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Synthesis and characterization of organic–inorganic hybrid composites from poly(acrylic acid)-[3-(trimethoxysilyl)propyl methacrylate]-Al_2O_3

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ABSTRACT

Hybrid inorganic–organic materials are promising systems for a variety of applications due to their extraordinary properties from the combination of different building blocks. In this work, we present the synthesis and characterization of a hybrid material based on poly[acrylic acid] (PAA), 3-(trimethoxysilyl)propyl methacrylate (TMPM), and aluminum oxide (Al_2O_3). The synthesis was carried out using a two-step process: first, a polymerization via radical initiation, and subsequently, a sol–gel process. The hybrids were prepared by keeping constant the amount of acrylic acid and aluminum oxide precursor but changing the amount of TMPM. The physical and chemical properties of the hybrids were investigated using infrared spectroscopy (FT-IR), X-ray diffraction (XRD), N_2 absorption (S_{BET}), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). The results indicate that all of the materials were simultaneous interpenetrating networks (SIPNs) and that the morphologies and the properties depend on the amount of TMPM used. All materials showed good thermal stability, and the surface area of the composite decreased as more TMPM was incorporated in the network.

1. Introduction

It is well known that organic polymers usually have some superior characteristics with respect to their toughness, flexibility, and processability. On the other hand, inorganic materials have high heat resistance and good mechanical and optical properties. Because many of the well-established materials, i.e., metals, ceramics or plastics, cannot fulfill all technological desires, a new class of materials has to be developed. With regard to tailoring new materials, scientists and engineers realized early on that mixtures of materials could exhibit enhanced properties compared to their pure counterparts [1–3]. The simplest way to realize such a composite is to incorporate, for instance, inorganic particles into a polymeric matrix. If the interaction of the inorganic and organic phases is suitable, the material will combine the advantages of the inorganic material (e.g., rigidity, thermal stability) and the organic polymer (e.g., flexibility, dielectric, ductility, and processability) [4–10].

The term “hybrid” is often used if the inorganic units are formed in situ with the polymeric matrix, for example, by the sol–gel process [11,12]. This process is similar to an organic polymerization starting from molecular precursors resulting in a bulk material. Unlike many other procedures used for the synthesis of inorganic materials, this procedure uses mild experimental conditions, i.e., a low reaction temperature, leading to industrial interest in the procedure [11–16]. In particular, the silicon-based sol–gel process was one of the major driving forces for what has become the broad field of inorganic–organic hybrid materials [17–22]. The reason for the special role of silicon was its good processability and the stability of the Si—C bond during the formation of the silica network, which allowed for the production of organic-modified inorganic networks in one step [23,24].

Kickelbick has reported different synthesis methodologies to obtain hybrid materials [25]. Particularly interesting for our work are those for interpenetrating networks (IPNs). For example, IPNs are formed if the sol–gel material is formed in the presence of an organic polymer or vice versa. In this way, IPNs could be Class I hybrids (materials characterized by weak interactions between the two phases, such as van der Waals or hydrogen bonds) or Class II hybrids (where there is evidence of strong chemical interactions, such as covalent bonds, between the components) [11].

Depending on the strength or level of interaction, two types of organic–inorganic hybrid materials can be obtained. Hence, to enhance the compatibility between the components, the organic and the inorganic components have to be modified. This modification consists of adding to either the organic or the inorganic component functional groups similar in nature to the other constituent. Such modifiers are also known as coupling agents [20,26,27]. Of the in

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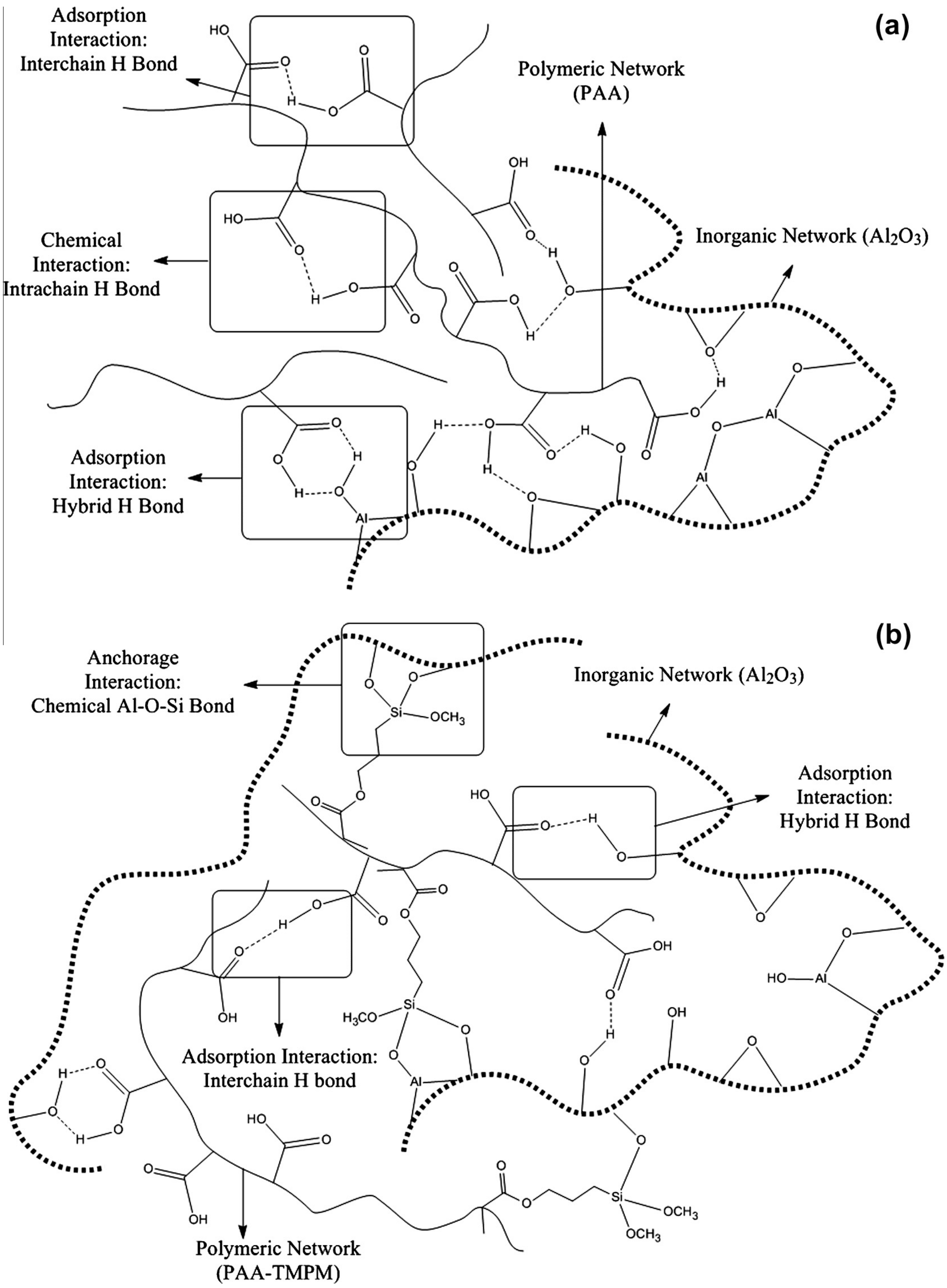
silica-based hybrid materials, silane coupling agents are the most used type of modifier agents. They generally have hydrolyzable and organofunctional ends. The general structure of the coupling agents can be represented as $RSiX_3$, where the X represents the hydrolyzable groups, which are typically chloro, ethoxy or methoxy groups. The organo, R, group can have a variety of functionalities chosen to meet the requirements of the polymer. These functionalities are involved in the formation of the inorganic network.

A different approach to the production of IPNs is denoted as the SIPNs (Simultaneous Interpenetrating Polymer Networks) process. In this case, the material is produced by performing the sol–gel process in combination with free radical polymerization of the polymeric phase [28,29]. This approach allows for the in situ formation and thus the homogeneous incorporation of polymers that normally would not be miscible. The use of coupling agents made it possible to observe the same beneficial effect in thermoset, i.e., epoxy resin, cellulose matrices [18,30,31], and others matrices.



Scheme 1. Schematic diagrams of simultaneous interpenetrating networks (SIPN) in the composites PAA/TMPM(x)/Al_2O_3 synthetized. (a) SIPN Class I, with $x = 0$ and (b) SIPN Class II with x: 0.05–0.5.