Colloid Polym Sci (2002) 280: 779–782
DOI 10.1007/s00396-002-0690-3

SHORT COMMUNICATION

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Mechanical degradation of polyisobutylene under turbulent flow

Received: 23 June 2001
Accepted: 1 March 2002

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Abstract Turbulent drag reduction (DR), induced by oil-soluble polyisobutylene (PIB) in kerosene, and chain degradation of PIB in a turbulent flow field are examined via a rotating disk apparatus. The DR efficiency decreases with time owing to the mechanical degradation of the PIB molecules. The DR efficiency and the amount of degradation are fitted to an exponential function and are compared with molecular weights measured by size-exclusion chromatography.

Keywords Drag reduction · Mechanical degradation · Polyisobutylene · Polymer degradation · Kerosene

Introduction

Because of the possible wide range of practical applications, intensive theoretical and experimental studies have focused on the turbulent drag reduction (DR) phenomenon, which arises when small amounts of polymer additives are introduced to a turbulent flow [1, 2, 3, 4, 5, 6, 7, 8, 9]. The most recent of these DR studies investigated DR in one- and two-dimensional turbulent flows [10, 11, 12]. In spite of such intense interest, however, our current understanding of the fundamental DR mechanism remains limited, and we find that various applications of polymer-induced turbulent DR are inevitably hampered by polymer degradation. In a turbulent flow, polymer additives are exposed to high elongational strain as well as high shear, which in some cases leads to scission of polymer chains over time and decreased DR effectiveness [13, 14, 15, 16]. This molecular degradation in turbulent flow is affected by a variety of factors, including the polymer molecular-weight distribution (MWD), temperature, polymer–solvent pairs, polymer concentration, turbulent intensity, and flow geometry.

Although there have been numerous investigations on mechanical molecular degradation in turbulent flow conditions, previous studies on degradation mechanisms were performed under nonuniform and uncontrolled shear flows, such as high-speed mixers and pipe flows that included entrance effects. Brostow [17] related macromolecular conformations in the flow field with DR efficiency and mechanical molecular degradation. Zakin and Hunston [18] monitored DR efficiency in a capillary tube, which is very sensitive to polymer molecular weight. In addition, Culter et al. [19] indicated that much of the mechanical degradation occurs at the entrance of the tube. To reduce entrance effects, Horn and Merrill [20] installed a conical funnel at the entrance of the tube from the feed solution reservoir.

Several theories have postulated that degradation is caused by extremely large extensions of polymer chains [21]. Molecular degradation is related to polymer–solvent interactions, for example, polymer molecules degrade more rapidly in a good solvent. In contrast to this intuitive argument, Moussa et al. [22, 23] found that polymer molecules degraded more rapidly in poor solvents at low Reynolds numbers, while the opposite trend was observed at high Reynolds numbers. They conjectured that their findings were attributed to two possible scenarios: polymer stretching and intramolecular entanglements [24].

Another factor that influences molecular degradation is the MWD of the polymeric additives. We know that DR occurs for higher molecular weights [2]. Den Toonder et al. [25] investigated the molecular degradation mechanisms of poly(ethylene oxide), polyacrylamide, and partially hydrated polyacrylamide.

In contrast to pipe flows (internal flows) the DR phenomenon in external flows has not been well studied. Therefore, we have investigated polymer-induced turbulent DR with various polymeric additives using a rotating disk apparatus (RDA) [15, 26, 27, 28] to examine DR phenomena in external flow. For a homologous series of polyisobutylene (PIB) in three different solvents (cyclohexane, kerosene, and xylene), we examined the solvent effects on DR characteristics [28].

In this study, we examined DR and mechanical molecular degradation of PIB in kerosene using an RDA. We then determined the relationships between the MWD curve and mechanical molecular degradation.

Method

The RDA was used to study both the DR efficiency of PIB and the degradation of the polymer chains in a turbulent flow. The RDA specifications have been reported previously [15, 27, 28, 29]. The turbulence is generated by a Couette flow system [30] or between two counter-rotating disks spaced one disk-diameter apart in a closed cylindrical cell [5, 31].

Turbulence is produced for high rotational Reynolds numbers, $N_{Re} > 3 \times 10^5$, or, equivalently, a rotational speed of the disk, ω, above 77.8 rad/s (or 743 rpm). Here, $N_{Re} \equiv \rho r^2 \omega / \mu$, where ρ is the fluid density, μ is the fluid viscosity, and r is the radius of the disk. The temperature of the system was maintained at 25 ± 0.5 °C. Since the DR phenomenon occurs only in the turbulent region, all the measurements in our study were taken at 1,800 rpm to ensure that they were confined to this region.

We first measured the torque required to rotate the disk for pure solvent, T_S, at a given ω. The percentage DR was then calculated by measuring the corresponding torque required for a dilute polymer solution, T_P, at the same ω [32, 33]:

$$\%\mathrm{DR} = \frac{T_S - T_P}{T_S} \times 100. \qquad (1)$$

The PIB sample for our study (PIB L140) was acquired from Exxon Chemical Americas and had a weight-average molecular weight, $\bar{M}_w$, of 2.52×10^6 g/mol [34, 35]. A small amount of antioxidant was added by the producer to avoid peroxidation of PIB.

For the DR measurement, 1 wt% stock solutions of PIB dissolved in kerosene was initially prepared by stirring the sample for 24 h with a magnetic stirrer. The percentage DR was then obtained as a function of elapsed time by injecting measured quantities of stock solution directly into the turbulent flow field generated in the RDA.

We used size-exclusion chromatography to determine the $\bar{M}_w$ of the polymer in the solution before and after the sample had been exposed to the turbulent flow. The size-exclusion chromatograph used in our study consisted of four Waters ultra-Styragel columns (HR 1, 2, 4, and linear columns), a Waters Rheodyne injector, a 510 high-pressure liquid chromatography pump, and a Waters R410 refractive index detector. Tetrahydrofuran was chosen as the solvent, and the flow rate was maintained at 1.0 ml/min. In order to obtain better resolution, the experiments were performed at 40 ± 1 °C. Before testing the samples, a calibration curve was constructed to obtain molecular-weight curves for the injected polystyrene samples using a polystyrene standard calibration kit (Polyscience, PA, USA).

Results and discussion

We measured the percentage DR as a function of time for PIB L140 in 100-wppm solution. As shown in Fig. 1, the percentage DR decreases as time elapses and then levels off to approximately 55% of the initial percentage DR. Note that for polysaccharide xanthan gum, known to exhibit high shear stability, the DR efficiency retains above 70% of its initial DR level even after 1 h [36]. To obtain better correlation between the percentage DR and the molecular weight, we measured the molecular weight of PIB and MWD several times. Figure 2 illustrates that the molecular weight of the PIB L140 in 100 wppm solution decreases over time, as the chains degrade. Each polymer solution was sampled in situ using a syringe during the DR experiments to determine the polymer molecular weight [15]. We precipitated each sampled polymer solution by adding acetone as a nonsolvent for PIB to determine the molecular weight and the MWD. We repeated this dissolving and precipitation process to purify our samples, and then dried them in a vacuum oven. As shown in Fig. 2, the molecular weight at time t, MW(t), decreases exponentially with time. To

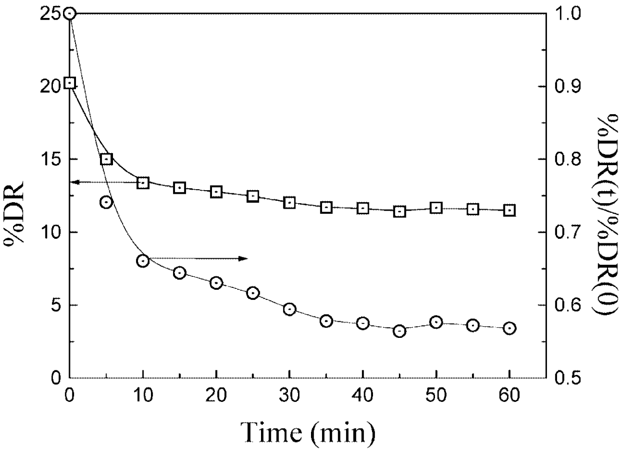

Fig. 1. Percentage drag reduction (*%DR*) and the normalized DR, %DR(t)/%DR(0), versus elapsed time for 100-wppm PIB L140 in kerosene

determine a final limiting molecular weight, $\mathrm{MW}(\infty) = \lim_{t\to\infty} \mathrm{MW}(t)$, we propose the following exponential equations:

$$\frac{\mathrm{MW}(t) - \mathrm{MW}(\infty)}{\mathrm{MW}(0) - \mathrm{MW}(\infty)} = \exp\left(-\frac{t}{\lambda_\mathrm{M}}\right) \tag{2}$$

or

$$\frac{\mathrm{MW}(t)}{\mathrm{MW}(0)} = \frac{\mathrm{MW}(\infty)}{\mathrm{MW}(0)} + \left[1 - \frac{\mathrm{MW}(\infty)}{\mathrm{MW}(0)}\right]\exp\left(-\frac{t}{\lambda_\mathrm{M}}\right), \tag{3}$$

where $\mathrm{MW}(0) = \lim_{t\to 0} \mathrm{MW}(t)$ is the initial molecular weight and λ_M is the relaxation time parameter. From Eqs. (2) and (3) and Fig. 2, MW(∞) of 0.55×10^6 g/mol and λ_M of 43.48 min were obtained for PIB L140.

The variation of the MWD of PIB L140 for the 100-wppm solution in kerosene during the DR experiment is shown in Fig. 3. This result agreed with that Wu et al. [37], who studied the ultrasonic degradation of poly(methyl methacrylate) in tetrahydrofuran, and Kim et al. [15], who studied the mechanical molecular degradation of polystyrene in three different solvents. They observed that an initial narrow polydispersity index ($\mathrm{PDI} \equiv \bar{M}_\mathrm{w}/\bar{M}_\mathrm{n}$, where $\bar{M}_\mathrm{n}$ is number-average molecular weight) or MWD became broader as degradation progresses. It has also been found that chain scission typically occurs around the midpoint of the chain, indicating that the polymers are highly extended when they break [17, 38, 39, 40]. A similar trend for the MWD for polystyrene in three different solvents has been also observed [15]. The degradation of PIB broadens the MWD owing to breakage in high-molecular-weight portions of the chain. Yu et al. [40] showed that monodisperse high-molecular-weight polystyrene molecules are preferentially broken from their degradation study.

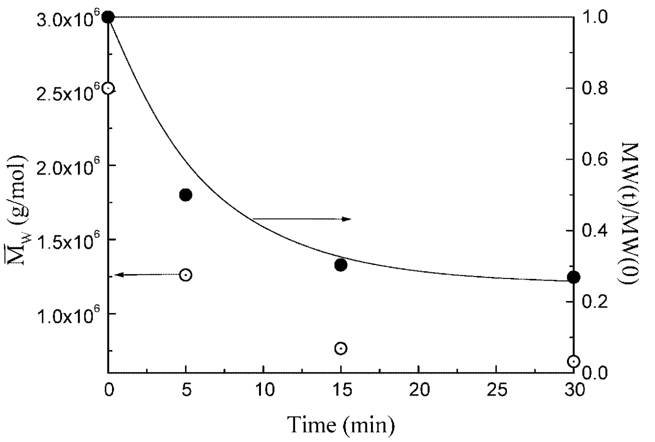

Fig. 2. The weight-average molecular weight, $\bar{M}_\mathrm{w}$, and the normalized molecular weight, MW(*t*)/MW(0), as a function of time for 100-wppm PIB L140 in kerosene at 1,800 rpm. The *open symbols* represent $\bar{M}_\mathrm{w}$, while the *filled symbols* represent MW(*t*)/MW(0)

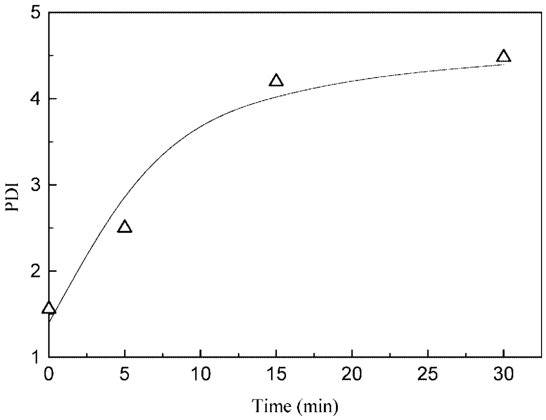

Fig. 3. Variation of the polydispersity index (*PDI*) with time for 100 wppm PIB L140 in kerosene

To illustrate the time evolution of the MWD, the MWD is represented by a Gaussian distribution of a molecular weight fraction. The time-dependent MWD obtained from the Gaussian distribution assumption for PIB L140 [41] is shown in Fig. 4. The calculation was based on the $\bar{M}_\mathrm{n}$ of PIB L140 obtained from size-exclusion chromatography as a function of time. As the high-molecular-weight portions of the chains degrade, they break apart to produce low-molecular-weight chain fragments [19, 20]. As a consequence, the number of these fragments increases with time.

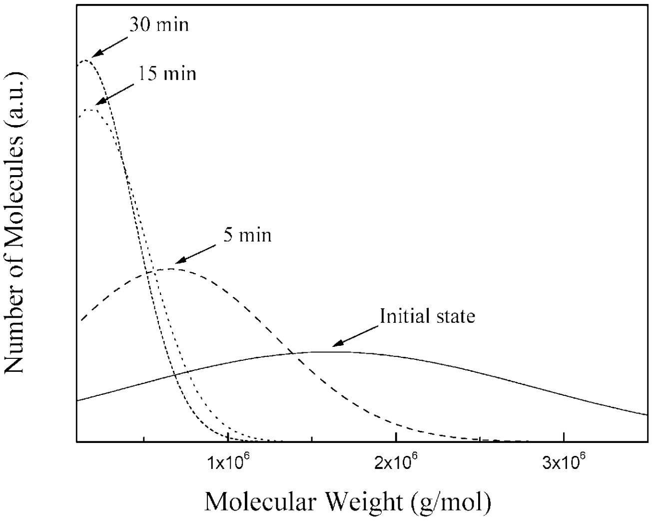

Fig. 4. Evolution of the molecular-weight distribution, before degradation (initial state) and after degradation for 5, 15 and 30 min. The *arrows* indicate the number-average molecular weight

Conclusion

The DR efficiency via polymeric additives was observed to decrease with time owing to the mechanical degradation of the polymer molecules. The mechanical degradation for PIB in an external flow was examined via an RDA and size-exclusion chromatography. Excellent correlation between the percentage DR and the molecular weight or the MWD (or PDI) over time was observed.

Acknowledgement This study was supported by research grants from the Korea Science and Engineering Foundation through the Applied Rheology Center at Korea University, Seoul, Korea.

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