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Oxygen barrier and blending properties of blown films of blends of modified polyamide and polyamide-6 clay mineral nanocomposites

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ABSTRACT

Investigations of oxygen barrier and blending properties of the modified polyamide (MPA) and nylon-6 clay (NYC) blends (MPANYC) were systematically investigated. After blending NYC in MPA, the oxygen barrier properties of the MPANYC film specimens are significantly better than those of the MPA and NYC film specimens. At 20 wt.% optimum content of NYC, the oxygen barrier improvement of MPANYC film specimen reaches the maximum, which is in the same order of magnitude of barrier improvement as those of PVDC film specimens. A similar relation on the NYC content was found on the plots of free free-volume properties (i.e. R_f, V_f, I_3 and F_v) vs. the NYC contents of MPANYC specimens. The minimum R_f, V_f, I_3 and F_v values of MPANYC specimens were found as their NYC contents reach about 20 wt.%. The characteristic X-ray reflections of α form PA crystals originally associated with the MPA resin almost disappear after blending varying amounts of NYC in MPA resins. Further morphological investigations showed that demarcated structures of elongated (ca. 700 nm) and overlapped clay mineral layers were found on the microtomed surfaces of MPANYC specimens as their NYC contents reach 20.0 wt.%. However, at NYC contents lower than 20.0 wt.%, the lengths of these “elongated and overlapped” clay mineral layers reduce significantly as the NYC contents continue to reduce. These improved oxygen barrier properties of the MPANYC film specimens were explained in terms of the reduced free-volume properties and demarcated structures of the elongated and overlapped clay mineral layers caused by the presence of the nanometer clay mineral layers.

1. Introduction

Non-polar hydrocarbon solvents, such as, xylene, toluene, white spirit, gasoline and cleaning naphtha can easily permeate through polyolefin (e.g. polyethylene and polypropylene) containers to result in pollution, safety and health problems. Alternative technologies, such as multilayer co-extrusion (Jabarin and Kollen, 1988; Kamal et al., 1995), and laminar-blend-blow-molding (Subramanian, 1983, 1984) are two of well proven technologies to improve this poor permeation resistance of polyolefin containers, wherein barrier materials, such as polyamide (PA) and/or ethylene–vinyl alcohol copolymer (EVOH) were used to enhance their barrier properties against the permeation of hydrocarbon solvents. It is well known that nylon has good barrier properties against hydrocarbon solvent permeation and good adhesion to a variety of resinous substrates or coatings. After blending proper amounts of EVOH in modified polyamide (MPA) resin, our latest investigation (Yeh and Chen, 2007) found that the oxygen permeation resistance improved consistently as the EVOH contents in MPAEVOH film specimens increase. In fact, at an EVOH content of 80 wt.%, the oxygen permeation rates of the MPA_1EVOH_4 film specimens are even lower than that of the pure EVOH film specimen with a vinyl alcohol content of 52 wt.%, wherein the vinyl alcohol contents present in the virgin EVOH of MPA_1EVOH_4 film specimens are equal to or more than 56 wt.%. Presumably, the significant reduction in the oxygen permeation rates of MPAEVOH specimens with increasing EVOH and/or vinyl alcohol contents is due to their gradually reduced R_f and F_v values, as the EVOH and/or the vinyl alcohol contents of MPAEVOH series specimens increase. However, the amounts of EVOH added in MPAEVOH film specimens are still too high to significantly reduce the cost of the MPAEVOH resins.

In order to reduce the cost while still maintaining good processibility and barrier properties of the barrier resins, modification of the barrier properties of polymers using nanoscale filler particles with a high surface area to thickness aspect ratio has drawn much attention recently (Okada et al., 1988; Usuki et al., 1995). Along with talc and mica, clay minerals have been used in a variety of polymers to reduce oxygen permeability (Cussler et al., 1988; Bissot, 1990; Sekelik et al., 1999; Chang

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et al., 2001; Bharadwaj et al., 2002; Krook et al., 2002), wherein the filler particles (e.g. smectites) are typically approximately 1 nm thick with laterally dimensions of the order 200–1000 nm. Significant improvements in modulus and heat deflection temperature were first found in polyamide-6 clay mineral nanocomposites (NYC) by addition of 2–8 wt.% of smectites (Okada et al., 1988; Usuki et al., 1992). Later investigations found that polymer nanocomposites exhibit significant better barrier performance to diffusing species in comparison with the unmodified polymers (Okada et al., 1988; Kojima et al., 1993; Usuki et al., 1995; Morgan et al., 2000). Presumably, this improvement in barrier properties of polymers is based on the tortuosity arguments, wherein the permeant molecules must travel the longer diffusive path in the presence of the clay fillers (Michaels et al., 1975; Wakeman and Mason, 1979; Cussler et al., 1988; Falla et al., 1996; Chang et al., 2001; Yang et al., 2001).

The main objective of this study is to investigate the blending and oxygen barrier properties of the blends of modified polyamide (MPA) and NYC resins, which will be referred to as MPANYC in the following discussion. The effects of MPANYC compositions on the oxygen permeation rates of their blown films were investigated. In fact, by using proper MPANYC compositions, MPANYC blown films exhibit significantly better oxygen permeation resistance than PE, MPA and NYC blown film specimens. To understand these interesting oxygen barrier properties of MPANYC film specimens, X-ray diffraction and free-volume properties of the MPA, NYC and MPANYC specimens were carried out. Possible mechanisms accounting for the interesting oxygen barrier properties of MPANYC blown films are proposed.

2. Experimental

2.1. Materials and sample preparation

The polyamide (PA) and compatibilizer precursor (CP) used in this study were obtained from Formosa Chemicals and Fiber Corporation, Taiwan, wherein PA is nylon-6 with a trade name of Sunylon 6N and CP is a 40% zinc-neutralized ethylene/acrylic acid copolymer. The M1030D (the first word "M" means Montmorillonite) nylon-6 clay mineral (NYC) was cited with a weight-average molecular weight (Mw) of 62,000 and 4.6 wt.% exfoliated montmorillonite, which was purchased from Unitika LTD., (Tokyo, Japan), and is a nanocomposites of nylon-6 and uniformly dispersed silicate layers of montmorillonite. As cited in the patents of Unitika LTD. (Kojima et al., 2000; Fujimoto et al., 2001), the bentonite contains montmorillonite (>80%), quartz, K-feldspars, plagioclases, carbonates, mica and other minerals, which was obtained from Yamagata, Japan. The bulk bentonite is composed by 86% of particles in a size <2 µm, 9% of those in a size of 2–50 µm, and 5% of those in a size >50 µm. The bentonite was crushed by jet-mill and dispersed in water, wherein the coarse particles were eliminated by sieving and repeatedly crushed until the particle size could pass through a 400 mesh sieve. The purified montmorillonite was then obtained by elutriation of the collected fine particles. The quaternary alkylammonium ($-NH_4^+$) solution was prepared by dissolving dodecylamine (i.e. $C_{12}H_{25}NH_3^+$) in de-ionized water, mixing and stirring with 2 mol HCl solution until a clear solution was obtained. The purified montmorillonite was then ion-exchanged using quaternary alkylammonium solution at pH 7, wherein the cations (mainly Na^+) between the laminates of montmorillonite were substituted with NH_4^+. The cation exchange capacity of the starting montmorillonite is 115 meq/100 g, which was determined by titrating the eluted NH_4^+ of dodecylamine with 0.1 N sodium hydroxide solution. The layered silicate in NH_4^+ form was thoroughly washing washed with water and ethanol and then soaked in a 10 wt.%wt% potassium chloride solution to replace NH_4^+ in the sample by K^+. The above organo-montmorillonite was swollen by ε-caprolactam (i.e. monomer of nylon-6) and then polymerized with the intercalated of montmorillonite at 260 °C for 6 h, to yield the nylon-6 clay mineral (NYC). The modified polyamide (MPA) resin was prepared by reactive extrusion of the CP and PA resins. The PA resins were blended with CP at 80:20 weight ratio using a Nanjing Jiant SHJ-20 twin-screw extruder to make MPA resin. The detailed experimental procedures used to prepare the MPA resins were described in our previous investigations (Yeh et al., 1995, 1997). The polyethylene (LDPE Taisox 6030F) and antioxidant (Irganox B225) used in this study were obtained from Formosa Plastic Corporation (Taipei, Taiwan) and Ciba-Geigy Corporation (Basel, Switzerland), respectively.

The CP modified polyamide (MPA) resins prepared by reactive extrusion from twin twin-screw extruder were quenched in cold water at 15 °C and cut into the pellet form. The blends of MPA and NYC (MPANYC) were prepared by melt blending the dried MPA and NYC resins at varying ratios using a Nanjing Jiant SHJ-20 twin-screw extruder. Before melt blending, MPA and NYC resins were dried in vacuum oven at 80 °C for 16 h. The dried components of varying weight ratios of MPA to NYC resins were then fed into the twin-screw extruder operating at 230 °C in the feeding zone and 220 °C towards the extrusion die with a screw speed of 200 rpm. The extruded MPANYC resins were then quenched in cold water at 15 °C and cut into the pellet form. The compositions of the MPANYC specimens prepared in this study are summarized in Table 1.

The MPA and MPANYC barrier resins were co-extruded with the LDPE and then film-blown using a Queen's Machinery QN-35/2E-650 double layers blown film machine, since it is well known that the melt viscosities of the PA related barrier resins are too low for film-blowing. Before film-blowing, MPA, NYC and MPANYC resins were dried at 80 °C for 16 h. The extruders used for LDPE and PA related barrier resins were operated at 170 °C and 200 °C in the feeding zone, respectively, 230 °C toward the extrusion die and at a screw speed of 75 rpm. The co-extruded films were then blown up at a blow-up ratio of 3, wherein LDPE and the PA related barrier resins were in the inside and outside layers, respectively. The barrier layers were then detached from the LDPE layer after film-blowing. The LDPE and barrier film specimens prepared in this study have a thickness of 25 µm.

2.2. Permeation properties of blown film specimens

The oxygen permeation rates of PE, PA, MPA, NYC and MPANYC films were determined using a Yanaco GTR-10 manometric gas permeability analyzer equipped with a Varian CP-3380 gas chromatography in accordance with ASTM D-1434 standard. The film specimens were cut into a circular shape with a diameter of 10 cm and a thickness of 25 µm, and then tested at 25 °C and 50% relative humidity for the permeation experiments. The oxygen permeation rate of each film specimen was estimated based on the average permeation rate of at least three film specimens. The areas (A_o) were obtained from GC spectrum corresponding to the oxygen permeation volumes of MPANYC film specimens in 24 h. The oxygen permeation volumes per day of MPANYC film specimens were then calculated by multiplying the A_o values with an instrument constant. The oxygen permeation rates of the film specimens were then evaluated by

Table 1
Compositions of MPANYC.

Compositions	MPA (wt.%)	NYC (wt.%)
MPA	100.0	0.0
$MPA_{48}NYC_1$	98.0	2.0
$MPA_{24}NYC_1$	96.0	4.0
$MPA_{16}NYC_1$	94.1	5.9
$MPA_{12}NYC_1$	92.3	7.7
MPA_8NYC_1	88.9	11.1
MPA_4NYC_1	80.0	20.0
MPA_2NYC_1	66.7	33.3
MPA_1NYC_1	50.0	50.0
MPA_1NYC_2	33.3	66.7
MPA_1NYC_4	20.0	80.0
NYC	0.0	100.0