

Fire-shielding Properties of Flexible, Transparent Laponite–PEG Hybrid Film

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Flexible and transparent hybrid film consisting of Laponite and poly(ethylene glycol) has flame-resistant and fire-shielding properties regardless of the absence of halogen, nitrogen, and phosphorus atoms. The film adhered to plastics with polar surface and inhibited the deformation of plastics upon exposing to fire.

Specialty materials that exhibit excellent mechanical strength, gas-barrier properties, ionic conductivity, and so on^{1–7} are sometimes obtained by mixing clays and polymers as “nanocomposite (NC).” NCs are achieved by, for example, clay–polymer multilayer formation^{8–12} through secondary interacting forces between clay surfaces and polymer strands. The properties of NCs usually depend on the feed ratio and the disperse uniformity of the components. In particular, it is expected that the physical properties of NCs are drastically improved by an increase in the amount of clay with anisotropic shape (fibril, disc, etc.) because of the formation of ordered structure. However, an increase in the clay component often causes structural inhomogeneities (e.g., entirely turbid dispersion) that have negative effects on the optical and mechanical properties. Therefore, the general NCs contain only a few wt/wt% of clay, and the addition of ordered structure is achieved by limited cumbersome techniques such as stepwise multilayer formation.^{8–12} More recently, some NCs were obtained by the direct mixing and subsequent doctor-blade processing of montmorillonite (MMT)/polymer mixtures.¹³ This method gave NC materials carrying a high content and unidirectional alignment of MMT platelets. Unfortunately, such NCs often lack flexibility and transparency.

Hybridization between a clay and a polymer by applying organic modification to the clay nanounits is another method to prepare new materials.¹⁴ Laponite, a relatively uniform disc-shaped synthetic clay of 25 nm in diameter and 1 nm thick,¹⁵ is widely used as a component of NC.^{6,7,16} Since the surfaces of Laponite platelets have negative charges and the sidewall carries positive charges at neutral pH, the platelets can disperse randomly in water. Because of the electrostatic attraction between the platelet surfaces and sidewalls, an aqueous solution of Laponite of a few wt/v% undergoes spontaneous and unavoidable gelation.

Recently, we reported the preparation of flexible and transparent hybrid films with a large content of Laponite RD (hereafter referred to as Laponite).¹⁷ The organic modification of the silanol functionalities on the Laponite sidewalls, to which protonation is the origin of positive charges, is one methodology to prevent such gelation. The authors reported the modification of Laponite sidewalls by poly(ethylene glycol) (PEG) strands through Si–O–Si linkages in the previous paper,¹⁷ according to the earlier investigation that reported the sol–gel reaction

between the sidewall Si–OH and triethoxysilyl-terminated PEG.¹⁸ Upon casting from the aqueous dispersion of the resulting PEG-modified Laponite gave the hybrid films with about 60% inorganic component. As the PEG strands were known to interact strongly with the Laponite surfaces,¹⁹ the resulting hybrid films were macroscopically almost transparent, flexible, and solvent-resistant, i.e., once dried, no dissolving nor swelling in water. The disco-nematic liquid crystalline structure of Laponite platelets in a cast film was observed from X-ray scattering analyses.¹⁷

In the present letter, we report the heat- and fire-shielding properties of hybrid film based on the high composition of inorganic component. Since the hybrid adheres to polar plastics [e.g., poly(ethylene terephthalate)] during the casting process, the versatility to the ant flame coatings was estimated. Such heat- and fire-shielding film is of broad interest because of demand in various industrial fields such as building and home furniture.^{20,21}

We recently discussed¹⁷ the methodology to follow the organic modification of clays²² that might give interesting inorganic–organic hybrids, where silane-modified PEG with reactive triethoxysilyl groups (sPEG, see experimental procedures and Scheme S1²⁴) was prepared as a useful polymer reagent that could be anchored to Laponite sidewalls through a sol–gel reaction as shown in Figure 1. The resulting hybrid, i.e., PEG-modified Laponite, had the inorganic component of 57 wt/wt% as reported in the previous paper.¹⁷ The sol–gel reaction between sPEG and Laponite gave the Si–O–Si self-crosslinks among the terminal –Si(OEt)₃ groups of sPEG besides the desired anchoring reaction between the terminal –Si(OEt)₃ groups and Si–OH groups of Laponite sidewalls.¹⁷ The hybrid films obtained by casting the 3 or 5 wt/wt% aqueous opaque dispersions according to the experimental procedure of Figure 1 exhibited high flexibility and high transparency of 90% transmittance at 400–800 nm. At the same time, once dried in air, they also became insoluble and less swelling in water due to dense packing of Laponite platelets and PEG strands in the manner of disco-nematic arrangement.²³ Lower than 1 wt/wt%

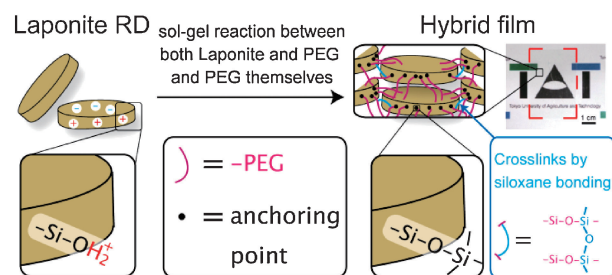


Figure 1. Schematic image of experimental procedure of hybrid film preparation.

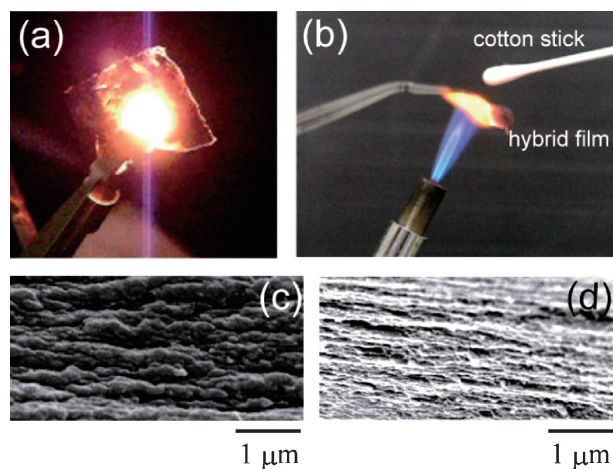


Figure 2. (a) Photograph of an initially 0.11-mm thick film exposed to a city gas/oxygen burner (ca. 1500 °C) from the back side, after the PEG strands were burnt out. (b) Self-extinguished hybrid films (the PEG strands were already burnt out) used as a heat- and flame-shield to protect a cotton-tipped stick positioned at about 8 mm behind the shield. (c) Cross-sectional SEM images of the hybrid film before burning. (d) Cross-sectional SEM images of the hybrid film after burnt.

content of water in the cast films was found from the thermogravimetric analysis even after the films were equilibrated in water.¹⁷ Meanwhile, the films prepared by casting the dispersion of mere Laponite/sPEG mixtures easily collapsed in water because of gradual dissolution.

The hybrid film showed strong fire-resistance properties due to its high content of clay platelets (Figure 2). By exposing to high-temperature city gas/oxygen flames (ca. 1500 °C), the ca. 0.1-mm thick hybrid film first caught fire for a short moment (ca. 1.4 s) as the PEG strands burnt off, but immediately self-extinguished upon removal of the flame. This result indicated that the hybrid film exhibited high fire-resistance despite the absence of halogen, nitrogen, and phosphorus atoms. The hybrid film after burning the organic portion completely still kept its shape and showed excellent heat- and flame-shielding capabilities (Figure 2a). As a cotton-ball stick placed behind the film did not catch fire even upon prolonged exposure (Figure 2b) for at least 120 s, the hybrid film acted as an efficient heat- and flame-shelter similar to ceramic plates. The film prepared from the dispersion of the mere mixture of Laponite and sPEG immediately broke by exposing to fire. The self-crosslinking among the terminal $-\text{Si}(\text{EtO})_3$ groups of sPEG would induce the strength of hybrid film after exposing to fire. As shown in the cross-sectional SEM images of the hybrid film (Figures 2c and 2d), the densely packed layered structure before burning was maintained even after burning without notable expansion but with generation of vacancies where the PEG strands had been. The reason for the layered structure remaining after burning was plausible due to the crosslinking among the terminal $-\text{Si}(\text{EtO})_3$ groups of sPEG. In Figure 3, the energy-dispersive X-ray mapping images of Si atom (EDX, Figures 3a and 3c) and the SEM images of the same area (Figures 3b and 3d, respectively) are illustrated. Because the Si atoms before burning distributed quite uniformly both in the cross section and surface, the border

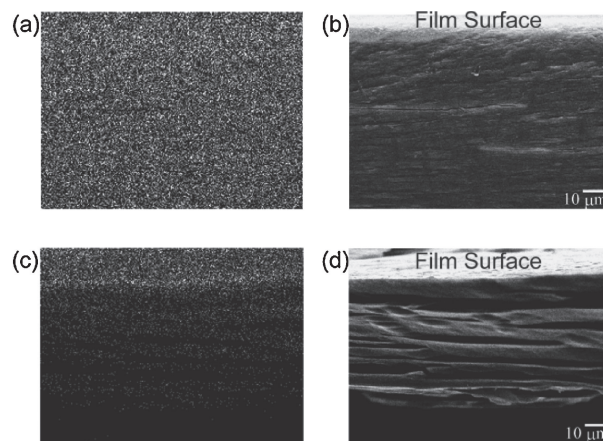


Figure 3. Cross-sectional view of the hybrid film. Energy-dispersive X-ray (EDX) maps of silicon atom (a, c) and corresponding SEM images (b, d). Before burning: (a) and (b), after burnt: (c) and (d).

that was clearly seen in the SEM image of Figure 3b was indistinguishable in the EDX image of Figure 3a. After being burnt (Figures 3c and 3d for EDX and SEM, respectively), the dense distribution of Si atoms was obviously seen in the outermost (skin) layer. The similar dense distribution of O atoms in the outermost layer and no existence of C atoms all over the area were noticed after burning (data not shown). Such SiO_x skin layer formation was likely to be promoted by the recombination of fragments that were generated by the decomposition of Si–O–Si root linkages on the Laponite sidewalls. The excellent heat- and flame-shielding properties of burnt hybrid film were brought about not only by the layered inorganic platelets with cellular vacancies but also the SiO_x skin layer.

The hybrid films prepared by casting and drying of the aqueous opaque dispersion on apolar plastics such as Teflon® and amorphous polyolefins were easily peeled off from the surface, but those cast on polar plastics such as poly(ethylene terephthalate), PET, and poly(vinyl chloride), PVC, adhered tenaciously. The tendency to pack densely, as already described, by the strong interaction among the Laponite platelets and anchored PEG strands minimized the water content in the bulk and/or interface of the hybrid films. As a result, no interference of nuisance water brought about the better contact of the hybrid components to the polar plastic surfaces. On the other hand, the films prepared from the aqueous dispersion of the Laponite/sPEG mixture only were turbid due to macroscopic inhomogeneity, and they never adhered to apolar or polar plastic surfaces. Although the water content of such mixture films varied according to the drying conditions, the reason of the weak adhesion was their high swelling properties that could be understood from easy collapsing and dissolution of the films in water. Due to the fire-shielding property of the hybrid film, the drip (instillation by heating) of PET almost disappeared by coating the films (Figure 4a). Furthermore, the deformation of PVC films during burning was prevented by the surface coating. Because the transparency of hybrid film did not diminish the light transmittance of the PET and PVC films by coating (Figure 4b), the present hybrid is a good candidate for coatings that add ant flame properties to plastic walls, ceilings, etc.

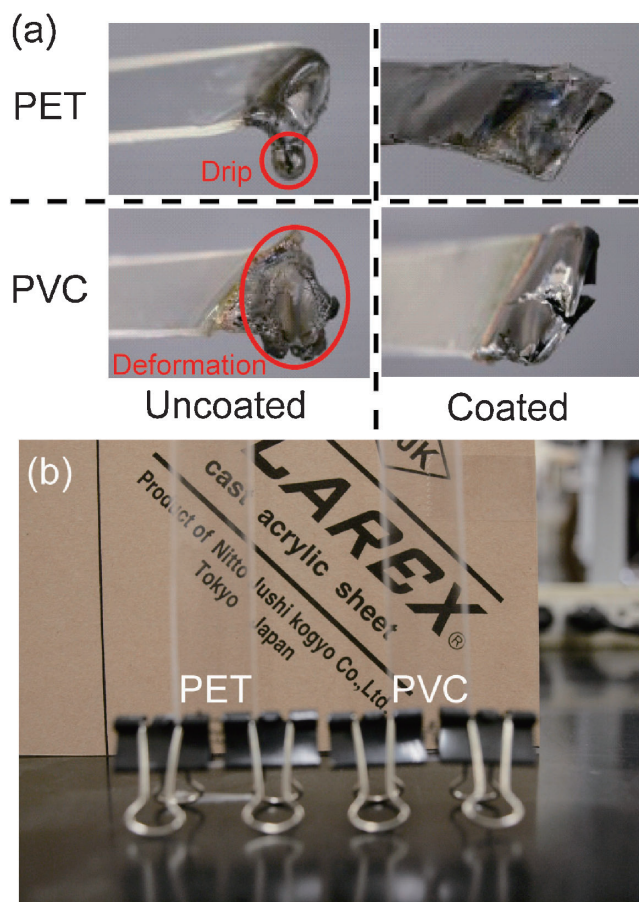


Figure 4. (a) Coated and uncoated PET and PVC test pieces after the UL94/HB flaming test. (b) “Transparent” PET and PVC test pieces of which front and reverse surfaces were coated with the hybrid.

In this letter, it was revealed that a flexible and transparent hybrid film consisting of Laponite and PEG has fire-shielding property regardless of the absence of halogen, nitrogen, and phosphorus atoms. The hybrid film adhered to plastics with polar surface, and the film inhibited the deformation of plastics upon exposing to fire. Such coating gives flame-resistant properties to the plastic films, as the hybrid contains no halogen, nitrogen, and phosphorus atoms. Thus, the present hybrid can be utilized as environmentally friendly fire-resistant materials.

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