Viscosity and creep compliance of polyoxymethylene copolymers of various average molecular weights

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Abstract: The effect of average molecular weight ($\overline{M}_w$) of polyoxymethylene (POM) on melt viscosity and solid state creep compliance were investigated. Viscosity follows the power function of $\overline{M}_w$. Creep compliance results indicate that time-temperature superposition applies to POM copolymers. Creep compliance in a short time (0.25 s) is independent of $\overline{M}_w$, but in a longer time (10 years) it follows an inverse power law relation with $\overline{M}_w$, up to a critical value of $\overline{M}_w = 81\,100$, where creep compliance becomes independent of $\overline{M}_w$. At intermediate time (17 min), similar to short one, no effect on susceptibility to creep compliance was observed. It was also stated that the activation energy is independent of $\overline{M}_w$.

Keywords: polyoxymethylene, molecular weight, viscosity, creep compliance, activation energy.

Lepkość i podatność na pełzanie kopolimerów polioksymetylenowych o różnych średnich ciężarach cząsteczkowych

Streszczenie: Zbadano wpływ średniego ciężaru cząsteczkowego ($\overline{M}_w$) wybranych kopolimerów polioksymetylenowych (POM) na lepkość stopu i podatność na pełzanie próbki w stanie stałym. Stwierdzono, że w przypadku wszystkich badanych kopolimerów POM zależność lepkości od $\overline{M}_w$ opisuje funkcja potęgowa. Wyniki badań podatności na pełzanie wykazały zgodność z zasadą równoważności temperaturowo-czasowej. Podatność na pełzanie w krótkim czasie (0,25 s) była niezależna od $\overline{M}_w$, natomiast w czasie dłuższym (10 lat) wielkość ta zmniejszała się ze zwiększaniem $\overline{M}_w$, aż do wartości krytycznej $\overline{M}_c$ = 81 100, po której nie zależała już od $\overline{M}_w$. W średnim czasie (17 min), podobnie jak w czasie krótkim, $\overline{M}_w$ nie wpływał na podatność na pełzanie. Zaobserwowano również, że energia aktywacji nie jest funkcją $\overline{M}_w$.

Słowa kluczowe: polioksymetylen, ciężar cząsteczkowy, lepkość, podatność na pełzanie, energia aktywacji.

Polyoxymethylene (POM) is an engineering polymer of formaldehyde with hydroxyl end groups stabilized by esterification or etherification. It is sometimes also referred to as polyacetal or less commonly as aldehyde resins [1]. POM can be a homopolymer or copolymer. The homopolymer consists solely of alternating oxymethylene structures. POM homopolymer is synthesized from formaldehyde or trioxymethylene using cationic polymerization. The acetal copolymer has oxymethylene monomers occasionally interrupted by a comonomer unit, such as an oxyethylene linkage [2]. POM copolymers are synthesized *via* trioxane and dioxolane using the ring-opening cationic polymerization technique [3]. POM is distinguished from other engineer polymers by its crystallinity level that can be between 60 to 90 % [4, 5]. High crystallinity induces very good mechanical properties such as high modulus, stiffness, hardness, fatigue resistance and creep resistance [5, 6]. Other desirable technological properties of POM include dimensional stability, corrosion resistance, superior tribological properties and capability of operating at temperatures above 90 °C [7—9]. All of these properties combined with good moldability allow the use of POM as a structural material in many different applications. In many occasions, POM is used as a substitute for metals or nylons [10, 11]. In fact POM can compete with nylons, which can show some serious deficiencies in dimensional stability in humid environments [12].

The use of POM has been growing steadily in the automotive and electronics industry. It has been replacing metals in pressure-loaded parts, such as window regulators or gear wheels and pinions [13]. POM has also found a niche in the production of office, electric and electronic devices as a structural or dielectric material [14]. POM has even found applications as a binder for feedstock material used in metal or ceramic injection molding [15—18]. It is in this last application that POM requires a better processability since it is filled with metal or cera-

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mic powders normally in more than 50 vol. %, which greatly increase its viscosity. This was the main motivation to develop POM copolymers with lower molecular weight than the currently available ones ($\overline{M}_w < 80\,000$).

It is well known that many properties of polymeric systems in general are greatly influenced by their molecular weight [19—23]. However, there is a gap in the literature with respect to POM copolymers, since low molecular weight POM copolymers were not commonly produced due to technical difficulties during the polymerization. A new polymerization technique has been developed and patented in order to overcome these limitations [24]. Properties of particular interest are viscosity and creep compliance, which are linked to processability and to the long time load-bearing capacity of a polymer, respectively.

Thus, the aim of this paper is to describe how the viscosity and creep compliance are affected by changing the average molecular weight of recently developed POM copolymers.

EXPERIMENTAL PART

Materials

For this investigation eight POM copolymers with different average molecular weights ($\overline{M}_w$) were synthesized by BASF (Ludwigshafen, Germany). The polymerization method of copolymers is described in a recent patent by the producer [24]. The nomenclature and $\overline{M}_w$ values of all the POM materials used in this study are shown in Table 1. $\overline{M}_w$ were measured by the supplier using gel permeation chromatography.

Table 1. Average molecular weights $\overline{M}_w$ of POM copolymers

Copolymer symbol	$\overline{M}_w$	Material shape as supplied
MW010	10 200	powder
MW026	26 700	powder
MW043	43 100	powder
MW081	81 100	pellets
MW092	92 400	pellets
MW109	109 000	pellets
MW129	129 000	pellets
MW204	204 000	pellets

Viscosity measurements

Viscosity measurements in oscillatory mode were performed in a HAAKE MARS-II (Thermo Scientific, Germany) at 180, 190, 210 and 230 °C. These four temperatures are within the range of processing temperatures of POM. A truncated cone-plate measuring-geometry with a diameter of 20 mm and angle of 1° was used in all measurements. Two frequency sweeps were performed in each repetition. The first one increasing from 0.01 to 100 Hz (from 0.0628 to 628 rad/s) and the second one decreasing from 100 to 0.01 Hz. This was done in order to monitor any possible flow instabilities. All measurements were performed applying the shear stress of 100 Pa, previously determined to be within the linear viscoelastic region of all materials investigated. Measurements at a given temperature were performed six times per material. In this study, viscosity results are presented as the magnitude of the complex viscosity ($|\eta^*|$), which is related to the constant rotational viscosity (η) through the Cox-Merz rule [25], which has been previously determined to apply to POM copolymers [26].

Creep compliance measurements

In order to perform creep compliance measurements cylindrical specimens with diameter $D = 5.8 \pm 0.1$ mm and length $L = 29.0 \pm 2.0$ mm were prepared by gravimetrical casting. The gravimetrical casting procedure was developed to avoid orientation of molecules caused by melt flow when using injection molding or extrusion during sample preparation. The casting procedure and the schematics of the equipment used have been described before elsewhere [17, 27]. A mass between 200 and 600 g was put on the unmolten polymer to push it into the melt, thus removing any possible trapped air. The pressing mass was varied due to the large changes in viscosity of materials with different molecular weights. The temperature of the heater was set to 200 °C. The heater was moved at a relatively slow speed of 1 mm/min, giving the pellets/powder enough time to melt.

After casting specimens were cut to the required length and glued with acrylate-based glue (F524 black and activator B, Kemis Plus, Radomlje, Slovenia) to custom made metal holders for gripping the cylindrical specimen to the measuring device. Three specimens were prepared for each type of material listed in Table 1.

Shear creep compliance measurements were performed in a HAAKE MARS II controlled stress rheometer fitted with solid clamps (Thermo Scientific, Germany).

Initial part of the creep measuring procedure started with an annealing phase at 120 °C for 2 h to equalize the mechanical stress—strain history of all materials. Annealing was followed by slow cooling to the first measuring temperature, -20 °C at the rate of 0.028 deg/min to minimize the effects of physical aging.

After cooling down, shear creep measurements were performed in segmental form at eight different temperatures between -20 and 120 °C with step 20 deg. Each specimen was shear loaded with a constant stress of 30 000 Pa for 1000 s, once the desired temperature had stabilized for approximately 15 min. The level of applied stress was previously determined to be within the linear viscoelastic region. The experimental window (*i.e.*, useful segment length) was set between 1 and 1000 s. Three repetitions were performed on different samples for each molecular weight under consideration and their results at a given temperature were averaged.

Following the time—temperature superposition principle, averaged segments were shifted along the time scale in relation to the segments measured at two nominal reference temperatures (T_{ref}) of 20 and 60 °C. Shifting was executed by using the closed form shifting (CFS) procedure [28].

In addition to the segmental creep measurements, long term (75 h) creep measurements were performed at 60 °C, after the sample was annealed at 120 °C for 2 h and cooled at the rate of 0.28 deg/min to the temperature of 60 °C. These measurements were performed in triplicate on a randomly selected POM copolymer, *i.e.*, MW109. These measurements were performed to make sure that time—temperature superposition was valid for POM copolymers since this information was not available in the available literature.

RESULTS AND DISCUSSION

Viscosity

The magnitude of the complex viscosity as a function of angular frequency for all POM copolymers was measured at 180, 190, 210 and 230 °C. The exemplary results obtained at 210 °C are shown in Fig. 1. It can be seen, that almost all of the POM copolymers investigated display Newtonian behavior in the frequency range investigated (0.0628 to 628 rad/s). Only the material with the highest $\overline{M}_w$ (MW204) shows a clear deviation from Newtonian to shear thinning behavior starting at approximately 20 rad/s. This is not unexpected, since in the molten state $\overline{M}_w$ increases, the level of entanglement increases and the amount of free volume decreases [29]. Reduction of free volume and increase of entanglement density lead to chain mobility reduction and as a consequence viscosity increases [30]. However, as the frequency of excitation or shear rate increases these entanglements break and the viscosity starts to decrease, *i.e.* shear thinning. Polymers with higher $\overline{M}_w$ have a higher number of entanglements and therefore can be more susceptible to shear, leading to an onset of shear thinning at lower frequencies, as observed in Fig. 1 for MW204. The viscosity curves become shorter as the $\overline{M}_w$ decreases since flow instabilities develop at larger frequencies when the values of viscosities become too small on the current experimental set-up.

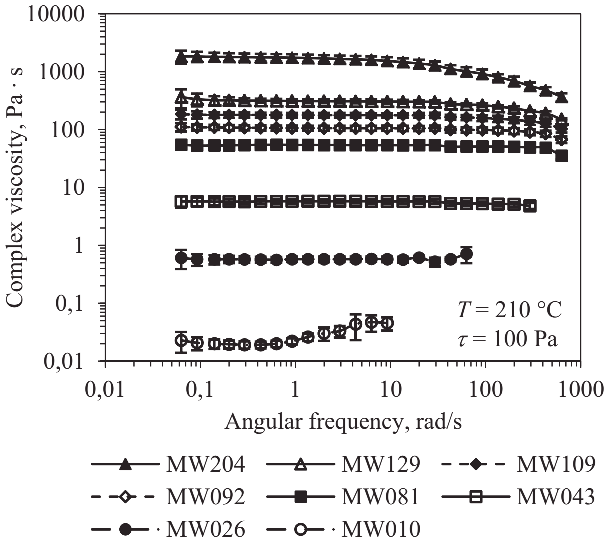

Fig. 1. Dependence of viscosity on angular frequency at temperature of 210 °C and applied stress of 100 Pa for POM copolymers with various $\overline{M}_w$

Polyoxymethylene can be classified as a linear entangled polymer. It is well known that for entangled polymers the shear Newtonian viscosity (η_0), as a function of $\overline{M}_w$ shows a scaling behavior [31]. Such relation follows a power law of the form proposed by Fox and Flory [19]:

$$\eta_0 = K \cdot M_w^a \qquad (1)$$

where: K — the parameter which quantifies the temperature and pressure dependence of the Newtonian viscosity of molten polymers, a — the parameter which relates to the level of entanglement of the polymers.

In this particular study η_0 was estimated as the average of complex viscosity ($|\eta^*|$) measured between 0.06 and 9 rad/s at a given temperature for a particular POM copolymer. The results are presented in Fig. 2. It can be seen that the Fox-Flory equation applies also for POM copolymers at the temperatures here investigated. The values of a parameter has been reported for several polymers to be between 3.3 and 3.7 when $\overline{M}_w > \overline{M}_c$ and ≈ 1 when $\overline{M}_w < \overline{M}_c$, where $\overline{M}_c$ is a critical average molecular weight [20, 30, 21]. Below $\overline{M}_c$ the flow units are single macromolecules, while above $\overline{M}_c$ the flow units are chain segments since the macromolecules are entangled [20]. The parameters for power law fitting for various temperatures are listed in Table 2. As can be seen from these results all the POM materials investigated appear to be

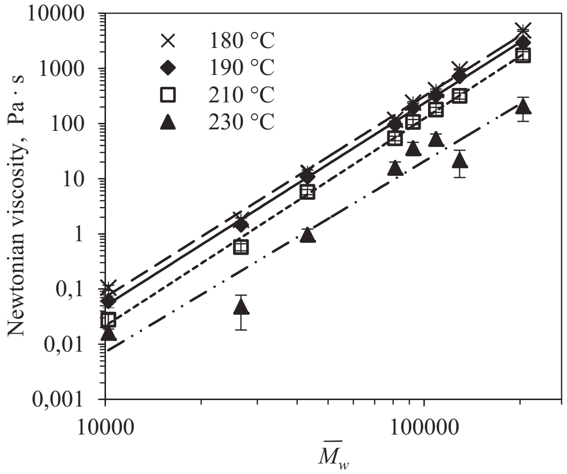

Fig. 2. Power law dependence of Newtonian viscosity and $\overline{M}_w$ for POM copolymers at 180, 190, 210 and 230 °C

characterized by $\overline{M}_w$ higher then $\overline{M}_c$, since the value of *a* is higher than 1.

It was expected that the value of *a* will be greater than 1 since it has been estimated that the molecular weight for entanglement ($\overline{M}_e$) of POM copolymers is 3100 [32]. In addition, it is generally believed that $\overline{M}_c$ is between 2 and 3 times larger than $\overline{M}_e$ [20, 30, 21]. In this particular study the lowest $\overline{M}_w$ available is around 10 000, which is more than 3 times greater than estimated $\overline{M}_e$.

Table 2. Parameters for power law fitting for shear Newtonian viscosity determined at various temperatures

Temperature, °C	*a*	*K*	R^2 of power fitting
180	3.64	$1.94 \cdot 10^{-16}$	0.996
190	3.67	$9.87 \cdot 10^{-17}$	0.999
210	3.76	$1.98 \cdot 10^{-17}$	0.998
230	3.46	$1.05 \cdot 10^{-16}$	0.943

From data presented in Table 2, it can be concluded that with temperature increase a slight increase in the value of *a* is observed. This is true until the temperature reaches 210 °C. Decrease of *a* at 230 °C could be attributed to the onset of degradation. It is known that POM is strongly sensitive to chemical degradation above its melting temperature (~180 °C). For this reason low molecular weight compounds such as melamine and dicyandiamide are used as thermal stabilizers. However, at temperatures 230 °C and higher these thermal stabilizers start to volatilize, thus reducing their thermal stabilizing efficiency [33]. In addition, the *a* value determined at 230 °C may be smaller because of larger error of its determination which shows smaller, than for other isotherms, R^2 value for the power law fit (Table 2). Therefore the viscosity values at 230 °C could be considered as unreliable due to chemical changes in the samples.

The temperature dependence of Newtonian viscosity for POM copolymers is shown in Fig. 3. As expected, an increase of temperature causes the viscosity of POM copolymers to decrease. However, it appears that different copolymers are more susceptible to changes in temperature than others. For example, the viscosity of MW129 when temperature is increased to 230 °C reduced their value by 98 % relatively to the value at 180 °C. For MW043 and MW204 viscosity decreased by 97 and 96 %, respectively, while the rest of the copolymers decreased its initial viscosity by approximately 85 %. As previously mentioned, bigger errors (marked by bars) might be an indication that the copolymers are starting to degrade [5]. If this is the case then the copolymers most sensitive to degradation might be MW026 and MW129.

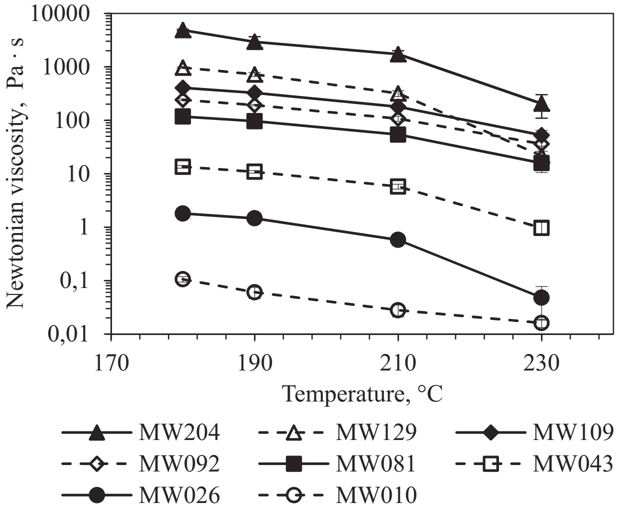

Fig. 3. Temperature dependence of Newtonian viscosity for POM copolymers with various $\overline{M}_w$

Creep compliance

The shear creep compliances segments at different temperatures (-20—120 °C) for the lowest molecular weight sample MW010 are shown as an example in Fig. 4. All other copolymers followed a similar behavior. As expected, the higher the temperature the higher the creep compliance, which is linked to an enhanced chain mobility due to an increase in free volume [34, 35].

After the segments were collected they were shifted using the CFS methodology [28] to two different temperatures 20 and 60 °C to construct the corresponding master curves utilizing the principle of time—temperature (*t*—*T*) superposition or correspondence [36, 37]. The master curves for all the POM copolymers at the reference temperature T_{ref} = 20 °C can be seen in Fig. 5.

In order to check the validity of the master curves prepared by *t*—*T* superposition, long term creep measurements were performed on MW109, which was randomly selected from the list of copolymers available. The com-

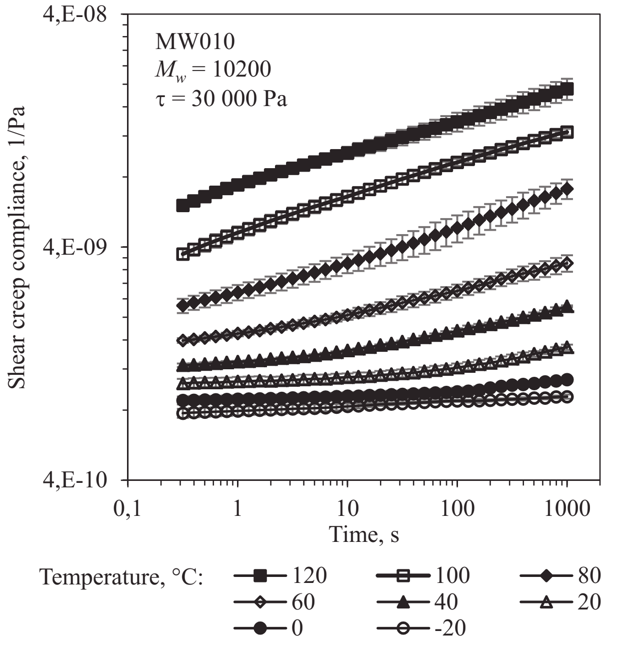

Fig. 4. Shear creep compliance segments determined for MW010 at various temperatures

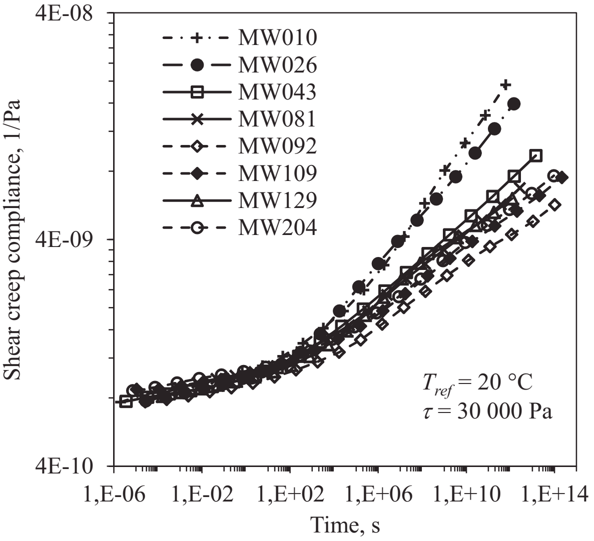

Fig. 5. Shear creep compliance master curves for POM copolymers with different $\overline{M}_w$ at T_{ref} = 20 °C

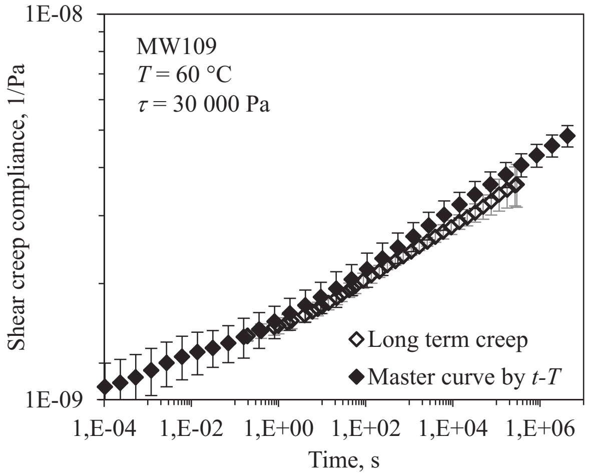

Fig. 6. Comparison between master curve by time—temperature (t—T) superposition and long term creep curve

parison between the master curve prepared by t—T superposition and the long term creep measurement for MW109 is shown in Fig. 6.

As it can be seen in Fig. 6 both shear creep compliance curves are within the experimental error of each other, suggesting that t—T superposition is valid for POM copolymers, despite the fact that they are semicrystalline materials. This is in contradiction to what is reported in the classic polymer literature and it is still believed that t—T superposition is not valid for semicrystalline materials and copolymers [34, 36]. Even though, it has been shown that t—T superposition is applicable to miscible and partially immiscible semicrystalline and amorphous polymer blends [38], polymer liquid crystals [35] and polymer liquid crystals blended with semicrystalline polymers [37]. These measurements were performed to make sure that t—T superposition is valid for POM copolymers, since this information was not available in the literature.

With respect to the effect of $\overline{M}_w$ on the creep compliance of POM copolymers, it can be said that during the first three decades the change in creep compliance is almost negligible. Hence, material's time-dependent behavior at short times is independent of molecular weight. This is important information from the point of view of POM applications that require further processing after initial shaping, for example powder injection molding technology (PIM). In PIM the molded ("green") parts are handled between the injection molding and debinding/sintering step and it is important that the parts creep as low as possible to maintain their geometrical stability [23]. Moreover, after the period of 10 years the increase in creep compliance is only between 7 and 25 times higher, and the highest increase occurs for the POM copolymer with the lowest $\overline{M}_w$. Therefore, Fig. 5 demonstrates that even POM copolymers with low $\overline{M}_w$ have the ability to retain mechanical properties over a long time. Just as a comparison, creep compliance of soft thermoplastic polyurethane loaded under similar conditions for 10 years increases by approximately 50 times [39].

In order to compare the effect of molecular weight on the creep compliance of POM copolymers, isochronal

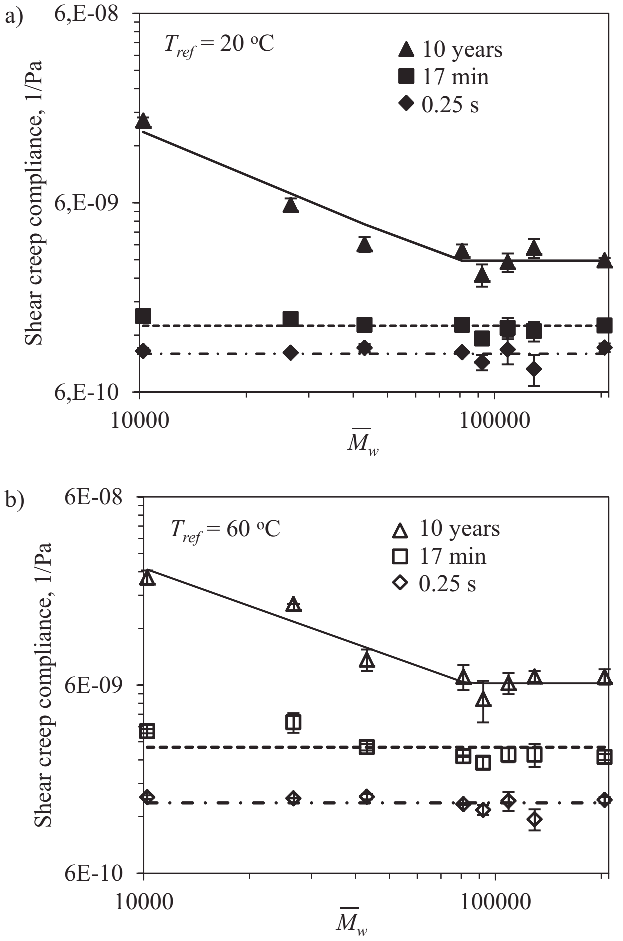

Fig. 7. Dependence of shear creep compliance on $\overline{M}_w$ of POM for three reference times (t = 0.25 s, 17 min, 10 years) at two reference temperatures (T_{ref}): a) 20 °C, b) 60 °C

T a b l e 3. Equations for shear creep compliance dependence on $\overline{M}_w$

Time, s	Equation	T_{ref}, °C	Values	R^2
0.25	J = constant when $10\,200 \le \overline{M}_w \le 204\,000$	20	$J = 9.57 \cdot 10^{-10}$ Pa^{-1}	1.000
		60	$J = 1.38 \cdot 10^{-9}$ Pa^{-1}	1.000
1000 (17 min)	J = constant when $10\,200 \le \overline{M}_w \le 204\,000$	20	$J = 1.35 \cdot 10^{-9}$ Pa^{-1}	1.000
		60	$J = 2.81 \cdot 10^{-9}$ Pa^{-1}	1.000
$3.15 \cdot 10^8$ (10 years)	$J = bM_w^c$ when $10\,200 \le \overline{M}_w \le 81\,100$	20	$b = 1.18 \cdot 10^{-5}$ $c = -0.733$	0.923
	J = constant when $81\,100 < \overline{M}_w \le 204\,000$		$J = 2.96 \cdot 10^{-9}$ Pa^{-1}	1.000
	$J = bM_w^c$ when $10\,200 \le \overline{M}_w \le 81\,100$	60	$b = 7.89 \cdot 10^{-6}$ $c = -0.629$	0.929
	J = constant when $81\,100 < \overline{M}_w \le 204\,000$		$J = 6.14 \cdot 10^{-9}$ Pa^{-1}	1.000

creep compliance curves at three reference times are shown in Fig. 7, at two reference temperatures: 20 and 60 °C. At shorter times (t = 0.25 s and 17 min) the creep compliance is independent of $\overline{M}_w$ at both selected reference temperatures. The horizontal lines that run through the data points in Fig. 7 represent the average value of the measured creep compliances at the selected times, such lines fit very well with the experimental data. However at longer times (t = 10 years), it was observed that creep compliance decreases until $\overline{M}_w$ = 81 100, followed by a plateau until the maximum $\overline{M}_w$ investigated (Fig. 7). The experimental data has been fitted using a combination of power and linear functions (*i.e.*, constants) as shown in Table 3.

The decrease in creep compliance with increasing $\overline{M}_w$ has been reported for other polymers such as polypropylene [40, 41], polyimides [42], poly(1,3-trimethylene carbonate) [43], fiber glass reinforced polyester [44] and even for polyoxymethylene homo-, co- and terpolymers [45]. However, current results show that after a critical $\overline{M}_w$ = 81 100 creep compliance at longer times ($t \approx$ 10 years) becomes independent of $\overline{M}_w$, at least up to $\overline{M}_w$ = 204 000 (Table 3 and Fig. 7). Also at very short times (t = 0.25 s) and intermediate times (t = 17 min), shear creep compliance is independent of the average molecular weight (Fig. 7).

Temperature dependence of creep

The temperature dependence of the creep compliance of POM copolymers is shown in Fig. 8. The isochronal curves at t = 1000 s ~ 17 min (Fig. 8) have a similar shape and a similar trend as the master curves shown in Fig. 5. All copolymers have a similar value of their creep compliance at the lowest two temperatures (-20 and 0 °C), and $T \ge 20$ °C the copolymers with $\overline{M}_w \ge 81\,100$ have creep much less than copolymers with the lowest $\overline{M}_w$. The copolymer with the lowest $\overline{M}_w$ (MW010) has the biggest sensitivity to temperature since the creep compliance increases by 21 times as the temperature increases from -20 to 120 °C. The copolymer with the second lowest $\overline{M}_w$ (MW026) showed an increase by 18 times, followed by the copolymer with the third lowest $\overline{M}_w$ (MW043) with an increase by 11 times. In comparison, the rest of the copolymers have an increase by between 7 and 8 times. Therefore, it can be said that $\overline{M}_w$ has a significant effect on the temperature sensitivity of POM copolymers.

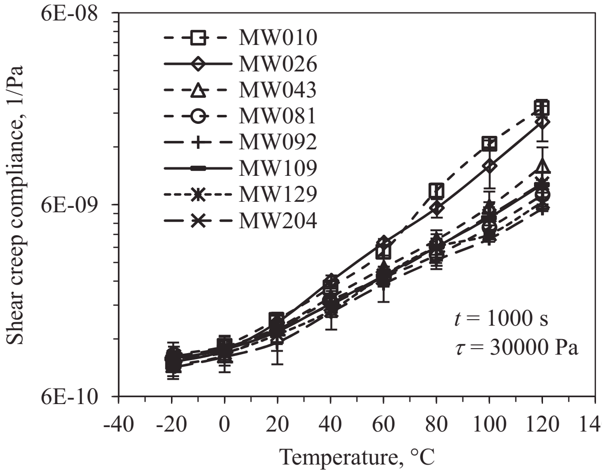

Fig. 8. Dependence of isochronal creep compliance on temperature at reference times of 17 min for POM copolymers with various $\overline{M}_w$

Arrhenius equation for activation energy

The activation energy (ΔE) is the minimum energy required for a process to occur. This includes movement of molecular segments in a polymeric chain [35]. ΔE indicates the sensitivity of the deformation rate to temperature. Using the shift factors (a_T) needed to construct the creep compliance master curves it is possible to estimate the ΔE through an Arrhenius-type of equation as follows:

$$\log a_T = \frac{-\Delta E}{2.31R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right) \tag{2}$$

where: R — the universal gas constant, T_{ref} — the reference temperature.

By plotting the calculated values of $\log a_T$ as a function of the inverse of the temperature difference ($1/T - 1/T_{ref}$),

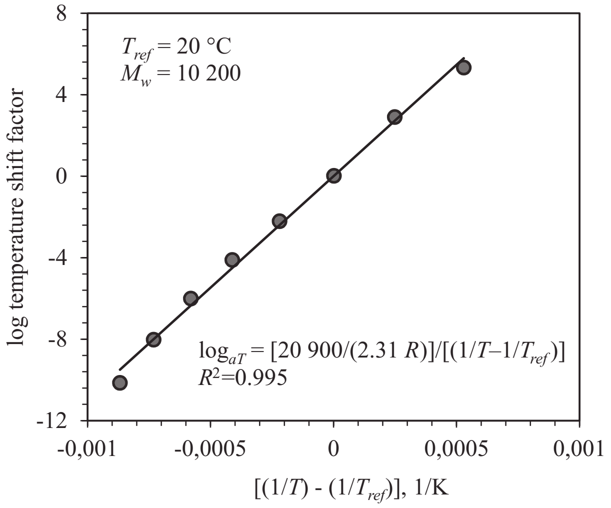

Fig. 9. Logarithm of shift factors (a_T) fitted by a linear function of ($1/T - 1/T_{ref}$) used to estimate the activation energy (ΔE) of POM MW010 at T_{ref} = 20 °C

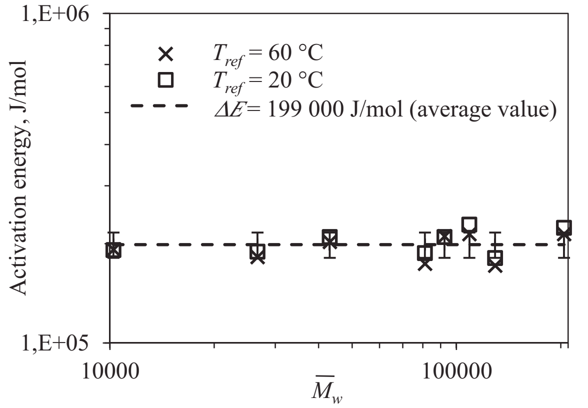

Fig. 10. The effect of $\overline{M}_w$ of POM copolymers on the activation energy (ΔE) estimated using the Arrhenius equation

it is possible to estimate ΔE from the slope of the obtained line for POM copolymers here measured. This procedure has been used for other semicrystalline polymers [46]. An example of such a plot is shown in Fig. 9.

The calculated values of ΔE as a function of $\overline{M}_w$ are shown in Fig. 10. It can be seen that all ΔE values lie within one standard deviation (positive and negative error bars) from the average of all calculated values at the two selected reference temperatures (20 and 60 °C). Therefore, it can be concluded that ΔE is independent of molecular weight within the range of $\overline{M}_w$ here investigated ($10\,200 \le \overline{M}_w \le 204\,000$) and at the selected reference temperatures.

The results of ΔE as a function of $\overline{M}_w$ are in line with the viscosity results and the fact that the Fox-Flory exponent is larger than 1, which indicates that the flow units are chain segments between entanglements rather than individual chains. Since all POM materials here investigated are beyond $\overline{M}_c$ for entanglement then it is expected that the energy required for chain mobility should be similar (ΔE ≈ 199 000 J/mol).

CONCLUSIONS

It has been observed that the Newtonian viscosity of POM copolymers increased with $\overline{M}_w$ according to the power function with exponent values between 3.4 and 3.7, depending on the temperature. Such behavior is similar to other linear entangled polymers. The shear creep compliance at shorter times (0.25 and 1000 s) appears to be independent of $\overline{M}_w$. However, at longer time (10 years), the shear creep compliance decreases with $\overline{M}_w$ following the power law relationship with exponent values between -0.26 and -0.35, depending on the temperature. There seems to be a critical $\overline{M}_w$ after which creep compliance becomes once again independent of $\overline{M}_w$, in this study it appears to be around 81 100. Also it has been shown that POM copolymers with $\overline{M}_w$ below 81 100 are much more sensitive to temperature changes. Results of ΔE calculated using the Arrhenius equation indicate that within $\overline{M}_w$ here investigated, the movable chain segments have a similar length since ΔE appears to be independent of $\overline{M}_w$.

Based on the results here presented appropriate applications could be found for each of the copolymers synthesized, such as binders for powder injection molding feedstock materials [47] and measured data could be used to model the behavior of products made with this polymers in solid and liquid state with finite element or finite volume software. It is important to notice that the viscosity and creep compliance of these polymeric materials could be modified by adding fillers [47] or by modifying the processing conditions, as it has been shown for other thermoplastics [48, 49].

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