Designed structure and functions of the hybrids between smectites and water-soluble polymer

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INTRODUCCIÓN

Materials design based on polymers has been examined extensively in order to overcome the limitations and to satisfy the current demands on the environmental impacts, cost, and emerging functions. The incorporation of filler to obtain polymer-based nanocomposites (hybrids) in a useful way to modify the performances of polymers (or overcome the limitation of polymers), so that the addition/incorporation/dispersion of various fillers into polymers has been done to tune the functions such as mechanical, thermal, optical, chemical and electrical ones. Motivated by the successful development of nylon-montmorillonite nanocomposite (Fukushima & Inagaki, 1987; Usuki et al., 1993), clay minerals of various structural types (and associating morphological characteristics) have been used as fillers. The anisotropic shapes of fundamental particles of clay minerals, which are composed of their crystalline structures, as fibrous and platy nanoparticles with varied aspect ratios are expected to lead versatile/controlled functions of the resulting hybrid materials. The modification of the surface of clay minerals (both external surface of the particles and internal surface of the nanostructure such as interlayer space of layered clay minerals and the lumen of halloysite) has been used to tune the affinity between polymers and clay minerals (Phuekphong et al., 2020; Tirayaphanitchkul et al., 2021) for the controlled dispersion of the fillers in polymer matrices.

The hybrids of layered clay minerals and water-soluble polymers have been reported and such characteristics as stabilities, adhesion, antibacterial, antifouling and self-healing were examined as the characteristics necessary for the practical applications. These functions/characters have been designed by the structure, which is controlled by the choices of layered clay minerals, polymers and their composition (polymer/clay ratio) as well as the processes. The hybridization of water-soluble polymers with layered clay minerals as exfoliated nanosheets (polymer-clay nanocomposites) has been examined to modify the functions of water-soluble polymers (Theng, 2012). On the other hand, water-soluble polymers are regarded as a guest species to be intercalated into the interlayer space as well as to connect the particles for the functional materials design in the application for gas barrier film for gasket and food packaging (Ebina, 2018), ion conductor (Ruiz-Hitzky, 1993), photofunctional materials, etc. (Imwiset et al., 2022; Teepakakorn et al., 2019; Teepakakorn & Ogawa, 2022; Saengdet & Ogawa, 2022). Here, our recent studies on the hybrids of water-soluble polymers and layered clay minerals will be introduced.

WATER RESISTANCE AND SELF-HEALING

The water-resistance of PVA or PVP-hectorite hybrid films were achieved by simple mixing of the components in the aqueous media and subsequent casting on the glass substrate without using chemical crosslinking agent or heat treatment (Teepakakorn & Ogawa, 2021a, 2021b). Low water permeation was explained as a result of the torturous path made by the clay platelets oriented parallel to the film. PVP and PVA chains was interacted with clay surface via the ion-dipole interactions and hydrogen bonding. The composition/structure of polymer and clay is a key parameter to achieve the water-resistance.

The recovery of material from being damaged by external mechanical force is one of the important characteristics for sustainable uses of materials. Self-healing polymer or polymer nanocomposite coating have been used as a protective layer of material surface in such applications as medical devices (electronic and sensing skin) and energy storage/conversion devices, together with anticorrosion and antifouling functions. The self-healing polymers are classified into nonautonomous and autonomous systems in which the damages are healed with and without the assistance from the external stimuli, respectively. Water-induced self-healing was found for the hybrid of PVA and a synthetic hectorite (Sumecton SWF, Kunimine Ind. Co., Ltd., Japan) (Teepakakorn & Ogawa, 2021b). Self-healing was observed by the immersion of the engraved film (the gap was a few tens of μm) in water (R.T. and 2 °C), seawater, steam, acidic (HCl pH = 1) and basic aqueous solutions (NaOH pH = 14) for only 1 min. The self-healing in water was repeatedly seen for 10 times, confirming the acceptable stability for practical uses.

THERMAL STABILITY

The thermal stability is a fundamental characteristic required in a wide range of applications. TG-DTA and DSC were normally used for the evaluation of the thermal stability. The composition-dependent thermal stability of water borne polymer-clay hybrid was investigated by examining the appearance and structural changes by the heat treatment. The PVP-hectorite hybrid films with varied PVP/clay weight ratio from 0.36, 1.08, 1.80 and 4.00 exhibited the changes of appearance upon heating (Teepakakorn & Ogawa, 2021a; Teepakakorn et al., 2022). No significant changes of the appearance and basal spacing were observed for PVP-hectorite films with the weight ratio of 0.36 after the heat treatment at 340 °C suggesting the carbonization of PVP occurred for the samples with higher PVP contents (weight ratio of 1.08, 1.80 and 4.00). The thermal stability of PVP was improved by the confinements into the interlayer space of smectites where the intercalated PVP is thought to interact with the silicate layer through hydrogen bonding and ion-dipole interactions.

CONCLUSIONS

Thanks to the swelling ability and the materials' variation, systematic structural design is possible in both perpendicular (interlayer expansion) and parallel (aspect ratio of platy particle) directions of the film cross-section. These structural design concepts have been successfully utilized to control the function (materials' performances) in such application as gas barrier, self-healing, anti-corrosion etc. Due to the eco-friendly nature of the components, clay-water soluble polymer hybrids are promising materials for practical uses especially in daily life products.

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