



ORIGINAL ARTICLE

Effect of waste wax and chain structure on the mechanical and physical properties of polyethylene



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Received 10 May 2013; accepted 13 January 2014

Available online 21 January 2014

KEYWORDS

Polyethylene;
Waste wax;
Mechanical properties;
Thermal properties

Abstract The influence of adding waste wax, produced as a by-product of the low density polyethylene manufacturing process, on the thermal and mechanical properties of three types of polyethylene (PE), high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE) and low-density polyethylene (LDPE), with 10, 20, 30 and 40 wt.% was investigated. Polymer-wax mixing was effective with no apparent leakage of the wax during sample preparation, which was evident from the agreement between the theoretical and experimental values of enthalpy for all types of PE.

The wax dispersion in the matrix strongly depends on the percentage of wax added to the polymer and the molecular structure of the polymer. It was found that increasing the wax content enhances the phase separation. LDPE undergoes less phase separation due to its highly branched structure composed of a network of short and long chain branches. The wax has no pronounced plasticising effect on the polymer. This is clearly manifested in LDPE as no change in the melting temperature occurred. LLDPE and HDPE were slightly affected by a high concentration of wax (30% and 40%). This is due to the non-uniform distribution of short chain branching along the LLDPE and HDPE main chains, which can interact with the wax structure.

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1. Introduction

Environmental protection and energy conservation represent two main challenges facing the world in the 21st century. Waste wax from Polyethylene plants has only found commercial use in limited applications. Developing new uses for it, especially in energy saving applications, should make significant contributions to meet the above challenges. Paraffin wax is a by-product of the high-pressure olefin polymerisation process (Pladis et al., 2006). It is a very low molecular weight

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Peer review under responsibility of King Saud University.



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polyethylene with a melting point ranging from 80 to 100 °C, depending on the average number of carbon atoms in the chains. As the mixture of polymer and unreacted ethylene gas exits the reactor and enters the separator, the solubility of the polymer in the unreacted ethylene is still high. The low molecular weight polymer chains are especially soluble in the unreacted ethylene gas at high pressure. As the regular polymer is separated from the unreacted gas, the low-molecular-weight polymer (wax) passes through the gas phase and is later separated and collected in metal drums as a by-product of the LDPE manufacturing process. This phenomenon is common in both autoclave and tubular technologies, but it is more common in autoclaves due, in part, to the short residence times in the reactor (Peacock, 2000).

Polyolefins have been extensively studied in combination with wax (Mpanza and Luyt, 2006). Several researchers have focused on the performance of these blends to act as phase change materials (PCM) (Molefi et al., 2010; Peng et al., 2004; Krupa et al., 2007a,b; Luyt and Krupa, 2009; Salyer, 1996). The interest in the use of wax is due to its many advantages, such as the possibility of high thermal energy storage and cost effectiveness in producing materials with new properties.

The carbon chain lengths of paraffin waxes with melting points between 30 and 90 °C usually range between 18 and 50 carbons. An increase in the length of the carbon chains increases the melting point of these waxes. Moreover, the melting enthalpy lies between 180 and 230 J/g, which is very high for organic materials (Molefi et al., 2010).

Wax/polymer blends can be used in many applications such as hot melt adhesives, coatings and phase change materials (Peng et al., 2004; Krupa et al., 2007a; Luyt and Krupa, 2009). The most common matrix used for blending paraffin waxes is polyethylene (Krupa et al., 2007b; Salyer, 1996; Xiao et al., 2001; Inaba and Tu, 1997; Sari, 2004). This is due to the chemical and structural similarities between polyethylene and paraffin wax, which ensure good compatibility between the two components.

Polyethylene (PE) is a commercially available low-cost polymer with excellent physical and mechanical properties. There are many types of PEs: high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE) and low-density polyethylene (LDPE). The main difference between them is the degree of branching they exhibit at the microstructural level. HDPE has the lowest degree of branching; LLDPE features short chain branches at regular intervals and LDPE is composed of both short and long, irregularly distributed branches. Changes in microstructure and the degree of branching result in several changes in properties such as the degree of crystallinity, morphology and lamellar thickness (Inaba and Tu, 1997; Sari, 2004).

AlMaadeed et al. (2012) showed that the properties of PE reinforced with glass fibres depend on chain branching. The stiffening effect of glass fibres was more pronounced in the case of LDPE due to the formation of a network between the filler and the long chain branching structure. This was clear from the significant increase in modulus of elasticity and storage modulus upon addition of glass fibres. Crystallinity also plays an important factor, as explained by the same authors. Molefi et al. (2010) studied three types of polyethylene (LDPE, LLDPE, and HDPE) with Fischer–Tropsch paraffin wax. They explained the immiscibility of the PE and wax as well as the plasticising effect of the molten wax on the PE matrix;

the authors mentioned that the wax affected the crystallisation behaviour of PE in terms of crystallinity and morphology without explaining the effect of structure and branching on the properties of the new material.

The properties of polymer-additive blends depend on the structure and degree of branching of the polymer (AlMaadeed et al., 2012), and in the case of adding wax to polyethylene, crystallinity plays an important role (Molefi et al., 2010).

The focus of this study was to understand the influence of the chain structure of polyethylene on the morphological, mechanical and thermal properties of new blends based on waste wax fillers.

2. Experimental

2.1. Materials

Three different types of polyethylene were used as a matrix: HDPE (MFI 0.35 g/10 min, density 0.955 g/cm³), LDPE (MFI 2.4 g/10 min, density 0.923 g/cm³) and LLDPE (MFI 2 g/10 min, density 0.918 g/cm³). They were graciously provided by QChem (Qatar) and QAPCO (Qatar). The waste wax, Q wax, was obtained from QAPCO (Qatar) and exhibited a density of 0.88 g/cm³. It is considered to be a high melting point paraffin wax. The Q wax exhibited one endothermic peak at 102 °C and a corresponding melting enthalpy of 20 J/g. This wax has a high average molecular weight (carbon chain lengths can be expected to be between C33 and C128). The very low degree of crystallinity indicates that the chains are highly branched, presenting obstacles for the regular folding of chains. This wax also has a wide molecular weight distribution resulting from the polymerisation process.

2.2. Preparation of PE- wax blend matrix

Blends were fabricated using a lab-scale twin screw extruder. Twin screw compounding is known to result in good dispersion in the polymer matrix. The throughput of the extruder and the screw speed were 0.7 kg/h and 110 rpm, respectively.

The blends were then dried for approximately 30 min at 70 °C before being fed into the injection moulding machine at 180 °C to make the final samples.

2.3. Characterisation

2.3.1. Scanning electron microscope (SEM)

The morphology of the PE/wax blends was characterised using a FEI Quanta 200 environmental scanning electron microscope (ESEM) at 2.0 keV. The samples were fractured perpendicular to the injection moulding direction in liquid nitrogen.

2.3.2. Atomic force microscopy (AFM)

The morphology of the samples was also studied by using AFM equipped with a Nanoscope IIIa controller (Digital Instruments, Santa Barbara, CA). All results were obtained in the tapping mode. A vertical engage scanner and Si probes were applied. The resonant frequency of the free-oscillating cantilever adjacent to the surface of the samples in the tapping mode was set as the driving frequency. The roughness of the samples was calculated from AFM images.

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