



Preparation and mechanical properties of polypropylene / montmorillonite nanocomposites - After grafted with hard/soft grafting agent[☆]

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ABSTRACT

Using a plastograph-mixer by the twin-screw mixed method to obtain the standard shaped specimens of polymer-clay nanocomposites (PCN), to prepare polypropylene (PP) / montmorillonite (MMT) nanocomposites pellets, grafting with two kinds of different surfactant – maleic anhydride (MA) or thermoplastic polyolefin elastomers (TPO). The chemical structure and polymer morphology of these as-synthesized PCN specimens were characterized by wide-angle powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). In addition, we prepare these experimental specimens in order to probe into its mechanical properties. These tests used are: layer distance of PCN, tensile, impact, shore-hardness, wearing tests, and so on.

In addition, use XRD to make the characterization analysis, compare it to scatter and layer-distance. It is found that increasing the MA into the MMT, layer-distance at 5 wt% increase from 2.09 nm to 3.94 nm; and increase the TPO into the MMT, layer-distance at 1 wt% increase to the 3.27 nm.

For the mechanical property, it is found that these specimens graft the MA have the following results: in the shore hardness test, the MMT weight percentage 5 wt% has the best result, increased by 51.2%. In the wearing test, the MMT 3 wt% strengthens by 81.48%. In addition, the specimens that graft the TPO, in the tensile test, increased by 5.79% have the best result.

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1. Introduction

Recently, layered materials such as smectite clay (e.g., montmorillonite, MMT) have attracted intense research interests for the preparation of polymer-clay nanocomposite (PCN) materials. PCN materials usually demonstrate unique properties superior to traditional composites and conventional materials. In general, they combine both the characteristics of inorganic nanofillers and organic polymers at the molecular level. Currently, the PCN material is found to be a promising system due to the fact that the clay possesses a high aspect ratio and a platy morphology. It can be employed to boost the physical properties (e.g., thermal stability [1], fire retardant [2], gas barrier [3], and corrosion protection [4]) of bulk polymers, mechanical properties is a particularly significant issue to study application and development for PCN materials. Kim and White [5] reported a variety of organic modified MMTs to understand the contribution of the organophilicity of organoclay on the formation of the polymer/clay nanocomposite.

Maleic acid (MA) is an organic compound that is a dicarboxylic acid (molecule with two carboxyl groups). Other names are malenic acid, maleinic acid and toxilic acid. In industry, MA is derived from maleic anhydride by hydrolysis. Maleic anhydride is produced from benzene or butane in an oxidation process. Maleic acid is soluble in water, has a

melting point of 139 - 140 °C. Both properties of maleic acid can be explained on account of the intramolecular hydrogen bonding [6] that takes place at the expense of intermolecular interactions.

Thermoplastic polyolefin elastomers (TPO) are unique elastomeric products designed to improve impact performance, melt strength, and overall processability for a variety of markets and applications. TPO combine highly desirable elastomeric properties in a pelletized form and are available in a wide range of grades to meet the most demanding processing and performance needs.

Polypropylene (PP) was first polymerized by Karl Rehn and Giulio Natta in March 1954 [7], serving as a preliminary work for large-scale synthesis from 1957 onwards. At first it was thought that it would be cheaper than polyethylene [8]. PP is reasonably economical, and can be made translucent when uncolored but is not as readily made transparent as polystyrene, acrylic, or certain other plastics. It is often opaque or colored using pigments. PP has good resistance to fatigue. The melting of polypropylene occurs as a range, so a melting point is determined by finding the highest temperature of a differential scanning calorimetry chart. Perfectly isotactic PP has a melting point of 171 °C. Commercial isotactic PP has a melting point that ranges from 160 to 166 °C, depending on atactic material and crystallinity. Syndiotactic PP with a crystallinity of 30% has a melting point of 130 °C [9].

PP is a thermoplastic polymer, made by the chemical industry and used in a wide variety of applications, including packaging, plastic parts and reusable containers of various types, loudspeakers, automotive components, and polymer banknotes. An addition polymer made from

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the monomer propylene, it is rugged and unusually resistant to many chemical solvents, bases and acids. However, major drawbacks in PP's applications are attributed to its poor native mechanical properties such as tensile, flexural, hardness and wear resistance. It should be particularly noted that the mechanical strength of polymers is the fundamental property needed to be fulfilled, before they can exhibit their major useful service properties.

Recently, several attempts have been reported to study the mechanical properties of PP–clay nanocomposite materials. For example, Wang and Sheng [10] prepared PP / org-attapulgitite (ATP) nanocomposites gave rise to a considerable increase of the storage modulus and a decrease of the $\tan\delta$ value demonstrating the reinforcing effect of clay on the PP matrix. Bao and Tjong [11] demonstrated that EWF concept can be used to evaluate the impact fracture toughness characteristics of the PP/MMT nanocomposites toughened with SEBS-g-MA elastomer. Thridandapani et al. [12] reported that under identical test conditions, the severity of surface deformation in PP–clay nanocomposites, which leads to stress whitening is significantly reduced. At lower loads, the periodic nature of tracks is retained together with ironing, while at higher loads, ploughing occurred.

Moreover, wear resistance of PET, nylon 66 and PS nanocomposite materials has been reported by Schadler et al. [13], Yu et al. [14] and Liu et al. [15], respectively. However, wear resistance of PP–clay nanocomposite materials have seldom been mentioned.

Therefore, in this paper we present the first evaluation of wear resistance of PP–clay nanocomposites and the first to make a comparative study on the mechanical properties of the effect of organoclay (MMTs) on impact strength, shore hardness and tensile strength of PP–clay nanocomposites.

2. Experimental

2.1. Chemicals and instrumentations

Commercial PP (Model No. TAIRIPRO K1011, melting point = 140–170 °C, specific gravity = 0.90 g/cm³) were purchased as pellets from the Formosa Chemicals & Fiber Corporation in Taiwan. The montmorillonite clay (Model No. I.30P) was purchased from Nanocor Company in USA. The surfactant of I.30P is derivative containing Octadecylamine modification. The maleic anhydride (MA) (molecular formula = O-COCH:CHCO, formula weight = 98.04, melting point = 131–139 °C, specific gravity = 1.48 g/cm³, assay = 99.5%) was purchased from First Chemical Works in Taiwan. The thermoplastic polyolefin elastomers (TPO) (Model No. ENGAGE™ 8100) was purchased from Dow Chemical Company in USA.

A wide-angle X-ray diffraction study of the samples was performed on a Rigaku D/MAX-3C OD-2988N X-ray diffractometer with a copper target and Ni filter at a scanning rate of 4°/min. The samples for the transmission electron microscopy (TEM) study were first prepared by putting the membrane of PCN (PP–clay nanocomposites) materials into low-viscosity embedding media epoxy resin capsules with four ingredients (ERL4206 5.0 g, DER736 3.0 g, NSA 13.0 g, and DMAE 0.15 g) and by curing the epoxy resin at 100 °C for 24 hr in a vacuum oven. Then the cured epoxy resin containing PCN materials were microtomed with a Reichert-Jung Ultracut-E into 60–90-nm slices. Subsequently, one layer of carbon about 10-nm was deposited on these slices on mesh 100 copper nets for TEM observations on a JEOL-200FX, with an acceleration voltage of 120 kV. Centrifugal Ball Mill (Retsch S100) was used to mill the size of organophilic clay. Twin roll mill (Kobelco, model KXY-30) was used to meltmix the organoclay and PP. A Plastograph-Mix and a Hot Press machine manufactured by Brabender Machine Company (Germany, Model no. PLE-331, co-rotating type, non-intermeshing, Max screw speed is 120 rpm, L/D ratio is 32, test temperature is 20 °C to 400 °C, Chamber maximum volume is 50 g) and Long-Chang Company (Taiwan, Model no. FC-60 TON) were used to make the as-prepared sample in the form of an ASTM D3039 standard

shape. A Scanning Electron Microscopy (SEM) with the model Hitachi S-4100 FE-SEM evaluates the surface morphology of as-prepared composite materials.

The tensile test of PCN membranes was carried out through a Universal testing instrument manufactured by Hung-Ta Company (Taiwan, Model no. HT-9102). The impact strength test of PCN membranes was carried out through an Izod Impact Tester manufactured by Hung-Ta Company (Taiwan, Model no. HT-8041B). The shore hardness tests were run on a Shore Hardness Test Machine by EXCELLENCE Company (Japan, Model D) for high and low hardness samples, respectively, under an indentation time of 10 seconds at 25 °C. The wearing resistance tests were run on a Wearing Test Machine by the TABER Company (Model 5130 ABRASER).

2.2. Preparation of PP–clay nanocomposite materials by melt intercalation

Before blending, PP and clay were dried at 85 °C inside vacuum oven for one hour. The proportion-grafting agent MA (or TPO) ratio to MMT is 2:1. Then, measure the weight of PP-MA-MMT and PP-TPO-MMT according to different proportions. MMT is 1, 3, 5 wt% respectively. PP, MA (or TPO) and MMT were prepared in a Plastograph-Mixer machine separately, at a screw speed of 30 rpm, melt temperature of 190 °C, blended for 5 minutes, 5 minutes, 5 minutes respectively, for a total blending time of 15 minutes.

The melt-mixing procedure of PP-MA-MMT and PP-TPO-MMT composites was performed by blending samples repeatedly, at least twice, to form products in the shape of pellets, with better combinations. A Plastograph-Mixer machine using the twin-screw

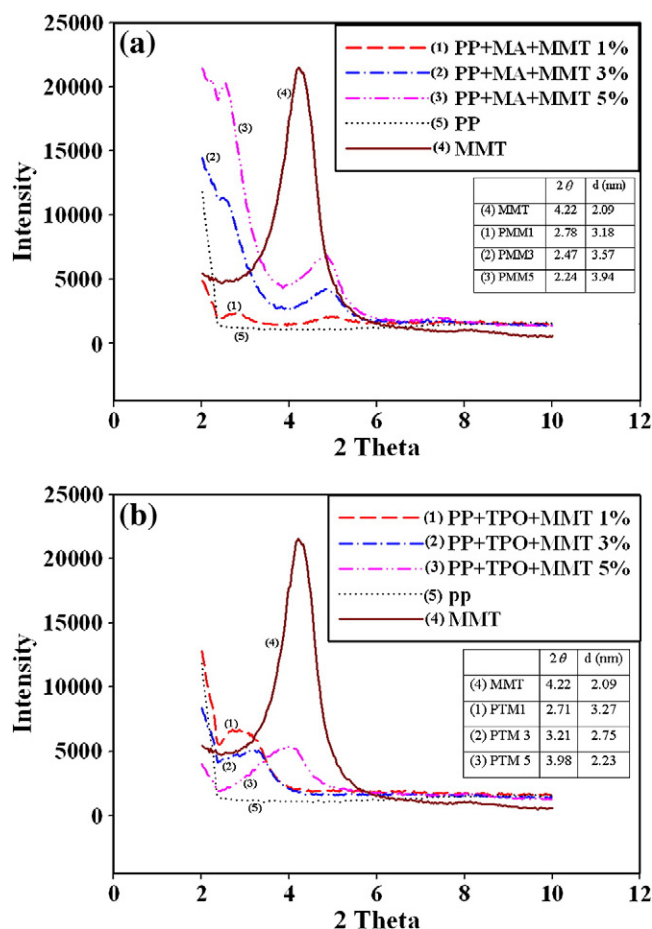


Fig. 1. (a) X-ray diffraction patterns of neat PP and PP-MA-MMT clay. (b) X-ray diffraction patterns of neat PP and PP-TPO-MMT clay.

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