Polymer Testing 45 (2015) 58–67

Contents lists available at ScienceDirect

Polymer Testing

journal homepage: www.elsevier.com/locate/polytest

Material properties

Rheological properties of ground tyre rubber based thermoplastic elastomeric blends

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ARTICLE INFO

Article history:
Received 15 April 2015
Accepted 21 May 2015
Available online 28 May 2015

Keywords:
Thermoplastic elastomeric blends
Ground tyre rubber
Recycling
Rheological properties
Cross-WLF model

ABSTRACT

This work analyses the rheological behaviour of thermoplastic elastomeric blends (TPE) based on ground tyre rubber (GTR), more specifically the rheological behaviour of binary and ternary polypropylene (PP) based blends with different rubber materials: an ethylene propylene diene monomer (EPDM), an ethylene propylene rubber (EPR) and GTR. The study was developed under steady-shear rate conditions by capillary rheometry at three different temperatures. Time–Temperature Superposition Principle (TTSP) was applied to the viscosity curves using a temperature dependent shift factor, allowing the construction of master curves for the analysed blends. The Cross-WLF model was used to predict the rheological parameters, giving numerical results for viscosity similar to the experimental data. GTR increased the blends viscosity. EPR showed rheological behaviour similar to PP, and EPDM presented higher power law behaviour. Pseudoplastic behaviour was observed for all the analysed blends. Incorporation of GTR in TPE blends for injection moulding purposes was found to be a feasible strategy to upcycle this type of potentially wasted material.

1. Introduction

Sustainable waste management policies have been implemented in recent decades to deal with end of life tyres (ELT). The use of complete, shredded or ground tyres in civil engineering projects, sports fields and moulded products are some of the implemented strategies to reutilise this potentially wasted product [1,2]. The use of injection moulding to recycle GTR, a by-product of ELT, can be a viable approach to upcycle this potential waste. For this purpose, the performance of thermoplastic blends with GTR has been studied by several authors [3]. However, due to the GTR being vulcanized and its lack of compatibility with polyolefins, the mechanical performance of these blends is still a limiting factor. Several strategies have been employed to improve the compatibility, such as regeneration techniques and the use of compatibilizing agents. TPE blends based on GTR, fresh rubber and polyolefin matrix (TPE^{GTR}) have also been studied, with special emphasis on their compatibility and morphology [4–13]. The majority of the studies has been focused on the mechanical properties of the blends and very few on their processability, which is a fundamental aspect for the development of TPE^{GTR} blends for the injection moulding industry.

Nowadays, numerical simulation of the injection moulding process is a powerful tool for the production of high quality products with enhanced productivity. The application of such simulation tools on the development of moulds for the injection of TPE^{GTR} blends requires the characterisation of these blends as regards flow and heat transfer. Rheology of polymer blends plays one of the most significant roles in the reliability of the numerical simulations and it is strongly influenced by the nature of the materials, their compatibility as well as their viscosity. A rheological study is, therefore, crucial to understand the influence of the different materials and compositions on the flowability of these blends under different processing conditions. By providing useful information about the material interactions and blend morphology, it can also contribute to better comprehension of their mechanical behaviour.

Prut et al. [14] analysed the dynamic rheological properties of binary PP/GTR composites containing different weight contents of GTR and PP with different molecular weight characteristics. Pseudoplastic behaviour was detected for all the blends with increasing

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http://dx.doi.org/10.1016/j.polymertesting.2015.05.006

GTR content, and a strong deviation from the Newtonian regime. Costa et al. [15] analysed the rheological behaviour of ternary blends based on low density polyethylene (LDPE) with EPDM and GTR in dynamic mode. They observed a decrease of viscosity with increasing frequency, characteristic of pseudoplastic behaviour, although they did not detect a Newtonian plateau even at low frequencies. GTR did not led to substantial increase of viscosity, which was explained by a probable encapsulation of GTR by EPDM. Kim et al. [16] studied the effects of GTR ultrasonic treatment and a compatibilizing agent on the rheological behaviour of polyolefin/GTR blends. The blends indicated pseudoplastic behaviour and the viscosity revealed higher dependence on the polyolefin material rather than on the GTR treatment and compatibilizing agent. The influence of different compatibilizers and bitumen on PP/GTR blends was analysed by Zhang et al. [17]. Bitumen was found to have a plasticizing effect, whereas the compatibilizers increased the viscosity. They concluded also that the polar compatibilizers have a higher effect on the viscosity increase than the non-polar compatibilizers. Scafaro et al. [18] analysed the processability of polyolefin/GTR blends prepared in a twin screw extruder without any additives. Different extrusion parameters such as temperature and mixing speed were set trying to promote the GTR thermo-mechanical devulcanization and, therefore, better compatibilization and mechanical properties. Results indicated a viscosity increase and most pronounced non-Newtonian behaviour for increasing GTR content. Different extrusion parameters and mixing procedures, such as mixing speed and mixing steps have only small effects on the blend rheology. A high processing temperature (300 °C) was found to have some disrupting effect on the three-dimensional network of the crosslinked GTR, and could also lead to some thermal degradation.

This work is part of an ongoing study that aims to contribute on the sustainability of the GTR recycling process, through the development of GTR based blends for injection moulding, without resorting to thermochemical methods. The mechanical and thermal properties of TPE^{GTR} blends based on a high melt flow PP, suitable for injection moulding of thin or/and complex parts, have already been studied by the same authors [19,20]. EPDM and EPR were chosen as the fresh rubber materials due to their toughening effect on the PP based blends and to their compatibility with GTR.

The purpose of the present work is to study the processability of TPE^{GTR} blends by evaluating their rheological behaviour. The effects of the blend composition is analysed by capillary rheometry. The Cross-WLF model is used to predict the flow behaviour of these TPE^{GTR} blends.

2. Rheological analysis

2.1. Theoretical principles

Capillary rheology allows determination of the material apparent viscosity (η_a) defined as

$$\eta_a = \frac{\tau_a}{\dot{\gamma}_a}\ (\mathrm{Pa \cdot s}) \tag{1}$$

where τ_a is the apparent wall shear stress and $\dot{\gamma}_a$ the apparent wall shear rate. These parameters can be calculated accordingly to the Poiseuille Law, based on the barrel diameter, plunger speed and length and diameter of the capillary.

The apparent wall shear rate is given by

$$\dot{\gamma}_a = \frac{4Q}{\pi R^3}\left(\mathrm{s}^{-1}\right) \tag{2}$$

where Q is the volumetric flow rate of the polymer melt and R the capillary die radius.

The volumetric flow rate can be calculated as

$$Q = \pi R_b^2 S_p \left(\mathrm{mm}^3.\mathrm{s}^{-1}\right) \tag{3}$$

where R_b (mm) is the radius of the barrel and S_p (mm.s^{-1}) is the plunger speed. The pressure drop, ΔP (*Pa*), measured across the capillary length, L (mm) is used to determine the apparent shear stress as

$$\tau_a = \Delta P \frac{R}{2L} (\mathrm{Pa}) \tag{4}$$

This model assumes fully developed flow along the entire capillary length, disregarding the extra pressure drop at the entrance of the capillary die. The entrance and exit effects on the rheological data can be corrected using Bagley's correction [21] which allows the determination of the true wall shear stress (τ_W)

$$\tau_W = \frac{\Delta P - \Delta P_e}{2\,L/R}\ (\mathrm{Pa}) \tag{5}$$

ΔP_e – pressure drop at zero distance from the entrance.

The shear rate expression assumes a Newtonian parabolic velocity profile. Due to the polymer non-Newtonian behaviour, the real profile is non-parabolic, similar to a plug-like flow. Assuming no slip conditions, the velocity is higher at the centerline and zero at the wall, which implies the highest shear rate at the wall. The profile shape is defined by a power law index (n) which characterizes the pseudoplastic behaviour of the material. n values below 1 represent the transition from Newtonian flow to shear thinning behaviour. Smaller values imply higher shear thinning behaviour, thus a greater deviation from the (Newtonian) parabolic profile [22].

The Weissenberg-Rabinowitsch correction [23] can be used to determine the true shear rate at the wall as

$$\dot{\gamma}_W = \frac{3+b}{4}\ \dot{\gamma}_a\left(\mathrm{s}^{-1}\right) \tag{6}$$

b is obtained by derivation of the apparent shear rate *vs* the wall shear stress on a double logarithmic plot, and represents the slope of the curve on such plot.

$$b = \frac{d\log\dot{\gamma}_a}{d\log\tau_W} \tag{7}$$

The melt viscosity (η) is then calculated through the relation between both corrected shear stress and shear rate as

$$\eta = \frac{\tau_W}{\dot{\gamma}_W}\ (\mathrm{Pa \cdot s}) \tag{8}$$

Lab Kars software from Alpha Technologies [24] can be used to determine the true shear stress, the true shear rate and the melt viscosity, using capillary rheological data acquired over a 10 to 6000 (s^{-1}) apparent shear rate range. The melt viscosity values for each experiment correspond to the average of at least 3 trials.

2.2. Rheological behaviour modelling

Several constitutive models have been developed to predict the rheological behaviour of thermoplastic materials for injection moulding purposes, including Newtonian, Ostwald (Power-Law), Cross and Carreau models, all of them relating viscosity to other parameters, such as temperature, shear rate and pressure [25]. The Cross-WLF model is based on the equation: