Featured Letter

Molar mass and temperature dependence of rheological properties of polymethylmethacrylate melt

Zhili Lu [a], Yamin Pan [a,b], Xianhu Liu [a,b,*], Guoqiang Zheng [a], Dirk W Schubert [b], Chuntai Liu [a]

[a] National Engineering Research Center for Advanced Polymer Processing Technology, Zhengzhou University, Zhengzhou 450002, China
[b] Institute of Polymer Materials, Friedrich-Alexander University Erlangen-Nuremberg, Martensstr. 7, 91058 Erlangen, Germany

ARTICLE INFO

ABSTRACT

The influence of molar mass and temperature on the rheological properties of polymethylmethacrylate (PMMA) melts was investigated by dynamical mechanical and creep-recovery experiments. The results shown that the steady state viscosities obtained from both experimental modes were in good agreement, and a well linear relationship between the activation energy and molar mass was obtained. The creep compliance of PMMA increased with the molar mass increased or temperature decreased, while the linear steady state recoverable compliance was found to be independent of the molar mass and temperature. Moreover, it was found that the master curves followed the time-temperature superposition principle well in the whole frequency range or time scale.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

Polymethylmethacrylate (PMMA) is a transparent thermoplastic with low gas permeability and good dimensional stability. For these reasons, it is widely used for applications in optical, actuation, sensor, biomedical applications, polymer electrolytes, conductive devices and so on [1–3]. It is also good compatibility, low-cost and amenable to a variety of fabrication methods which makes it suitable for mass production in the development of nanocomposites and nanotechnology [4–9]. PMMA could be synthesized in isotactic, atactic, and syndiotactic forms. The amorphous nature of PMMA is governed by its tacticity in the following order: syndiotactic > atactic > isotactic. The glass transition temperature goes in descending order [10]. Commercial PMMA is the cross-linking mixture of different tacticities.

Rheology is a well establish science to get an insight into the deformation behavior of materials. Dynamic mechanical or creep-recovery experiments are commonly used [4–9]. So far, it has been demonstrated that dynamic mechanical experiments are powerful methods for the rheological characterization of polymer melts and particle-filled polymers. The viscosity and the elastic compliance of a polymer which enable important insights into the molecular structure can be determined in a straightforward way.

Creep, as a time and temperature dependent phenomenon, also is of importance for material applications requiring long-term durability and reliability. Some studies on the creep performance of PMMA materials filled with different nanoparticles were carried out [6–8]. However, the influence of the molar mass or temperature dependence on rheological properties of pure polymer could not be observed. Therefore, in this study, the influence of molar mass and temperature on the rheological bheavior of PMMA melts was investigated by dynamical mechanical and creep-recovery experiments.

2. Experimental

Commercially available PMMA Plexiglas 6 N, 7 N and 8 N with a density of 1.19 g cm^{-3} were supplied by Evonik Röhm GmbH, and their number-averaged molar masses were 84, 92 and 99 kg/mol, respectively. The materials were prepared by melt mixing and compression molding. Before the sample preparation and measurements, the materials were dried at 80 °C under vacuum for 24 h. The rheological measurements were carried out with the materials in the molten state under a nitrogen atmosphere using a modified stress-controlled shear rheometer Gemini from Malvern Instruments. Before starting any experiment, the sample was allowed to equilibrate for 10 min.

3. Results and discussion

To gain insight into the flow behavior of the pure polymer matrices, the mobility of PMMA matrices at different temperatures was measured. In Fig. 1 the magnitude of the complex viscosity as
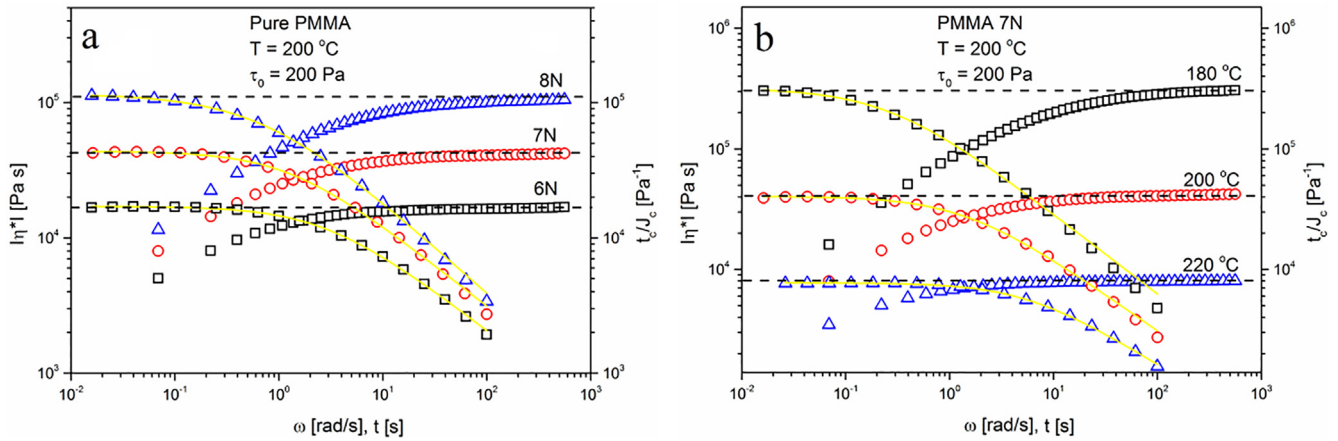
Fig. 1. Complex viscosity vs. angular frequency in compared with t_c/J_c vs. creep time for different PMMAs at 200 °C (a) and PMMA 7 N under different temperatures (b). The lines are fits to Eq. (1).

a function of the angular frequency was compared with t_c/J_c as a function of creep time for the different PMMAs and PMMA 7 N at different temperatures. It was seen that the steady state viscosities obtained from both experimental modes were in good agreement. Moreover, it was observed that the viscosity decreased with decreasing molar mass or increasing temperature. The viscosity increased with the decrease in frequency until a constant value, called zero shear viscosity η_0 was attained. For example, at 200 °C the zero shear viscosity of PMMA 6 N is 17.1 ± 0.1 kPas whereas it is 42.4 ± 0.5 kPas for PMMA 7 N and 110 ± 5 kPas for PMMA 8 N, respectively. Therefore, the Carreau equation was introduced to extrapolate η_0.

$$|\eta^*| = \frac{\eta_0}{\left(1 + \left(\frac{\omega}{\omega_0}\right)^m\right)^{n_0}} \tag{1}$$

where ω_0 is the critical angular frequency, at which the viscosity function begins to decrease; n_0 and m are the fit parameters. As shown in Fig. 1, the fit line was in good agreement with the experimental data.

The Arrhenius plots of η_0 against the temperature are revealed the flow activation energy of PMMA mobility. In our case, the Arrhenius equation can be expressed as

$$ln\eta_0 = lnA - E_a/RT \tag{2}$$

where R is gas constant, A is arbitrary constant, and T is absolute temperature. Fig. 2 shows the Arrhenius plots of η_0 as a function of the inverse of temperature for different PMMAs. It was observed that $ln\eta_0$ held a well linear relationship with the inverse of the temperature. The value of E_a was estimated by Eq. (2) to be about 154, 162 and 171 kJ/mol for PMMA 6 N, 7 N and 8 N, respectively. Moreover, it was found that E_a showed a well linear relationship with the molar mass (insert of Fig. 2). The differences in activation energy can be explained by differences in the mobility of the polymer chains [11–13].

Fig. 3 shows the creep and recoverable compliances of the different PMMAs at 200 °C and PMMA 7 N at different temperatures. The creep compliance J_c increased with increasing the creep time and reached the terminal flow zone, which was characterized by a double-logarithmic slope of one. The recoverable compliance J_r grew with recovery time, too, and reached a stationary value J_e^0 at longer times. Morevoer, a decrease of creep compliance with increasing molar mass or decreasing temperature was observed due to the higher viscosity. The linear steady-state recoverable compliance J_e^0 of pure PMMA was found to be independent
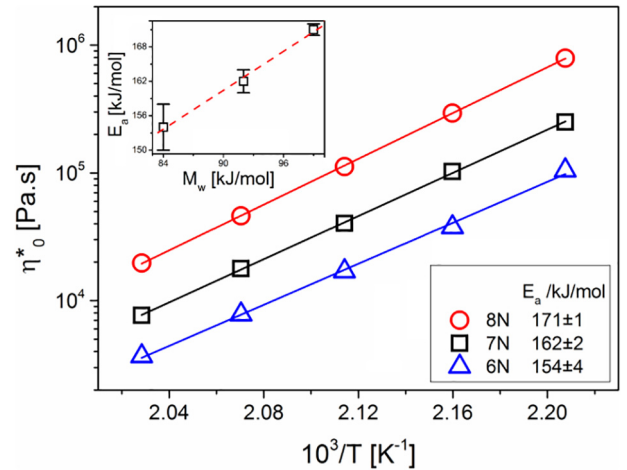
Fig. 2. Arrhenius plots of η_0 vs. $1/T$ for different PMMAs. Insert: E_a vs. M_w.

of the molar mass and temperature, and attained a value of $2.9 \pm 0.2 \times 10^{-5}$ Pa^{-1}. Those results were in good agreement with the literature [6–8] from which it was known that the linear steady-state recoverable compliance was independent of the molar mass and temperature for linear polymers.

The time-temperature superposition (TTS) is a valuable tool for describing the viscoelastic behavior of linear polymers over a broad range of times or frequency through shift of the experimental data at various temperatures to a common reference temperature [14]. The shift factor a_T is a function of temperature and follows the so-called Williams-Landel-Ferry (WLF) equation at processing temperatures, i.e.

$$loga_T = -\frac{c_1(T - T_0)}{c_2 + (T - T_0)} \tag{3}$$

T and T_0 are the actual and reference temperature, respectively; c_1 and c_2 are material-specific parameters. For pure PMMA, a_T in the dynamic mechanical experiments can be determined as

$$a_T = \frac{\eta_o(T)}{\eta_o(T_0)} \tag{4}$$

For the creep-recovery experiments, the shift factors were calculated as shown in Figure S1a. Within the accuracy of the measurements, a_T should be the same in both experimental modes (Figure S1b).