Research paper

Effect of nanoclay localization on the peel performance of PE based blend nanocomposite sealants

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ABSTRACT

Polyethylene (PE) based clay polymer nanocomposites (CPN) are of great importance to generate peelable seals in packaging industry. This study shows the significant effect of organoclay (OC) localization in PE-based blend sealants on their peel properties, for the first time. Two different immiscible blends composed of PE/ethylene-methyl acrylate copolymer (EMA) and PE/ethylene-methyl acrylate-glycidyl methacrylate terpolymer (EMA-GMA) were examined for their potential to generate peelable seals upon addition of organo-modified montmorillonite (OMt). WAXD results and TEM observations reveal that OC is localized at the interface of PE/EMA phases while it is localized within the dispersed EMA-GMA phase in the PE/EMA-GMA blend, which is in agreement with the thermodynamic predictions. The incorporation of 4 phr OC converts the lock seal behavior of the PE/EMA blend seal to a peelable behavior over a wide peelable heat seal temperature range (over 35 °C). In contrast, the OC/PE/EMA-GMA nanocomposite sealant, in which OC is mostly located within the EMA-GMA phase, shows lock seal performance similar to the PE/EMA-GMA neat blend.

1. Introduction

Packaging, as an important sector of plastic industry, has a crucial effect on consumer purchase behavior (Ahmed et al., 2014) and could be an entire reason for a brand existence (Gómez et al., 2015; Han, 2005). Due to modern life style, easy-open packaging with peelable sealants is increasingly developed for variety of applications (Berbert, 2012; Kinigakis et al., 2016; Laske, 2016; Liang et al., 2017; Longo, 2002; Rivett et al., 2003; Ursino, 2009). Monolayer and multilayer films along with a peelable sealant layer provide a good solution to produce user friendly packaging. A peelable sealant can be opened upon peeling either from the interface of the seal layer and its adjacent layer, which is called adhesive peel (Ernesto Mendoza-Navarro et al., 2013; Frihart, 2004; Nase et al., 2014; Santos et al., 2001), or within the seal layer, which is called cohesive peel (Liewchirakorn et al., 2017; Nase et al., 2008b), or combination of both (Martínez-García et al., 2008). In an adhesive peel, separation takes place at the interface of two sealed layers and no residue is left on the opposite side. In addition to the poor seal that is provided by adhesive materials, the seal strength of adhesive sealants is more sensitive to the seal parameters i.e. heat seal temperature, pressure and dwell time (Nase et al., 2014). A cohesive peel, however, is made by blending two or more immiscible polymers (Longo, 2002; Ursino, 2009) or by incorporation of solid particles in seal area (Liang et al., 2017). In this approach the seal layer is strongly

welded to a substrate to provide a reliable seal while peel initiation and propagation upon peeling is controlled by the presence of weak interfaces in the seal layer (Liebmann et al., 2012; Nase et al., 2008b). Cohesive peelable films provide stronger seals and have received a great deal of attention in the packaging of perishable products. Furthermore, the peel strength can be adjusted through controlling process conditions (Nase et al., 2009) and seal materials formulation (Nase et al., 2008b; Zhang et al., 2009) for different applications.

Polyolefins, particularly polyethylene (PE), are the best candidates for the seal layer due to their easy processability, low cost, and low heat seal initiation temperature (Coles et al., 2003). Accordingly, blends that are used for cohesive peelable films are usually made of polyolefins such as blends of poly(ethyl methyl acrylate) (PEMA) with propylene co-ethylene copolymer or blends of PE or ionomer with polybutene-1 (PB-1) (Liebmann et al., 2012). Such blends suffer from a narrow peelable heat seal temperature window (ΔT_p) (Liebmann et al., 2012) or aging in sealants containing PB-1 (Nase et al., 2015; Nase et al., 2008a). Incorporating organomodified nanoclays in the seal layer is an effective approach to achieve a cohesive peelable sealant with a wide ΔT_p of over 30°C (Zhang et al., 2009). Nevertheless, it was shown that such a broad ΔT_p is only achieved through well dispersed and distributed organoclay (OC) in the sealant matrix (Zhang et al., 2009). For PE based sealants, incorporating PE grafted maleic anhydride (PE-g-MA) as well as blending PE with a functionalized polymer such as PE

copolymers and/or terpolymers have been shown to improve the dispersion of the nanoclays in the seal area and consequently increases ΔT_p (Zhang et al., 2009). Manias et al. (Manias et al., 2009) showed that blending PE with ethylene vinyl acetate (EVA) is much more effective than PE-g-MA compatibilizer in increasing the dispersion of nanoclay in the PE sealant and broadening ΔT_p.

When solid particles are added to an immiscible binary polymer blend, solid particles either locate at the interface of phases or within one of the components, depending on their interaction or wettability by the blend components. Theoretical predictions and experimental results demonstrate that the morphology and dynamic phase behavior of a polymer blend and thus its properties can be tailored depending on the localization of solid particles in the blend (Aghjeh et al., 2016; Ali et al., 2016; Grande and Pessan, 2017; Lee et al., 2012; Si et al., 2006; Thankappan Nair et al., 2015; Vo and Giannelis, 2007; Yoo et al., 2010). In general, the domain size increases when nanoparticles are located in dispersed phase due to an increase in viscosity and breakup suppression (Dasari et al., 2005; Hong et al., 2006). By contrast, the dispersion of solid particles in a polymer matrix can suppress the coalescence due to the barrier effects of solid particles (Khatua et al., 2004) or increase the break-up due to the increase in viscosity of the matrix (Hong et al., 2006). Localization of fillers at the interface of a blend components can reduce the domain size through various mechanisms, i.e. the barrier mechanism, change in the viscosity ratio, or compatibilization effect of solid particles (Ammar et al., 2017; Martín et al., 2010; Trifkovic et al., 2015). Nanoparticles can also intercalate in both polymer phases and at the interface and thus result in a strong compatibility between components and reduce the dispersed phase size (Sinha Ray and Bousmina, 2005). Although thermodynamic considerations are the main drivers determining the localization of solid particles in an immiscible multiphase system, this stable equilibrium state dictated by thermodynamics is not always reached (Dasari et al., 2005). The final localization of solid particles is strongly influenced by kinetic effects including the mixing strategy (Nofar et al., 2016; Zhao et al., 2013), viscosity ratio (Elias et al., 2008a; Elias et al., 2008b; Jalali Dil and Favis, 2015), composition (Ojijo et al., 2012), mixing time (Göldel et al., 2012; Gubbels et al., 1998; Xiong et al., 2013) and shear rate (Hong et al., 2008; Jalali Dil and Favis, 2015; Taghizadeh and Favis, 2013). Due to unfavorable localization dictated by kinetic effects, solid particles migrate from one phase to another phase as soon as they collide with the interface through hydrodynamic forces (Elias et al., 2008a).

It has been shown that various properties of polymer blends such as electrical (Wu et al., 2009; Zhang et al., 1998; Zhao et al., 2013), thermal (Ojijo et al., 2012) and mechanical (Ebadi-Dehaghani et al., 2016; Mallick et al., 2010; Mallick and Khatua, 2011; Ojijo et al., 2012) properties can be tailored through solid particle localization. To our knowledge, the effect of localization of nanoclay on the peel performance of PE-based blend films has not been reported in the literature. The present work investigates the localization of OC and its effect on morphology and peel performance of two different PE-based blends composed of OC/PE/EMA and OC/PE/EMA-GMA.

2. Experimental

2.1. Materials

Low density polyethylene (LDPE) with the trade name of Novapol LF-0219-A was provided by Nova chemicals. Ethylene-methyl acrylate copolymer (EMA) with the trade name of Elvaloy AC 1224 is a copolymer of ethylene with 24 wt% of methyl acrylate (MA) as comonomer was obtained from DuPont. Ethylene Acrylic ester- Glycidyl Methacrylate terpolymer (EMA-GMA) containing 24 wt% of MA and 8 wt% of Glycidyl Methacrylate (GMA) with commercial name of Lotader AX8900 was purchased from Arkema. EMA and EMA-GMA are commonly used for seal applications due to their thermal and

mechanical properties as well as low softening and melting temperatures (Chou, 2011; Galloway, 2008; Hawes and Sasthav, 2006; Hwo, 1987; Lee and Hausmann, 2005; Schell and Pockat, 2006). Surface modified Mt. with the trade name of Cloisite 15 was provided by Byk Company. The organomodifier is dimethyl dihydrogenated tallow in which tallow is approximately 65% C18, 30% C16, 5% C14 with cation exchange capacity (CEC) of 125 meq/100 g.

2.2. Clay polymer nanocomposite film preparation

Two master-batches of OC/EMA-GMA and OC/EMA containing 20 mass% Cloisite 15 were prepared using a twin screw extruder (TSE) Leistritz ZSE 18HP, with an L/D ratio of 40 equipped with a separate nanoclay feeder and at a melt temperature of 190°C and rotor speed of 100 rpm. The master batches were then diluted by LDPE to achieve OC/PE/EMA nanocomposites (PE and OC refer to LDPE and Cloisite 15 organonoclay respectively) and OC/PE/EMA-GMA containing 4 phr OC with a mass composition of 84/16/4. Blends of PE/EMA and PE/EMA-GMA with a mass composition of 84/16 were also prepared for comparison. Then, the blends and CPN were processed into films and co-extruded with linear low-density PE (LLDPE) and high density PE (HDPE) as support layers through a cast line. In this process, each layer was extruded using a single screw extruder LE20–30 from Labtech at screw speeds of 40, 25, and 60 rpm for the seal layer, LLDPE, and HDPE, respectively. The temperature zones of the extruders were set at 170/180/190/200 °C. The molten polymer passed through a 5 layer ABCDA feed block connected to a 12″ coat hanger cast die with a die opening of about 500 μm in average. Afterwards, it was stretched in air and directed trough calendar rolls chilled with cold water. The calendar rolls speed and draw ratio were adjusted to obtain uniform films with a thickness of 90 μm consisting in the seal, LLDPE middle and HDPE support layers of 30, 20 and 40 μm respectively.

2.3. Contact angle (CA) measurements

CA measurements were carried out using the sessile drop technique with the FDS contact angle system OCA Data Physics TBU 90E. CA was measured through placing 2 μl of liquids on films of PE, EMA and EMA-GMA such that three drops in several positions of a sample were tried and for each time the sessile drop CA was stabled over 1 min time. For each drop, the average of the right and left angles was used as CA. Then, the surface tensions of polymer components were calculated using contact angle (CA), θ, measurements according to Owens-Wendt equation (Owens and Wendt, 1969):

$$\gamma_l\,(1 + \cos\theta) = 2(\sqrt{\gamma_i^d \gamma_l^d} + \sqrt{\gamma_i^p \gamma_l^p}) \tag{1}$$

where, γ_l is the surface tension of liquid and γ_i is surface tension of polymer i. γ_l^p and γ_l^d are polar and dispersive portions of the surface tension of the liquid, γ_l, respectively. γ_i^p and γ_i^d are polar and dispersive portions of the surface tension of the polymer, γ_i, respectively. The average of the CA of the liquids on each polymer film was used in Eq. (1) to calculate the surface tension of the sample. In this work, deionized water and Formamide (FM) were used to measure the contact angle of the polymers with the liquids. Dispersive and polar portions of the surface tension for water are 22.1 and 50.7 mN/m and for FM are 39.5 and 18.7 mN/m respectively (Shimizu and Demarquette, 2000). The surface tension of Cloisite 15 at room temperature was obtained from literature (Kooshki et al., 2013). The surface tensions of the polymers and the OC at melt process temperature (200 °C) were extrapolated based on their surface tension at room temperature and its rate of thermal variation, i.e. dγ/dT, that was considered − 0.067 mN/m·K for LDPE, − 0.07 mN/m·K for EMA and EMA-GMA (Wu, 1982) and − 0.1 mN/m·K for organo-modified montmorillonite (Picard et al., 2007).

The interfacial tension between components i and j were then