A Experimental Study on the Rhelogical and Mechanical Properties of Blends of Polyethylene and Modified Oil Shale Ash (MOSA)

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Abstract: Blends of Polyethylene (PE) and modified-oil shale ash (MOSA) with different fractions of MOSA were prepared by the melting blend method. The effects of MOSA content on the rheological and mechanical properties of the blend were properly assessed via direct experimental analysis (more precisely, all rheological measurements were performed using a laboratory-scale XSS-300 torque rheometer with single screw extruder; the temperatures were maintained at 170°C, 180°C and 190°C under continuous extrusion). The prepared samples were observed to display a shear-thinning behaviour. Moreover, with increasing the MOSA content, we found the yield strength of the blends to increase, while its elongation at break tends to decrease. Notably, by adding 3 wt.% MOSA only, the tension yield strength of the blends was 61.18% higher than that of pure PE.

Keywords: oil shale ash, polyethylene (PE), shale ash (MOSA) blends, rheology, mechanics

1   Introduction

China is one of the countries that have largest oil shale deposits, which are estimated at 6×10^{13} tonnes and mainly located in Fushun Northeast China. It is estimated that 3.7×10^9 tonnes of oil shale can be mined by open pit mining in Funshun, while about 5%–8% of this quantitity can be extracted as shale oil. The process that involves the pyrolysis of the block oil shale at 500°C is known as Fushun Retort process in china. Every year, large quantities of oil shale ash are discharged as a by-product of oil shale pyrolysis from shale oil plants. Efficient disposal of oil shale ash(OSA) has been all the country issue because of harmful effects on environment such as shortages of new space for landfill.

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In order to reduce the production cost of plastic products and improve certain characteristics, one or more filler is usually needed as an addition to the resin matrix. However, it should be noted that melt mixing and screw extruder are the most preferred method for preparation of PE/oil shale ash blends for industrial applications. Understanding the rheology of filled polymer melts is important for the prediction of material performance in many commercial applications. The investigation on the theology of the filled polymer blends is not only helpful to access the processing characteristics of the materials is but also helpful to understand the polymer-filler interactions and structure-property relationship in blends. As a result, rheology appears to be a unique technique for the study of polymer blends. Previous research concerned with this type of filler focuses on the coal fly ash (CFA), for example, Yang *et al.* (2006), Horiuchi *et al.* (2000) and Dilip *et al.* (2010). CFA containing globular particles with a reasonable size distribution, low density, good shape with good dispersity and fluidity is suitable as a polymer filling material. The usage of OSA in polymer industry will not only reduce its production cost but also may enhance its fresh and hardened properties. However, the use of OSA as a filler is still not widespread. So far little attempts have been made to study the rheological properties of polymer filled OSA. The literature is also limited in the correlation of capillary rheology and mechanics of the polymers filled OSA.

The aim of this paper is to investigate the effect of OSA on rheological properties of PE melt. In this work we studied the rheological and mechanical behavior of low density polyethylene mixed OSA. The rheological behavior was assessed using torque rheometer.

2   Experimental

2.1   Materials

PE samples were provided by DAQING petrochemical company, China. Chemically pure anhydrous ethanol and Industrial-grade silane coupling agent (KH550) were purchased from Sinopharm Chemical Reagent Shenyang Co., Ltd, china. Samples of OSA for this work were generated by the Fushun Retort process. Samples of OSA were ground, dried and sieved to give particles size of less than 200 meshes. The chemical composition of the OSA was listed in **table 1**. The mineralogical compositions of the OSA was shown by **Fig.1**. The composition of the OSA mainly consisted of quartz [SiO_2], kaolinite [$Al_2Si_2O_5(OH)_5$], nepheline [$NaAlSiO_4$].

2.2   Preparation of modified-oil shale ash (MOSA)

OSA was modified by the following process: 50 g OSA was dispersed in the aqueous solution, in which 20 g of silane coupling agent KH550, 72 mL anhydrous

Table 1: Chemical composition of oil shale ash

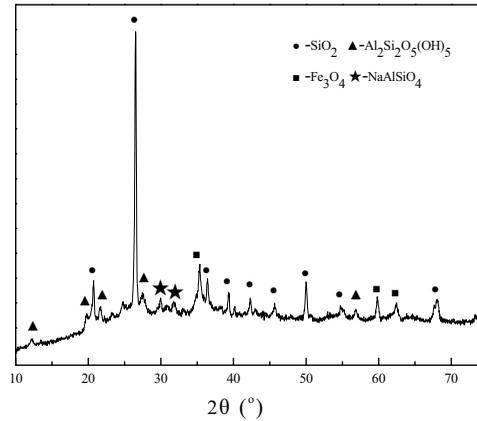| Component	SiO_2	Al_2O_3	Fe_2O_3	K_2O	MgO	TiO_2	Na_2O	CaO	SO_3	P_2O_5
w/%	64.8	20.60	8.20	1.26	1.09	0.96	0.93	0.78	0.78	0.29

Figure 1: XRD pattern of the OSA

ethanol and 8 mL distilled water were added. The suspension was mechanically stirred for 3 h, then filtration. MOSA was obtained after the filter cake was dried at 50°C for 8 h under vacuum.

2.3   Sample preparation

PE filled with four different MOSA concentrations (1, 2 and 3 wt%) were prepared by melt mixing in a Haibo AXN internal mixer for 30 min. The manufacturing temperature was kept at 120°C with 800 rpm of rotaton speed.

2.4   Rheological measurement

The rheological measurements were carried out using a laboratory-scale XSS-300 torque rheometer with single screw extruder. The temperatures were maintained at 170°C, 180°C and 190°C from the hopper to the die under continuous extrusion with a computer-operated screw extruder of length to diameter ratio of 5/1, 7/1, 10/1 and 15/1, respectively. The shear rate range was varied from from 10–30 rpm with a 5 rpm increment. The pressure drop (Δp) between capillary ends was measured with a dynisco pressure transducer. The volumetric flow rate (Q) was determined by collecting and measuring the ejected mass as a function of time. From these data, the wall shear stress (τ_{app}) and the apparent shear rate (γ_{app}) were calculated

as Eqs. (1) and (2):

$$\tau_{app} = (R\Delta P)/2L \tag{1}$$
$$\gamma_{app} = (4Q)/(\pi R^3) \tag{2}$$

where R denotes the radius of the die and L is the length of the die. Most polymers melt is non-Newtonian, meaning that their viscosity depends on factors other than the velocity gradient. Except for rare cases, the viscosity of polymer melts and solutions decrease as the shear rate increases. This could be explained by the alignment of the polymer molecules under the application of the shear. This molecular alignment will allow easier flow of the molecules, which reduces the viscosity at higher shear rates, which is called shear thinning. This phenomenon is described by the famous power law formulated by Ostwald and Waels shown in Eq. (3):

$$\tau_{app} = k\gamma_{app}^n \tag{3}$$

Where k and n are the characteristics of the rheological behaviour (k = consistency index, n = non-newtonian flow index). Thus the plot $\log \tau$ versus $\log \gamma$ should be a straight line whose slope can be used to evaluate non-mewtonian flow index. Non-mewtonian flow index is equal to unity when the flow is Newtonian. A value either greater or smaller than unity shows a shear thickening or a shear thinning, respectively.

Measurements performed suggest that an $L/D < 40$ is not enough to reach a fully developed flow and to make end effects ineligible. Therefore, the correction for end effects are performed using the proposition of Bagley and Rabinowitsch, Bryson. (1970), the real shear rate and the real shear stress are defined as the following Eq. (4) and Eq. (5):

$$\gamma_{real} = (3n+1)\gamma_{app}/4n \tag{4}$$
$$\tau_{real} = \Delta PR/2(L+Re) \tag{5}$$

where e is a multiplication factor according to the Bagley correction, the plot $\triangle P$ versus L/R for a constant value of shear rate should be a straight line whose extansion line can cross L/D axis, the horizontal intercept can be used to calculate e (intercept $= e$).

According to these values, the real shear viscosity η_{real} is then defined as Eq. (6):

$$\eta_{real} = \tau_{real}/\gamma_{real} \tag{6}$$

2.5 Mechanical characterization

The chemical compositions of the OSA was determined by X-ray fluorescence spectrometry (XRF) in a ZSS100e spectrometer (Japan). The mineralogical structure of OSA was determined by a Netherlands PW3040/60 X-ray diffraction (XRD, X-ray powder diffractometer, CuK radiation 40 kV, 50 mA). Tensile tests were carried out following GB/T 1040-92 in order to measure the yield strength and stress and strain at break. Dumbbell shaped specimens of dimensions 115 mm × 6 mm × 3mm in the narrow section were tested using a Reger 10kN electronic universal testing machine (Model RGWT, SHENZHEN, China) at a crosshead speed of 100 mm/min. For each treatment level, three replications were conducted.

3 Results and discussion

3.1 Melt rheological properties

Fig. 2. Real shear stress as a function of real shear rate of neat PE and PE/MOSA blends for various L/D ratios [(a) 5/1, (b) 7/1, (c) 10/1, and (d) 15/1] of the capillary die. Clearly, all of the sample materials exhibited the expected pseudo plastic behavior. Specifically, real shear stress increased abruptly with initial increase in the real shear rate, but it increased more gently with further increase in the real shear rate. For any given real shear rate, the addition of MOSA and an increase in the MOSA content generally caused the real shear stress to increase, suggesting that the presence of MOSA caused the blends to be more restricting to flow.

Fig.3 shows real shear viscosity as a function of real shear rate of neat PE and PE/MOSA blends at 190°C for various L/D ratios (i.e., 5/1, 7/1, 10/1, and 15/1, respectively) of the capillary die. Apparently, real shear viscosity of all of the sample materials exhibited a strong shear rate dependency in the shear rate range investigated, in which it decreased in a non-linear manner with increasing real shear rate, a result indicating a shear thinning behavior of the materials. Even at the very low shear rates investigated, all of the materials did not behave as a Newtonian fluid. On the other hand, at high shear rates, real shear viscosities of all of the sample materials seem to converge or start to converge to a common real shear viscosity. For any given real shear rate, the addition of MOSA and an increase in the MOSA content resulted in a slight increase in the real shear viscosity, indicating the greater viscous nature of MOSA in comparison with that of neat PE.

3.2 Mechanical properties

Table 2 shows yield strength, elongation at yield of neat HDPE and HDPE/MOSA blends. Generally, it can be observed that the mechanical properties of the compos-
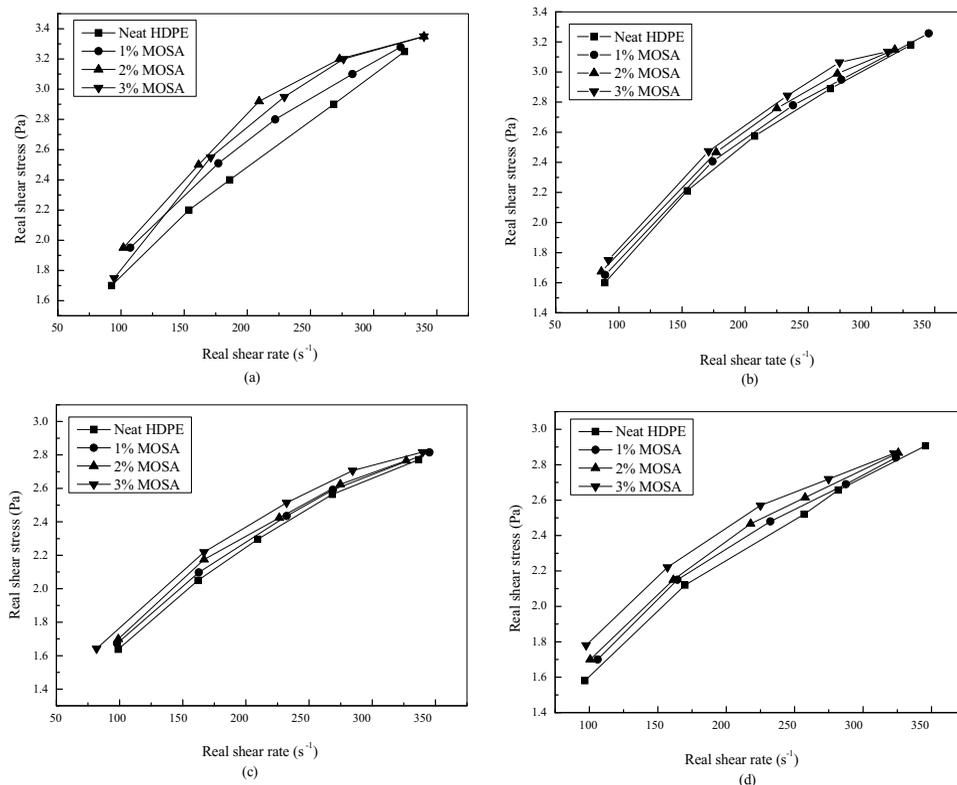
Figure 2: Real shear stress as a function of real shear rate of neat PE and PE/MOSA blends for various L/D ratios [(a) 5/1, (b) 7/1, (c) 10/1, and (d) 15/1] of the capillary die.

ite samples are close to the mechanical properties of neat HDPE. The yield strength of the composite was found to increase with the addition of MOSA from 1% up to 3 wt% and achieved the maximum 61.18% higher strength than that of neat HDPE. The elongation at break shows the reverse order of yield strength phenomena with the addition of OMSA. It is due to the fact that at higher MOSA content the silicon-rich areas become bigger and tend to show characteristics of forming an interconnecting network. When such network-density becomes higher at higher MOSA concentrations they can potentially lead to intense strain localization because of hindered plastic deformation/strain of the matrix. The strain localization around the dense network of silicon dioxide ultimately causes matrix cracking due to severe modulus mismatch between polymer and silicon dioxide and hence ductile yielding behavior that substantially reduced. Therefore, decrease of the ductility at higher MOSA content might be attributed to the presence of MOSA aggregates.
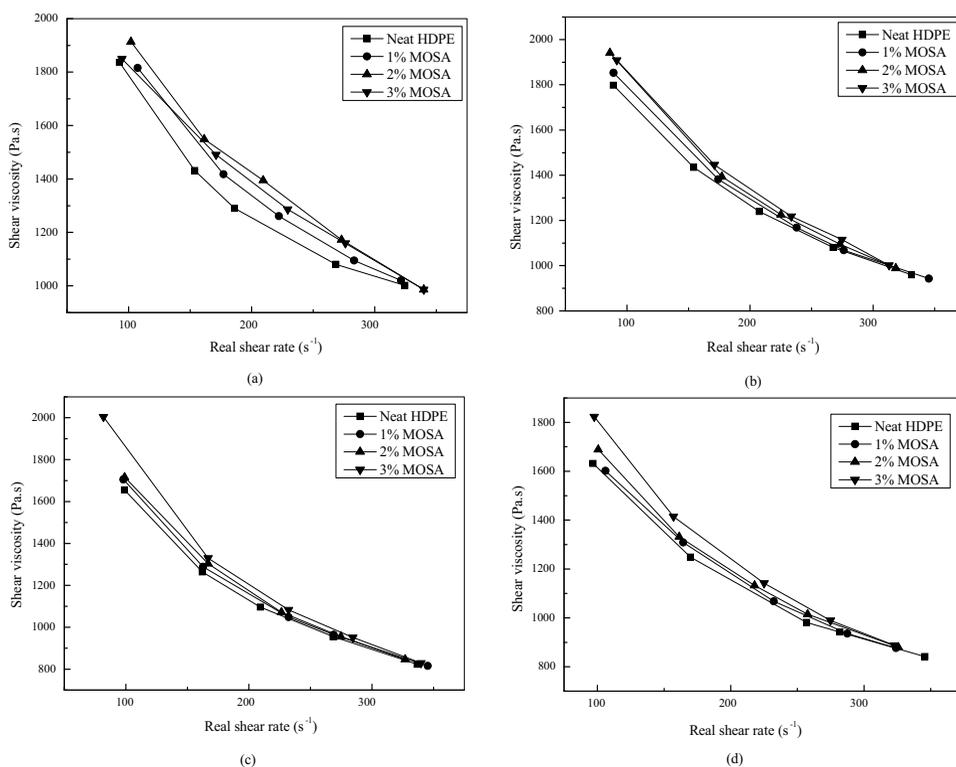
Figure 3: Real shear viscosity as a function of real shear rate of neat PE and PE/MOSA blends for various L/D ratios [(a) 5/1, (b) 7/1, (c) 10/1, and (d) 15/1] of the capillary die.

Table 2: Tensile properties of PE and PE/MOSA blends

MOSA content (wt. %)	Young's modulus (MPa)	Tensile strength (MPa)	Strain at break (%)
0	162.51	16.32	62.66
1	188.22	23.03	61.33
2	186.50	25.64	60.80
3	196.84	26.31	57.11

4 Conclusions

The melt rheological properties of PE/MOSA blends and their mechanical properties were investigated experimentally. For the given sample material, the real shear stress was found to increase with increasing real shear rate and the real shear stress

was generally found to increase with the addition of progressively larger amounts of MOSA. All of the sample materials exhibited a clear shear-thinning behavior.

Our study demonstrated that MOSA can play an important role in a PE matrix. Incorporation of the MOSA tends to improve the rigidity, strength, but it dramatically decreases the elongation at break.

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