of the pristine SLS calculated from the WAXS d_{001}-reflection is 0.95 nm [26]. ω-Aminododecanoic acid (ADA) (used for silicate swelling and polycondensation to form PA-12) was provided by EMS-CHEMIE AG, Switzerland. The SLS was dispersed in water and swollen with an excess of ADA with respect to the CEC for SLS (overall concentration: 40 mmol/l), 24 mmol/l HCl and 8.3 g/l SLS. The dispersions were filtered and dried at 80°C. The nanocomposites were prepared by polycondensation of ADA at 280°C in an autoclave in the presence of the swollen silicates. After 1 h the pressure was raised to 20 bar. In the subsequent 1.5 h the pressure was continuously reduced to ambient pressure. The mixture was stirred for another 7 h and degassed. The polymer was pelletized, dried, and injection molded.

Morphological studies were performed using a Jeol 200 kV transmission electron microscope (TEM). Ultrathin sections with a thickness of about 50 nm were microtomed at −80°C using a Leica Ultracut E cryo-ultramicrotome. The staining was carried out using OsO_4 in a water/formaldehyde mixture for 3 days [27].

To study mechanical deformation processes, samples were uniaxially deformed and investigated in situ by high voltage electron microscopy (HVEM, 1000 kV). All deformation tests under the microscope were performed at room temperature. The specimens for HVEM investigations were microtomed at −80°C, yielding samples with a thickness of approximately 0.5 μm.

3. Results and discussion

Fig. 1, which is obtained from an OsO_4-stained ultra-thin section, shows the typical morphology of a PA-12 nanocomposite with 2 wt% layered silicate. It is clearly visible that the silicate layers are homogeneously dispersed in the PA-12 matrix. In some areas of the polymer matrix the regularly intercalated silicate layers are locally stacked up to hundreds of nanometers in thickness and from several hundred nm to a few μm in length. Single stacks of silicate layers have an average thickness of about 150 nm. The orientation of silicate layers can also be recognized easily in the TEM micrograph, in which the injection molding direction is parallel to the long axis of the layered silicates.

Fig. 1. Typical morphology of synthetic layered silicate polymer nanocomposite stained with OsO_4 (arrow indicates the injection molding direction).

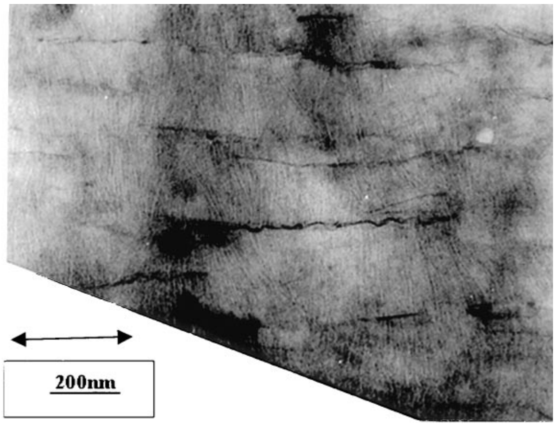

Fig. 2. Arrangement of layered silicates in the injection molding direction, and perpendicular oriented fine lamellae of PA-12 at the interfaces of layered silicates (arrow indicates the injection molding direction).

This forced orientation is a result of the high shear rates during injection molding.

Furthermore, another phenomenon can directly be observed by TEM. Where the layered silicates are arranged in the injection molding direction, the fine lamellae of the PA-12 crystals are oriented perpendicularly to the polymer/silicate interface, i.e. on planes lying normal to the injection molding direction (Fig. 2). The addition of layered silicates to the PA-12 matrix drastically affects the morphology of the matrix polymer. It is also interesting that the lamellae radiating perpendicular to the interface appear laterally well-organized parallel to each other. This interfacial ordering must be a result of the crystallization process and is similar to the well-known transcrystallization [28]. At the crystallization temperature of the matrix, the surfaces of layered silicates act as heterogeneous nucleation sites. Once nucleation of the oriented lamellae occurs at the surfaces of the silicate layers, the growing face of the lamellae, i.e. the hydrogen-bonded planes, becomes parallel to the interface. As a result, lamellae are orientated with chains lying tangential to the particle surface. The nucleation and oriented growth of lamellae occur predominantly in the matrix region between stacks. Similarly to our observations, it has been reported for PA-6 clay hybrids, that the γ-(020) hydrogen-bonded planes are oriented parallel to the interface with the montmorillonite inclusions [29–31]. The ends of the polymer chains are bonded by ionic interaction to the surface of the negatively charged montmorillonite [2,32]. The ionic interaction of polymer chains at the surface affects the crystallinity and produces lateral organization of the lamellae [32–34]. As a consequence, the end-tethered polymer chains at the silicate surfaces stabilize the overall structure.

Fig. 3. Void formation between the folded silicate layers during the microtoming of the bulk nanocomposite.

In general, the deformation behavior of semicrystalline polymers is strongly dependent on the crystalline orientation [35–38]. The morphological characteristics of polymer nanocomposites directly cause remarkable differences in deformation processes, which in turn determine ultimate macroscopic properties. More recent research by Lin and Argon has shown that the hydrogen-bonded planes of polyamides have the lowest slip resistance [37]. As a consequence, under external load the local deformation will be easily initiated on these planes, and the yield stress should be lowered in the regions of easy shear. This local softening of the material allows for deformation to large strains without initiating any critical fracture process, thus enhancing toughness.

It should be emphasized that although some molecules of the matrix polymer are intercalated into the galleries, crystalline lamellae could not be detected inside the galleries. This confirms that the matrix polymer molecules intercalated into the galleries should exhibit different characteristics, in terms of conformation, molecular weight, etc., from those of the neat matrix polymer [39], also they are non-crystallizable. Therefore, in such confinement between adjacent intercalated silicate layers the crystallization of polymer chains should be hindered especially when it is taken into consideration that the interlayer spacing is similar in dimensions to, or even smaller than, the lamellar thickness. Furthermore, the interaction between the silicate layers is relatively weak compared with that between polymer chains and the silicate layers in contact with the matrix. This is clearly revealed in Fig. 3.

During the microtoming of the bulk nanocomposite the stacked silicate layers split easily, as a result of the voids formed inside the stacks. Since the flexural rigidity of layered silicates is less than that of more isotropic spherical particles, they are subjected to large bending moments. As a consequence, the stacked silicate layers reveal highly folded structures. The regions with large curvatures will provide the weak points at which plastic deformation can occur under external load. For the development of morphology, the significant roles of silicate layers in the polymer

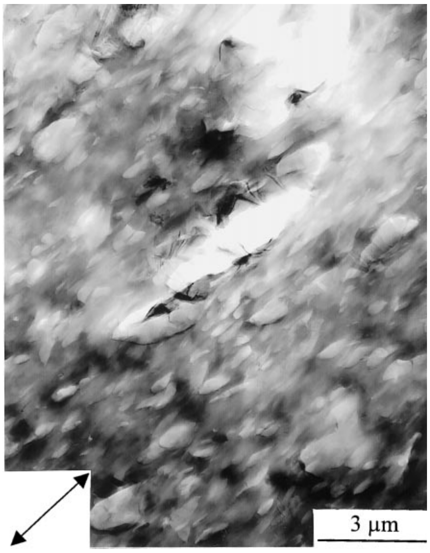

Fig. 4. TEM micrograph of a deformation structure at low magnification taken during in situ tensile tests of the synthetic layered silicate polymer nanocomposite.

nanocomposites can be summarized as follows: (i) the surfaces of the silicate layers act as nucleation sites for crystallization, which will be initiated preferably in the microenvironment of silicate layers [40], and (ii) the silicate layers tether organic substances onto their surfaces.

3.1. Mechanical deformation processes

Fig. 4 shows an HVEM micrograph of the deformation structure at low magnification taken during in situ tensile tests of the layered silicate PA-12 nanocomposite. The deformation structure reveals well-developed microvoid formation in the plastically deformed specimen. It is also clearly seen in the micrograph that larger voids have been formed around the larger inhomogeneities.

This association is reasonable, because under external load the stress fields around the large particles are strongly overlapped by interaction with those of adjacent small particles, which cause higher hydrostatic or triaxial stresses; therefore, void formation will easily take place around them. The microvoids appear randomly in the whole area of the uniaxially deformed specimen. There is no evidence of band-like deformation structures, such as shear bands observed for most rubber toughened polymer systems. Except for shear band formation, however, the structure strongly resembles the deformation structure in polyamide impact-modified with poly(butyl acrylate) particles (see Fig. 11 in Ref. [24]). Furthermore, owing to the weak interaction between silicate layers, the stacked silicate layers will be readily fractured when they are subjected to higher hydrostatic stress. However, as mentioned above, the matrix polymer is strongly tethered to the surface of a stacked silicate layer by ionic bonding. As a consequence, the nucleation of microvoids takes place easily not on the polar region of the stacked layers but directly inside them. Fig. 5 shows the characteristic deformation structures at higher magnification taken from in situ tensile tests under the electron microscope. The tensile direction is indicated by arrows attached to the pictures. During deformation, the orientation of the stacked silicate layers plays a crucial role. Fig. 5a shows a deformation structure in the case of layered silicates stacked perpendicular to the external load. Deformation starts inside the stacked silicate layers. Subsequently, microvoid formation takes place in-between the silicate layers. The small portions of stacked silicate layers appear at the fringes of microvoids, which are directly connected to the surfaces

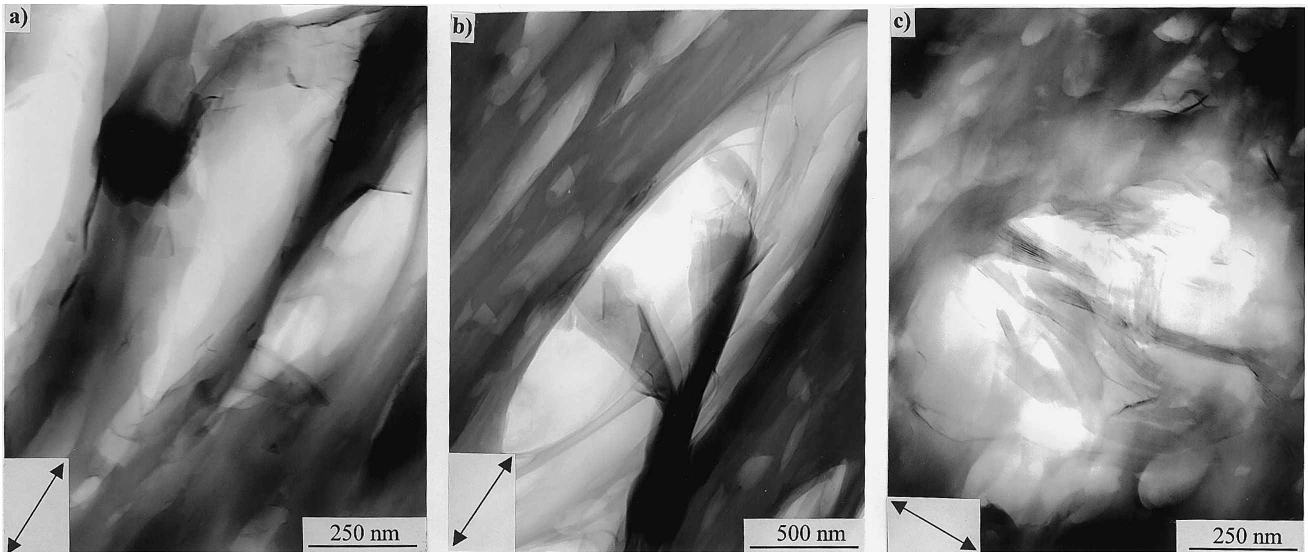

Fig. 5. Characteristic deformation structures in higher magnification taken from in situ tensile tests under the electron microscope. Tensile direction is in the arrow direction. (a) Deformation structure in case of layered silicates stacked perpendicular to the external load. (b) Case of stacked silicate layers orientated with a certain angle to the applied stress. (c) Stacked silicate layers that are orientated parallel to the applied stress.

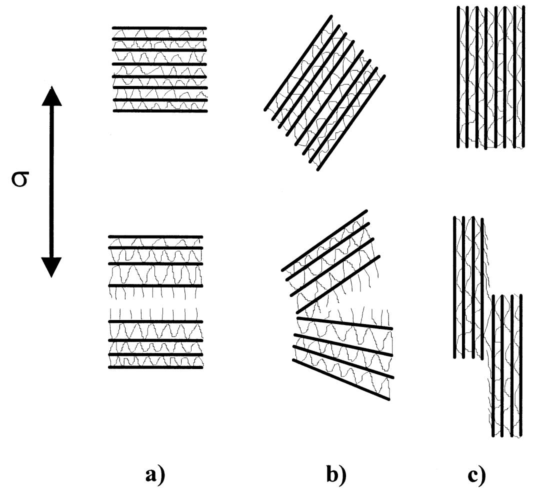

Fig. 6. Schematic models of micromechanical deformation processes of the stacked silicate layer depending on the orientation (arrow indicates the load direction): (a) splitting mode, (b) opening mode and (c) sliding mode.

of the microvoids. As the strain increases, the microvoids formed inside stacked silicate layers grow, but the propagation of the microvoids into the polymer matrix is strongly prevented. Through this particle-bridging mechanism the applied stress can be easily transferred to the polymer matrix. As a consequence, the stiffness of the nanocomposite is improved. In the case of the stacked silicate layers orientated at a certain angle to the applied stress, the stacked silicate layers are separated during plastic deformation (Fig. 5b). When the stacked silicate layers are orientated parallel to the applied stress, they will be broken up into several bundles. These bundles slide in the direction of applied stress and the microvoids form in these slip lines (Fig. 5c).

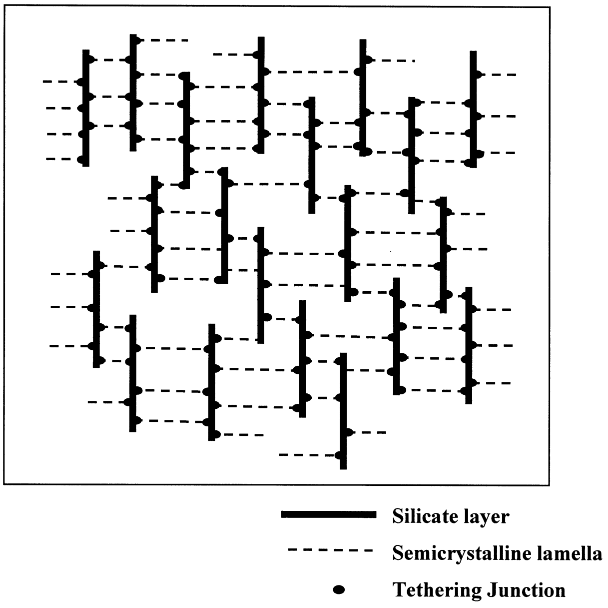

Fig. 7. Proposal for a new class of polymeric materials: nanostructured network in inorganic–organic nanocomposite.

These results of the in situ electron microscopic investigation of micromechanical deformation processes are schematically represented in more detail in Fig. 6. It has been found that the main initiation step for plastic deformation is microvoid formation inside the stacked silicate layers, since the individual silicate layers stacked in the polymer matrix are weakly bonded to each other. Since the orientation of the stacked layers plays a crucial role during deformation, three deformation modes can be observed depending on the stacked layers: (a) splitting, (b) opening, and (c) sliding of the layered structure.

Once the uniaxial load is applied at a stacked layer, which is orientated perpendicular to the applied load, deformation initiates at the middle region of the stacked layer, and splitting of the layer takes place in the middle region. Interlayer distances in the stacked layers increase with increasing distance from the middle region (Fig. 6a). In the case that the stacked layers lie at a certain angle to the direction of applied load, opening of bundles of the stacked layer occurs during deformation processes (Fig. 6b). When the stacked layers are oriented parallel to the applied load, sliding of bundles of the stacked layer takes place during deformation, by which the interlayer distances are kept constant (Fig. 6c).

3.2. Proposal for molecular network in layered silicate polymer nanocomposite: a unique combination of high strength, modulus and toughness

In general, stiffness/strength and impact strength work against each other in conventional polymer blends and polymer composites. The addition of rubber particles to a polymer matrix produces an increase in toughness but reduces the stiffness, whereas inorganic filler particles are added in an attempt to improve the stiffness but sacrifice the toughness [41,42].

It is well established in the literature that the introduction into a polymer matrix of inorganic nanofiller particles at a concentration of only a few wt% results in a remarkable combination of high stiffness and toughness. This synergy is caused by changes in the morphology of the polymer matrix due to the presence of nanofiller particles. Hence, if it is possible to control the structures at the level of different length scales, material properties can be tailored. The material should consist of a nanostructured network (Fig. 7): finely dispersed and uniformly oriented silicate layers should be aligned perpendicular to lamellae, and the two materials should be strongly bonded to each other. It can be assumed that such materials will have the desired superfunctional characteristics. In these polymer nanocomposites, the nanofiller particles have a dual function during deformation processes: (i) due to their intrinsic high modulus they act as rigid modifier particles, which are responsible for high strength and modulus, and (ii) due to the microenvironments of nanofiller particles (the well-organized structures), they could function as microvoid initiation sites, which are necessary for high toughness.

4. Conclusions

In the present work, the role of nanofiller particles during deformation processes in PA-12 nanocomposites containing intercalated synthetic layered silicates has been investigated. The studies on morphology of nanocomposites show that the introduction of synthetic layered silicates in the PA-12 matrix drastically affects the morphology of the matrix polymer in the 'nano' scale, since the thickness of the layered silicates is of about the same size as the polymer matrix molecules themselves. A very interesting result is the perpendicular orientation and organization of the PA-12 lamellae in the microenvironments of nanofiller particles. The intercalated silicate layers were locally stacked in the polymer matrix. The characteristics of the morphology of polymer nanocomposites directly cause remarkable differences in deformation processes, which in turn determine their ultimate macroscopic properties. It has been found from in situ deformation tests in the electron microscope that the main micromechanical deformation process in the PA-12 layered silicate nanocomposite is microvoid formation inside the stacked silicate layers. During the deformation processes the separated bundles in the stacked layers tilt perpendicular to the direction of applied load. Depending on the orientation of the stacked layers, some amount of applied energy is dissipated by splitting, sliding or opening of the separated bundles in the stacked layers. As a result the toughness of nanocomposites will be enhanced. The silicate layers bounded at the fringes of microvoids are load-bearing and prevent the microvoids from growing further. As a consequence, the stiffness of the nanocomposite is improved.

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