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Reactive melt blending of low-density polyethylene with poly (acrylic acid)

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KEYWORDS

Low-density polyethylene; Poly(acrylic acid); Reactive blend; FTIR; Rheological behavior; Flow index; Activation energy **Abstract** Reactive melt blending of low-density polyethylene LDPE with a low molecular weight poly (acrylic acid) PAA in the presence of benzoyl peroxide (BPO) free radical initiator was studied by means of a HAAKE torque rheometer and a capillary rheometer FTIR spectroscopy and was used to characterize the structure of LDPE/PAA blends. The rheological behavior of blends has been investigated at different temperatures (170, 190, 210 and 230 °C) and shear rates (5.43, 18.1, 54.3, 181 and 543 S⁻¹). With a rise of temperature and increasing shear rates the shear stress of blends increases nonlinearly. The melt viscosity increases with the increase in the PAA proportion but decreases with the increasing shear rate and shear stress. The melts of all the blends are pseudoplastic in nature. The flow behavior index (*n*) of the blends decreases with the increase in the PAA proportion and with the increase in the temperature. The temperature sensitivity of the flow behavior of the blends is studied using Arrhenius plots. The system exhibits relatively low activation energy which means less sensitivity to temperature with an increase in the PAA ratio.

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1. Introduction

Low-density polyethylene LDPE is the one of the most important thermoplastics today, it has gained an important position among other polymers due to its wide range of mechanical, physical and chemical properties.

Low-density polyethylene is a partially crystalline solid with a degree of crystallinity in the 50–60% range that leads to sev-

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eral properties such as opacity, rigidity (stiffness), tensile strength, tear strength, and chemical resistance (Billmeyer, 1971).

However, its use in blending with other polymers has been limited due to the absence of polar functional groups and lack of reactive sites on LDPE back bone. Chemical modification through functionalization or grafting leads to the introduction of polar group onto polymer main chain as pendent unites or short chain branching via free radical reactions initiated by organic peroxides to generate reactive sites on polymer chain for grafting (Ghosh et al., 1998). Another way of increasing the adhesion, compatibilization, wettability properties of LDPE is its modification in the bulk by the addition of small amounts of polar polymer or low molecular weight additives. Different monomers were grafted onto LDPE such as maleic anhydride, unsaturated carboxylic derivatives and vinyl or acrylic

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compounds containing more than one functional group (Ghosh et al., 1998; Ghosh and Dev, 1998). LDPE modified with polar monomer has found wide application as reactive compatibilizer in LDPE blends in which the second component of the mixture is a polar polymer.

Compatibility of the immiscible blend components can be greatly improved using peroxides, taking advantage of high reactivity of polyolefins to free radical that good starting point for promoting compatibilization between polypropylene PP/ polyethylene PE blends, although the individual component responds differently to peroxide (PP degraded &PE crosslink),on the other hand, low molecular weight compounds can be used by adding in the melt to initiate grafting – coupling reactions forming graft or block co-polymers during processing.

Compatibility between polyethylene with other polyolefins by addition of peroxide having been obtained in several researches, Vogel and Heinze studied effects of processing conditions on crosslinking LDPE/EVAc ethylene vinyl acetate copolymer by DCP when mixed in internal mixer at 150– 210 °C (Vogel and Heinze, 1993), Abraham et al., prepared LDPE/LLDPE blend in internal mixer at 160 °C by DCP dicumyl peroxide (Abraham et al., 1992), Yu et al., mixed LDPE/PP blend by internal mixer at 180 °C uses 2,5-dimethyl-2,5-di-t-butylperoxy hexane as radical coupling agent (Yu et al., 1990, 1992, 1994).

The main aim of chemical modification of LDPE molecules is to enhance blend compatibilization and to improve some useful properties such as compatibility polyethylene with polystyrene (Kim et al., 1997), polyamide, polyester (Karl Fink, 2005), starch (Huang et al., 2005) poly (butylenes terephthalate) (Yang et al., 2003). Functionalization of polyolfines for improving adhesion is usually carried out through carboxylation with unsaturated monomers (eig. Maleic anhydride, acrylic acid) used at low concentration (Ghosh and Dev, 1998) as well as the population and a proximity of the propagation poly(acrylic acid) chains increase (acrylic acid suffered homopolymerization when grafted onto polyolfines in the melt thus bringing in a reduction in the graft yield) (Ghosh and Dev, 1998; Kim et al., 1997; Bhattacharya and Inamdar, 2007) which lead to the higher rate of termination and consequently lower grafted degree on polymer backbone. On the other hand, if the amount of the functional group is too small, few graft copolymers are formed and thus cannot play efficient roles as compatibilizers; the final physical properties of the polymer blend become poor (Kim et al., 1999). In this work, preparation blend of low-density polyethylene LDPE with a much higher concentration of carboxylate (low molecular weight poly(acrylic acid))by reactive blending in the batch mixers is made in the presence of an organic peroxide. The react blends were examined by Fourier transform infrared (FTIR) spectroscopy in attempts to confirm the "in situ" formation of compatibility copolymers and study rheological characterization of the grafted copolymers.

2. Materials

Low-density polyethylene (LDPE grade SCPILEN 22004) of density 0.921 gm/cm³ and melt flow index 0.32 g/10 min was procured from state company for petrochemical industry, Basrah, Iraq. Benzoyl peroxide BPO has been used as graft and cross-linking agent supplied from Fluka. Acrylic acid (obtained from BDH) polymerized to low molecular weight poly

(acrylic acid) PAA in the store. Molecular weight (Mv) of this poly (acrylic acid) was determined with viscosity testing method in this case, Mark-Houwink Eq. (1) as used

$$[\eta] = KMv^{\alpha} \tag{1}$$

where η is a intrinsic viscosity, K is a constant dependent on solvent, Mv is a viscosity average molecular weight and α is a parameter dependent on molecular shape. Here solvent used is 2 mol/L NaOH, $K = 42.2 \times 10^{-3}$ and $\alpha = 0.64$.

By substituting these data in Eq. (1) the molecular weight was found to be 11,370–11,376 dalton.

About 2 g of gross LDPE (95 wt.%)/PAA (5 wt.%) product prepared in this laboratory was dissolved in 100 mL boiling xylene and precipitated in 100 mL acetone to remove unreacted PAA during melt mixing. The precipitated LDPE/PAA was filtered, washed, and then dried in an air oven.

Approximately 0.5 g of the purified LDPE/PAA sample mentioned above was dissolved in 50mL of hot xylene, and then titrated with 0.05N KOH in methanol using phenolphthalein as an indicator. The equation to calculate degree of grafting of PAA can be expressed as Eq. (2):

$$DG(wt.\%) = \frac{V \times N \times M}{W} \times 100$$
⁽²⁾

where V represents the volume of KOH/MeOH solution used for titration of grafted PE, N is molar concentration of KOH/ MeOH solution, M is the molecular weight of AA, and W is the weight of grafted LDPE(Yang et al., 2001). The DG (wt.%) for LDPE (95 wt.%)/PAA (5 wt.%) was 5.04 wt.%.

3. Blend preparation

All blends were prepared by melt-mixing of the components in an internal mixer (Haake Rheometer 90) with rotor speed of 50 rpm and at 160 °C. Benzoyl peroxide was added in four portions at 2 min, mixing was continued for 2 min after the last addition. The total mixing time was 10 min in all cases.

The blends having different compositions from PAA wt.% = 1-5 at the fixed peroxide concentration (0.2 g). In all cases, the blends were compression molded into sheets immediately after mixing was finished for FTIR analysis.

4. FTIR spectroscopy

Fourier transforms infrared ray FTIR measurement by Shimadzu FTIR – 8400S for neat LDPE and PAA besides LDPE/ PAA/BPO blends.

Unmodified LDPE film had absorption bands at the expected frequencies for saturated aliphatic groups, including strong intensities at 2936–2916, 2863–2843 and 720–750 cm⁻¹ for methylene vibration, as well as, less induce absorption at 1380–1375 cm⁻¹indicating methyl groups as shown in Fig. 1. FTIR spectrum of thin film of PAA observed a weak absorption peak at 1640 cm⁻¹ in PAA molecules indicates the presence of trace quantities of the -C=C- double bond stretching in the PAA molecules, Fig. 2. This confirms the availability of sites for reacting (cross-linking) with free radicals on LDPE chains. This band at 1640 cm⁻¹ disappears in the reactive LDPE/PAA blends spectra may be due to cross-linking reactions. Fig. 3 shows reactive blends spectra, strong band 3100–2900 cm⁻¹ and sharp absorption stretching carboxylic acid at 1725–1700 cm⁻¹, lower intensity absorption

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