Temperature dependent separation of immiscible polymer blend in a melted state

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ABSTRACT

The density and the spectral fingerprint of a compounded blend or composite vary widely depending on the type of the components and their composition. However, the currently used polymer separation techniques, such as density-based and optical sorting systems are not suitable for recovering these materials fully due to the physical-chemical bonding between the components. The application of a novel separation principle creates the opportunity to enrich the blend fractions to neat, homogeneous zones in a melted state by utilising centrifugal force. In this study three different types of plastics: high density polyethylene, polystyrene and polyethylene terephthalate were deeply investigated in order to understand the separability of their blends as a function of rotation time and melt temperature. The results showed that the separation of polymer mixtures and blends depends strongly on the viscosity and bulk density at a given temperature, and the initial particle size also has a significant impact.

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1. Introduction

The emission of plastics has taken on even larger industrial dimensions since the global economic crisis ended in 2010, the production has been increasing again by 4% annually. To meet the growing demands of the consumer society, manufacturers are responding with continuous development (Vasile et al., 2017; Wang et al., 2015). For example multilayer packaging hit the market in order to keep food (e.g. prepacked sandwiches or capsulated coffees) fresh for longer, by blocking the moisture and oxygen transport due to the better gas barrier property of multiple polymer layers (Alipour et al., 2015; Blanchard et al., 2017; Santana et al., 2017). In the electronic and automotive industry the properties of plastics are increasingly being modified with additives, fillers and reinforcements (Cholake et al., 2017; Mallampati et al., 2017); or polymers are blended in order to tailor the desired properties (Dobrovszky and Ronkay, 2016; Jose et al., 2015; Utracki et al., 2014; Szabó et al., 2017). Regardless of the durability of the developed materials, packaging and household products have short life cycles and more than half of the post-consumer polymeric materials appear in the household waste within one year (Blanco, 2016; Cafiero et al., 2015). The life cycle of electronics and automotive products also shows a decreasing trend (Sun et al., 2017).

Based on these facts, polymer recycling is desirable in all sorts of ways, since the waste should be treated in the highest level of the waste management hierarchy as it is required by the directives of European Union (Directive 200/98/EC, 2008). In addition, social expectations should also be taken into account (Pita and Castilho, 2016). Further advantage of utilising recycled polymers is that the energy demand for processing and the emissions of CO_2 can be reduced (Jimenez et al., 2016; Laurenti et al., 2017). However, achieving the required purity of the recovered materials is a key factor for a continuous, reproducible production of high quality products. This demand requires proper sorting and separation techniques in the case of mixed plastic waste in order to minimize the contamination in the separated fractions (Gundupalli et al., 2017; Zeghloul et al., 2017). Unfortunately, at industrial scale the applied technologies, which are based on mainly density-difference (Lupo et al., 2016) or optical sorting principles (Mauruschat et al., 2016), are not adequate in the case of polymer blends and composites. The density of a compounded blend or multilayer films may vary widely depending on the compositional ratio of the polymers, or especially, on the case when the blends contain filler or reinforcement (Chandran et al., 2014); not to mention the possibilities of foaming. Optical sorting is also not a suitable method for these products as the rays reflected from the product will not match with the database signs. Therefore, blends are unrecognizable for the separator. The degree of degradation and the presence of contaminants on the surface of a polymer

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further distort the received spectral signals (Zhang et al., 2017). Moreover, identifying dark coloured products are extremely difficult with optical sorting technologies due to the absorption of light (Brunner et al., 2015). Overall it should be stated that at the end of a recycling process only neat, homogenous and contamination free polymers can provide adequate mechanical properties for plastic products (Cruz et al., 2017; Singh et al., 2017). Furthermore, collecting, handling, washing and sorting the waste greatly increase the cost of recycling, which can result in an economically non-recoverable investment (Hopewell et al., 2009). When the cleaning and separation of polymer waste is more complex and expensive, or when the separation is not possible (as in the case of blends); the manufacturers refuse to recycle the plastics (Khodier et al., 2018).

If polymers with high amount of contamination are submitted to melt extrusion or injection moulding, the risk of degradation may increase during the processing. Impurities may also impair the mechanical properties of the end-products due to the emerging heterogeneities. In such cases, interactions between the phases are weak, which results in local weaknesses. Not to mention the migration possibilities of contaminants. Therefore, it is of utmost importance to determine the components and their composition in a waste stream. Several opportunities are available for this purpose. Analysing the waste stream by infrared spectroscopy is one of the most popular methods today. Infrared spectroscopic techniques are suitable not only for the determination of composition but also for the chemical characterization of the components including their configuration, conformation and miscibility (Bokobza, 1998). In the case of black coloured samples, plastic components, fillers and reinforcement can be identified by using an attenuated total reflection (ATR) setup during Fourier transform-infrared (FTIR) spectroscopy. Raman spectra and mapping are another solutions to receive information about contaminants. Raman mapping provides discrete chemical information at distinct positions within the sample. A laser spot scans the investigated area pixel by pixel, which results in a colour map containing highly precise structural and chemical information (Coman and Leopold, 2017). The characterisation of polymers by nuclear magnetic resonance spectroscopy (NMR) also provides a possibility to determine the content and purity of a sample as well as its molecular structure (Kun and Pukánszky, 2017). However, the latter two methods require expensive equipment. Samples can be monitored as a function of time or temperature in a specific atmosphere by thermoanalytical techniques, e.g. thermogravimetry and differential thermal analysis (DSC). The mentioned methods allow us to study chemical processes associated with heating or cooling in a small amount of sample. Thermogravimetry means the continuous measurement of the weight of a sample against temperature in order to follow its degradation or other reactions with the atmosphere. Different ranges of degradation temperature can give information about the composition while the residual mass provides data on the amount of filler or reinforcement. From the DSC curves, endothermic and exothermic energy changes can be read. By identifying the glass transition- and melting temperature, the composition of a sample can be determined as well. Pyrolysis-gas chromatography-mass spectrometry analysis provides information about the original composition of a sample from the oligomers, monomers and other characteristic gas-phase products arising from the pyrolytic decomposition (Bodzay et al., 2009).

High density polyethylene (HDPE), polystyrene (PS) and polyethylene terephthalate (PET) are among the most widely used commercial plastics (Geyer et al., 2016; Kunwar et al., 2016). Blending the mentioned plastics is in the focus of research, in order to set the desired properties of the materials, like higher elongation during tensile tests or greater resistance against dynamic impacts (Palacios et al., 2016). The emerging morphology can be classified into disperse/matrix phase or co-continuous structures in the case of an immiscible polymer blend (Bouquey et al., 2011). The final morphology depends on the processing parameters, the composition ratio and properties of the components. Adding filler, reinforcement (Mohammed et al., 2017) or coupling agents (Parameswaranpillai et al., 2015) to polymer blend also play an important role on the forming structure because of the exfoliation and intercalation (Chandran et al., 2015), hence determining other physical and mechanical properties. However, these material developments rarely deal with the later recyclability because of the lack of appropriate separation devices. According to today's widespread procedures, the components of the blends can only be recovered by utilising chemical solvers. Polystyrene can easily be dissolved in several solvents, like acetone, petrol, chloroform, tetrahydrofuran or terpinene (García et al., 2009). A suitable chemical solvent for PET is phenol/trichlorobenzene in 50:50 ratio (Fasce et al., 2005), while polyethylene can be etched by tetralin, toluene or xylene (Lei et al., 2009; Matsuda et al., 1984). Small wonder that the environmental and health risks of dissolving can be significant, that it becomes difficult to apply solvents during recycling due to the cause extra costs in industrial applications.

Although the own constructed density-based melt separator has not been manufactured on an industrial scale yet, the principle of melt separation creates the opportunity to enrich the components to neat fractions from a polymer blend without chemical solvents by utilising only centrifugal force (Dobrovszky and Ronkay, 2014; Dobrovszky et al., 2015). The aim of the present study is to show the separation possibilities of the compounded PET/HDPE and PS/HDPE polymer blends depending on the dispersed particle size, the rotation time and the applied heat temperature.

2. Experimental

2.1. Materials

Three different injection grade post-consumer plastics: high density polyethylene (HDPE), polystyrene (PS) and polyethylene terephthalate (PET) were chosen for this study. The 50/50 vol% mixtures of PET/HDPE and PS/HDPE were prepared, from PET type NeoPET 80 (density at room temperature 1.34 g/cm³, melting temperature 248 ± 4 °C) produced by Neogroup (Lithuania), PS type Edistir N 1840 (density 1.05 g/cm³, recommended melt temperature 210–240 °C in case of extrusion) supplied by Versalis S.p.A (Italy) and HDPE type Liten MB 87 (density 0.955 g/cm³, Vicat softening temperature 122 °C) provided by Unipetrol RPA (Czech Republic).

2.2. Sample preparation

In order to compare the effect of compounding, mixing of the components was implemented in two different ways: (i) making dry mixture from the granules by shaking and (ii) compounding the components in a melted state with a twin-screw extruder. In the latter case PET was dried in an air drying oven for 6 h at 160 °C before extrusion. The compounding was performed in a Labtech Scientific LTE 26-44 twin-screw extruder with 40 L/D ratio. The rotation speed was 75 rpm, the temperature profile was 230–255 °C in the case of PS/HDPE and 250–275 °C in the case of PET/HDPE blend, where the highest value means the die temperature. Granulation was realised after cooling in a water bath, therefore the 50/50 vol% PET/HDPE and 50/50 vol% PS/HDPE blends had to be dried again at 80 °C for 2 h, respectively, in order to remove moisture adhered to the surface. The resulting dispersed/matrix structure can be seen in Fig. 1. The HDPE formed the matrix in both cases, in which the shape of dispersed PS phase was mainly