



ORIGINAL ARTICLE

Effect of phenol formaldehyde resin as vulcanizing agent on flow behavior of HDPE/PB blend



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Received 21 July 2013; accepted 13 December 2013

Available online 25 December 2013

KEYWORDS

Thermoplastic elastomer;
Polyethylene;
Rheological properties

Abstract Thermoplastic elastomer (TPE) based on High density polyethylene (HDPE)/polybutadiene (HDPE/PB = 70/30 parts) blends containing 1, 3, 5, 7 and 10 wt.% of dimethylol phenolic resin as a vulcanizing agent in the presence of SnCl_2 as catalyst was prepared. The dimethylol phenolic resin was prepared in our laboratory. The blends were compounded in mixer-60 attached to a Haake rheochord meter-90. The rheological properties were measured at temperatures 140, 160, 180 and 200 °C. The linearity of the flow curve appeared for 5% of the vulcanizing agent. The shear stress and shear viscosity have increased upon increasing the shear rate over a range of loading levels of vulcanizing agent of 1%, 3%, 5%, 7% and 10%. This may be attributed to the increased vulcanization between polyethylene and the rubber blend. The flow behavior index of the system shows a pseudo plastic nature behavior (since $n < 1$). The consistency index (K) increased with the increase in the phenol formaldehyde resin content and the temperature. Hence, the increase in the value of the consistency index (K) of the polymer melts refers to more viscous materials prepared. The activation energy for the TPE blends fluctuated indicating that there is phase separation; where each polymer behaved separately. This study showed that HDPE/PB blends are characterized with good rheological properties, which can be recommended to be processed with the injection molding technique.

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1. Introduction

Polymer blending was recognized in the last few decades as the most promising way to prepare new material with tailored

individual properties (Nabil, 2014). Polymer blends are defined as a mixture of two or more polymers or copolymers. Blending of existing commodity or engineering polymers often can be implemented more rapidly and it is less expensive than realization of new polymer chemistry including development of monomer synthesis and polymerization technology (Drobny, 2007; Mohamad et al., 2006). Thermoplastic elastomer (TPE) is a new family in the field of polymer blending. Currently thermoplastic vulcanized (TPVs) are the fastest growing segment of the elastomer market and occupy a vital position in the family of TPEs due to their huge potential. However, there are still some unsolved technological problems, which are associated

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Peer review under responsibility of King Saud University.



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with a lack of proper understanding of the TPVs. Both the process of TPV production and the structure-properties relationship of the TPVs are still in the development stage (Babu et al., 2011). For this reason, the development of TPV-based products is generally pursued by a somewhat trial and error method. Extensive studies have been carried out in the area of polymer blend (De and Bhowmick, 1990; Mohamad, 2007). Thermoplastic elastomers from blends of poly butadiene rubber (BR) and polyethylene (PE) find applications in wire and cables, oil seals, hoses, automotive, household articles, footwear, military and other molded articles by virtue of their easy process ability, excellent oil resistance and good mechanical properties (Kear, 2003; Drobny, 2007; Saiah, 2012; Sikder, 2013). New application of polymer blend in the field of transport behavior of various organic solvents and gases through polymers is of great technological importance and it plays a vital role in a variety of barrier applications (Kumar et al., 2012; Bhattacharya et al., 2011). Hence, it is important to study the viscoelastic properties of these materials in order to understand the final processing properties of the materials. Goettler et al. (1982) were the first to study the technical importance of the TPVs in terms of rheological characteristics using a capillary rheometer. Han and White (1995) described the comparative rheological study of PP and PP/EPDM uncross-linked and dynamically cross-linked blends, using various rheological instruments to measure steady shear flow, uniaxial extension, and oscillation flow properties of the compounds. Steeman et al. (2000) reported that TPVs have a yield stress for flow and that the value increases with the

increase in elastomer component in the TPV. An extensive study of rheological response of PP/EPDM blends and the TPVs with phenolic resin as crosslinking agent has been carried out by Jain et al. (2000). Tanrattanakul et al. (2009) studied the effect of phenolic resin as a vulcanizing agent on mechanical properties and morphology of TPE prepared from PP/NR. In our laboratory, different materials (peroxide, phenol formaldehyde resin and maleated polyethylene) were used to control and eliminate the discontinuity of flow curve which was related to the surface distortion of the polymer extrudate. Using these materials had improved the viscosity which is an indication of the processing of the polymers.

The preparation of HDPE/PB blends using different % of phenol formaldehyde resin as a vulcanizing agent in the presence of SnCl_2 as catalyst forms the focus of this research. The prepared TPEs are evaluated by rheological, flow and activation energy properties.

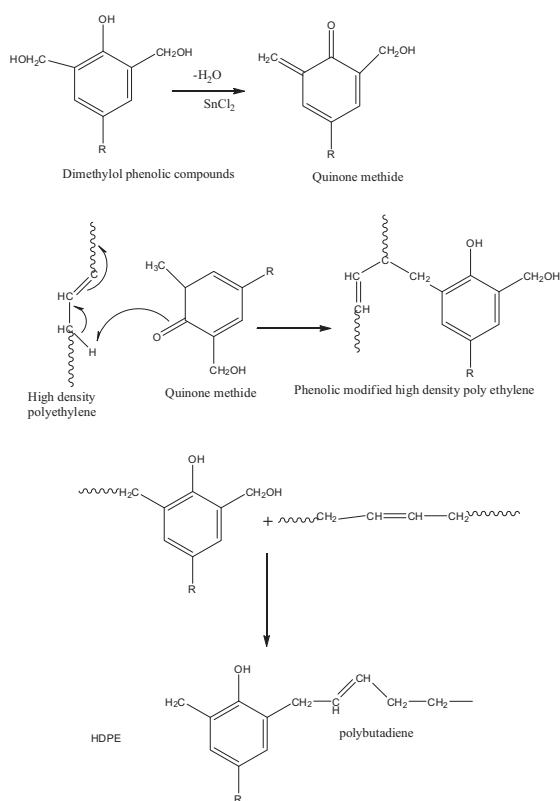
2. Experimental

2.1. Materials

Highdensity polyethylene (HDPE) SCPILEX 6003 was manufactured by the State Company for Petrochemical Industries (SCPI) in Basrah-Iraq (MFI = 0.3 gm/10 min, density = 0.960 gm/cm³). Polybutadiene was obtained from Kumho Petrochemical-Korea, KUMHO KBR has 34.5% of 1,4-cis content. Stannous dichloride (SnCl_2) was manufactured by Fluka Company and used as it is. Phenol formaldehyde resin was prepared in our laboratory.

2.2. Preparation of the thermoplastic elastomer

The thermoplastic elastomer has been prepared using a Haake rheocord meter 90 according to George et al. (1999) and Nakason et al. (2006). As conducted in previous studies (Hernández et al., 2006; Nakason et al., 2006; Mousa et al., 2005), HDPE (70 parts by weight) and dimethylol phenolic resin (1, 3, 5, 7 and 10 wt.%) were mixed at 180 °C with rotor speed of 60 rpm for 3 min. Stannous dichloride (SnCl_2) (2 parts) was added and mixed for 5 min. Then PB (30 parts by weight) was added and the mixing was continued for 5 min., the suggested mechanism is shown in Scheme 1. The products were later cut into small pieces. The prepared TPEs were characterized by Shimadzu FTIR model 2400S. Thin film was prepared by compression molding. The FTIR spectra (Fig. 1) show a weak absorption peak of a trace quantity of the $-\text{C}=\text{C}-$ stretching at 1640 cm^{-1} in HDPE molecules. The presence of the trace carbon double bond confirms the availability of sites for reacting with the methylol groups in phenolic molecules (Scheme 1). In Fig. 1, the spectra of TPE with 5% phenol formaldehyde resin show a combination of HDPE absorption ranges and a number of characteristic absorption peaks relating to phenolic molecules can be seen and indicated to the $-\text{OH}$ stretching vibration of monomeric phenol at 3600 cm^{-1} and hydrogen bonding of phenol at 3380 cm^{-1} and a peak at 1206 cm^{-1} contribute to $-\text{C}-\text{O}$. The peak at 1340 cm^{-1} is attributed to the stretching vibration of phenolic ($\text{C}-\text{OH}$). While the two peaks at 1600 and 1660 cm^{-1} are indicated to the stretching vibration of the $-\text{C}=\text{C}-$ of aromatic rings.



Scheme 1 The mechanism of preparing the TPE using phenol formaldehyde resin as vulcanizing agent.

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