Organic/Inorganic Hybrid Polymer/Clay Nanocomposites

The exfoliation and dispersion of clay particles are improved.

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A novel class of polymer/clay nanocomposites has been invented in an attempt to develop transparent, lightweight, durable materials for a variety of aerospace applications. As their name suggests, polymer/clay nanocomposites comprise organic/inorganic hybrid polymer matrices containing platelet-shaped clay particles that have sizes of the order of a few nanometers thick and several hundred nanometers long. Partly because of their high aspect ratios and high surface areas, the clay particles, if properly dispersed in the polymer matrix at a loading level of 1 to 5 weight percent, impart unique combinations of physical and chemical properties that make these nanocomposites attractive for making films and coatings for a variety of industrial applications. Relative to the unmodified polymer, the polymer/clay nanocomposites may exhibit improvements in strength, modulus, and toughness; tear, radiation, and fire resistance; and lower thermal expansion and permeability to gases while retaining a high degree of optical transparency.

The clay particles of interest occur naturally as layered silicates. In order to fully realize the benefits of a polymer/clay nanocomposite, it is necessary that the clay particles become fully exfoliated (delaminated) and uniformly dispersed in the polymer matrix. Concomitantly, it is necessary to maintain the exfoliation, counteracting a tendency, observed in prior formulations of polymer/clay nanocomposites, for dispersions of exfoliated clay particles to collapse back into stacked layers upon thermal treatment. One reason for the difficulty in achieving and maintaining exfoliation and uniform dispersion is the incompatibility between the silicate particle surfaces (which are hydrophilic) and the polymer matrix (which is hydrophobic). The present invention addresses these issues.

The figure depicts a process for making a polymer/clay nanocomposite film according to the invention. In one of two branches of the first step, a hybrid organic/inorganic matrix resin in a sol-gel form is prepared. The organic precursor of the hybrid is a compound or oligomer that contains both a cross-linkable functional group (e.g., phenylethynyl) and an alkoxysilane group. The inorganic precursor of the hybrid is also an alkoxysilane. Both precursors are mixed with a solvent to form the sol-gel matrix resin. In the other branch of the first step, a clay solution is prepared by initially dispersing layered clay particles in the same solvent as that used to form the sol-gel matrix resin. To achieve intercalation of the solvent into the stacked layers, the mixture is subjected to high-shear mixing and ultrasound. Suitable clays to provide compatibility with the organic polymer include chemically modified organophilic cation-exchanged smectite type clays and synthetic clays having hydroxyl functional groups on the edges and/or elsewhere on the surfaces of the particles.

In the second step of the process, the clay solution is added to the hybrid sol-gel solution and the resulting mixture subjected to high-shear mixing and ultrasound. The hydroxyl groups of the organic/inorganic hybrid react with hydroxyl groups on the surfaces and the edges of the exfoliated clay particles, forming covalent and/or hydrogen bonds that enhance exfoliation in the presence of high shear.

The third step involves a film casting process. For example, to make an unoriented film, one begins by simply casting the solution onto a glass plate or other suitable clean, dry surface. The solution is allowed to dry to a tack-free film in ambient, desiccated air, then further dried and cured in flowing heated air. During this thermal treatment, the remaining silanol groups of the hybrid undergo condensation reactions, forming a molecular network that prevents the reunion of the exfoliated particles into stacked layers. In addition, the organic matrix can be consolidated with further crosslinking among the cross-linkable functional groups during thermal cure. It may be possible to prepare oriented films and fibers by using shear, drawing, and fiber spinning processes.

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