

Melt-Rheological Behavior of High-Solid Cement-in-Polymer Dispersions

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ABSTRACT: The rheological behavior of a series of poly (ethylene oxide) melts containing nonhydrated cement is investigated using stress-sweep measurements. The influence of the polymer end-group—diol, monomethyl ether, and dimethyl ether—, molecular weight, and the particle volume fraction is examined. The data suggests that monomethyl ethers adsorb with their single OH group head-on on the cement surface, which reduces the interparticle friction and the viscosity, but mixtures based on monomethyl ethers exhibit shear-thickening behavior. The diols cause the formation of hydrogen-bonded particle networks leading to high viscosities, but these mixtures exhibit shear-thinning

behavior due to the collapse of the network upon shearing. On increasing the particle volume fraction, the samples feature a nonlinear increase in viscosity. Fitting these data indicated that the maximum particle volume fraction is close to the random packing density of spheres and decreases with decreasing shear stress. As coating for glass rovings, the mixtures match the reinforcing performance of solvent-based systems despite lower cement content. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 565–571, 2011

Key words: rheology; composites; polyethers; inorganic materials; melt

INTRODUCTION

Multifilament glass-fibers, so called rovings, are gaining increasing importance as reinforcement in concrete.^{1–3} However, to serve efficiently as reinforcement, the interfilament space inside the multifilament needs to be filled with a compound that binds the individual filaments to each other and to the surrounding matrix. For this, we have recently developed a reactive coating based on water or alkali soluble polymers and nonhydrated cement.^{4,5} The mode of operation is that in contact with cement paste, the polymer dissolves and exposes the embedded cement particles to the aqueous environment. This triggers the formation of a crystalline matrix inside the roving, which binds the filaments to each other and to the surrounding matrix.⁶ However, the previously reported systems rely on organic solvents to reduce the viscosity of these cement-in-polymer dispersions during preparation and application.^{4,5} In terms of a potential scale-up to industrial quantities, this is a less favored option due to cost, environmen-

tal, and safety reasons. A process from the melt would, therefore, be more desirable.

The rheological behavior of pure polymer melts below the critical molecular weight of entanglement is dominated by Newtonian behavior.⁷ Above this point, the elastic interaction between entangled chains lead to deviations from Newtonian behavior. When insoluble particles are suspended in Newtonian polymer melts, deviations from Newtonian behavior are only observed above a certain critical particle volume fraction ϕ_{crit} and/or higher shear rates.⁸ Experimental studies on spherical particles typically report shear-thinning effects.^{8–10} This indicates that above a certain shear force the viscosity-governing particle–particle interactions that hinder the flow decrease. On the other hand, a computational simulation calculated shear-thickening behavior on increasing ϕ by including particle surface roughness and low-distance repulsive forces.¹¹ Thus, under these conditions, friction determines the particle–particle interactions at high ϕ and/or shear stresses indicating that particles with geometries that are particularly susceptible to friction or jamming can give rise to shear thickening. However, shear thickening appears to be a general and reversible property of suspensions provided that the particles do not flocculate.¹² In fact, triggering particle flocculation externally can be used to switch from shear thickening to shear-thinning behavior.¹³ In addition, complex particle geometries amplify the shear-

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TABLE I
Structures and Molecular Weights (Numbers in g mol^{-1}) of the Linear Poly(ethylene oxide) Derivatives Used in This Study

PEO Diol	PEO MME	PEO DME
1000	1000 2000 5000	1000

thickening behavior, whereas broad particle-size distributions attenuate it.¹²

To compare the rheological behavior of different polymer melts containing insoluble particles, the influence of the pure polymer needs to be eliminated. This is achieved by using the reduced viscosity

$$\eta_R = \frac{\eta_\phi}{\eta_{\phi=0}}, \quad (1)$$

where η_ϕ is the viscosity at the volume fraction, ϕ , and $\eta_{\phi=0}$ the viscosity of the pure polymer melt.^{14,15} To describe the correlation of η_R and ϕ , Einstein proposed the equation $\eta_R = 1 + k_E\phi$, where k_E is a correction factor describing the particle shape. However, Einstein's formula is only valid for small ϕ . By introducing a maximum particle packing volume fraction ϕ_M and by considering the decreasing free volume upon increasing ϕ , the following general formula was developed:^{16,17}

$$\eta_R = [1 - (\phi/\phi_M)]^{-k_E\phi_M}. \quad (2)$$

At very low ϕ , eq. (2) can be approximated with Einstein's equation and, thus, k_E can be obtained from the initial slope when plotting η_R versus ϕ . k_E was found to be 2.5 in the case of spheres,⁹ and increases with increasing anisodiametricity to, e.g., 3.1 in the case of cubes.⁸ Perfect close packing of monodisperse spheres results in a volume fraction of $\phi_M = 0.74$. However, the random packing of spheres, which is basically a collection of tetrahedral aggregates, was found to result in an effective ϕ_M of ~ 0.61 – 0.65 .¹⁸ Additionally, ϕ_M further decreases with increasing anisodiametricity.¹⁹

Herein, we report the melt-rheological behavior of cement-in-polymer dispersions designed to improve the fiber-matrix adhesion in textile-reinforced concrete. These mixtures are an advancement of previous, solvent-based systems^{4,5} to meet industrial demands. Linear poly(ethylene oxide)s were chosen as dispersing medium due to their low-initial melt viscosity. Using stress-sweep measurements, the interactions of cement particles and the polymers

with different end-groups and molecular weights are studied. The dispersions under investigation obey eq. (2), which was used to quantitatively assess ϕ_M and k_E at different shear stresses. Based on the rheological and mechanical behavior, a mixture is recommended for the scale-up.

EXPERIMENTAL

Materials

The fine-grained cement with a particle size of $d_{95} \leq 6 \mu\text{m}$ was obtained from Dyckerhoff AG, Neuwied, Germany. The set of linear poly(ethylene oxide)s in the form of diol (PEO Diol), monomethyl ether (PEO MME), and dimethylether (PEO DME) listed in Table I was purchased from Fluka and Sigma Aldrich. The densities of the polymers were obtained from company's catalogs and the density of the cement particles from Ref.²⁰

Poly(vinyl alcohol) (PVA) $M_w = 9500 \text{ g mol}^{-1}$, saponification number 302, and poly(vinyl acetate)s (PVAc) $M_w = 12,000$ – $18,000 \text{ g mol}^{-1}$ and $M_w = 110,000$ – $150,000 \text{ g mol}^{-1}$ were obtained from Wacker. Poly(ethylene-co-vinyl acetate) (EVA) $M_w = 110,000 \text{ g mol}^{-1}$, with a vinyl acetate content of 40%, was purchased from Aldrich.

Methods

All cement-in-polymer (c/p) dispersions based on poly(ethylene oxide)s were prepared in an IKA HKD-T 0.6 laboratory kneader, by controlling the temperature of the mixing chamber with an external circulator. The cement content of the dispersions was calculated as weight fraction w or volume fraction ϕ according to

$$w = \frac{m_{\text{cement}}}{m_{\text{polymer}} + m_{\text{cement}}} \quad \text{and} \quad \phi = \frac{V_{\text{cement}}}{V_{\text{polymer}} + V_{\text{cement}}}.$$

In a typical preparation, 90 g of polymer were placed in the kneader and melted at 70°C , followed by a total of 210 g cement added in 10 portions.

TABLE II
Matrix of the Samples Under Investigation

w	0.0	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.75	0.77
ϕ	0.0	0.038	0.081	0.13	0.19	0.26	0.35	0.45	0.51	0.54
$M_w/\text{g mol}^{-1}$										
1000 (Diol)	X							X		
1000 (MME)	X	X	X	X	X	X	X	X	X	X
1000 (DME)	X							X		
2000 (MME)	X							X		
5000 (MME)	X							X		

X denotes the prepared samples.

After the final cement portion was added, the mixture was slowly cooled down to 15°C, while kneading to avoid solidification of the mixture into a solid block. This mixture had $w = 0.7$ ($\phi = 0.45$) and the appearance of fine, solid gravel. Mixtures with lower cement content are not hard but plastically deformable at ambient temperature. Table II shows the dispersions used in this study.

For the rheological measurements, a Rheometric Scientific DSR SR 200 stress-controlled rotational rheometer was used. The instrument was fitted with a 40 mm cone and plate geometry with a fixed lower plate and a rotating, truncated cone of 1 Rad cone angle. The temperature was controlled with an external circulator. The c/p samples were presheared using a steady stress of $\tau = 300$ Pa for 5 min immediately before running the stress-sweep measurements from 1 to 300 Pa and back. The temperature-viscosity curves in Figure 1 were recorded by heating the pure polymers in the rheometer to above the melting point and cooling at a rate of 2.6–5 K/min while constantly measuring the viscosity.

RESULTS AND DISCUSSION

Previous cement-in-polymer dispersions used to improve the fiber-matrix adhesion in textile-reinforced concrete were based on PVAc and its derivatives such as PVA or EVA for performance reasons.^{4,5} However, these polymers exhibit rather high melt-viscosities (Fig. 1). Because the addition of high amounts of insoluble inorganic additives increases the viscosity, low-molecular weight poly(ethylene oxide)s were chosen, for which the melt viscosities are 3–5 orders of magnitude lower. As poly(ethylene oxide)s are easily water soluble, the cement-in-polymer dispersions made from this group of polymers will work according to the mode of operation outlined before (see Introduction and Ref. 5). This was confirmed by pull-out tests (vide infra).

Figure 2(A) shows the linear stress-sweep measurements of the pure PEO-polymers at 70°C as reference. All exhibit Newtonian behavior. However, polymers of the same molecular weight but with dif-

ferent end-groups differ in their absolute dynamic viscosities. In such a series, the order reads dimethyl ether < monomethyl ether < diol. A similar trend was observed for solutions of poly(ethylene oxide)s in ethylene glycol or ethylene glycol ethers and was explained by the formation of intermolecular hydrogen bonds, which give rise to so called "apparent longer chains."^{21,22} Hydrogen bonding also seems to occur in the pure polymer melts in the case of the diol or the monomethyl ether as, e.g., for the 1000 g mol⁻¹ series, the dynamic viscosity of the diol is 54% and that of the monomethyl ether 30% higher than that of the dimethyl ether. However, due to hydrogen bonds being considerably weaker than covalent bonds, the dynamic viscosity of the 1000 g mol⁻¹ monomethyl ether is lower than the one of the 2000 g mol⁻¹ dimethyl ether.

Figure 2(B) shows the double-logarithmic plot of η versus M_w for the monomethyl ether series. Such plots are frequently used to determine the critical molecular weight of entanglement, expressed by a single significant jump in the slope.⁷ However, poly(ethylene oxide)s are known to show a different behavior, as the slope in the double-logarithmic plot continuously increases.²³ This was explained by a continuously increasing

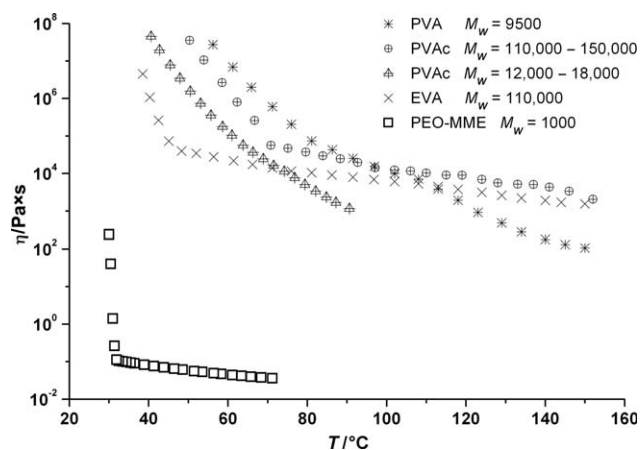


Figure 1 Melt-rheological behavior of pure poly(vinyl acetate) and its derivatives used in solvent-based c/p mixtures in comparison with PEO MME 1000 g mol⁻¹.

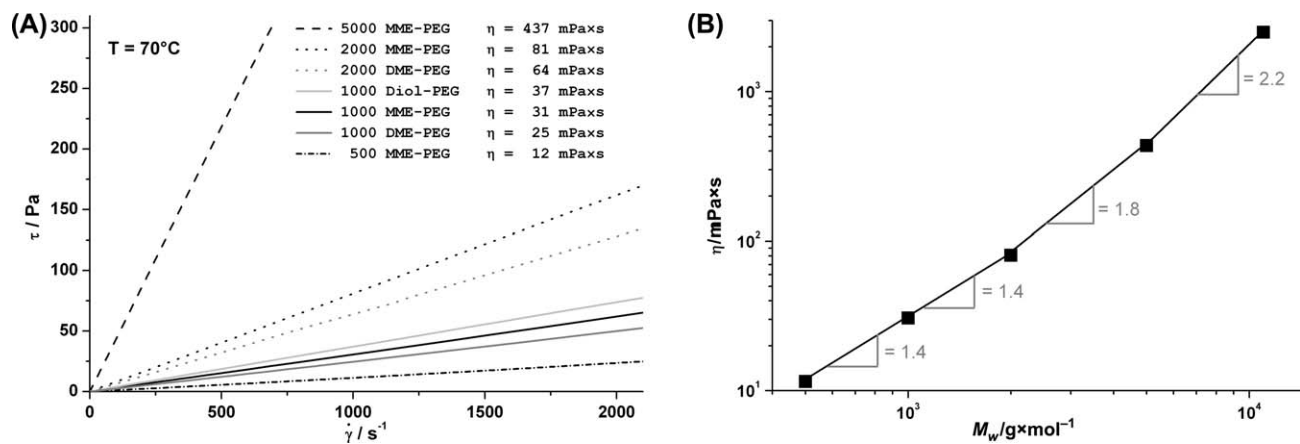


Figure 2 Rheological behavior of PEO melts. Influence of the molecular weight and end-groups (A) and the development of the melt viscosity for PEO monomethyl ethers (B).

content of intermolecular chain interactions, possibly due to hydrogen bonding.^{21,22}

The cement particles used as solid, insoluble additive in this study are highly irregular with sharp edges and a broad size distribution (Fig. 3). As a result, the dynamic viscosities of the cement-in-polymer dispersions at, e.g., constant $\phi = 0.45$ and $M_w = 1000 \text{ g mol}^{-1}$ exhibit an at least 15 times higher initial viscosity than the corresponding pure polymers (vide infra).

Within a given molecular weight, the dynamic viscosities follow the order of the pure polymers, i.e., $\eta_{\text{DME}} < \eta_{\text{MME}} < \eta_{\text{DIOL}}$, at low-shear rates. However, to eliminate any influence of the polymer, the reduced viscosities according to eq. (1) have to be compared (Fig. 4). With this normalization, the order of the viscosities changes. At $\phi = 0.45$, η_R of samples based on the dimethyl ether is slightly higher than η_R of the samples based on the monomethyl ether, even at low-shear rates. Upon increasing shear rate, both the mono- and the di-methyl ether sam-

ples show shear-thickening behavior, as a result of jamming and interparticle friction of the highly irregular cement particles. Shear thickening was found to be reversible in all experiments, but is less pronounced for the mixture based on the monomethyl ether. A control experiment using quartz sand of similar particle geometry, size, and size distribution as nonreactive, noncementitious additive also showed reversible shear-thickening behavior. This indicates that the shear-thickening effect is due to the particle form rather than, e.g., undesired hydration of the cement during the measurement.

Both findings, lower reduced viscosity and less pronounced shear thickening for the monomethyl ether, might be explained by the formation of H-bonds between the hydroxyl-group of the PEO monomethyl ether and the surface of the cement. This attaches the polymer to the particle surface and gives rise to a softer interphase around the cement particles, which acts as a lubricant to reduce the interparticle friction [cf. Fig. 5(A) for a proposed

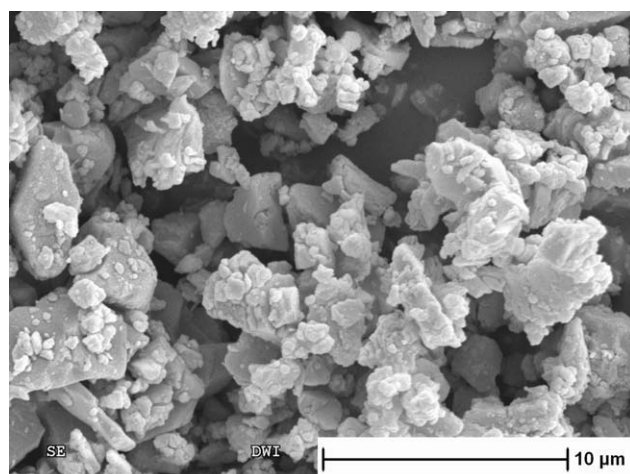


Figure 3 SEM image of the cement particles used in this study.

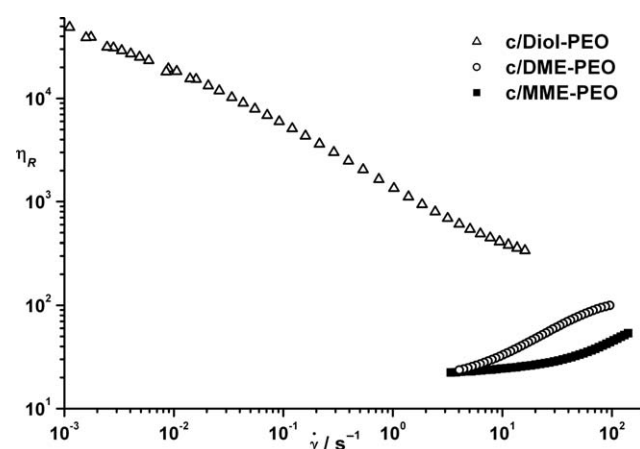


Figure 4 Influence of the end-group on the rheological behavior of cement-in-polymer dispersions with $M_w = 1000 \text{ g mol}^{-1}$ and $\phi = 0.45$ in all cases. $T = 56^\circ\text{C}$.

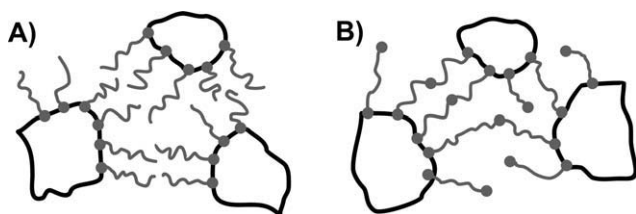


Figure 5 Schematic illustration of the adsorption of PEO monomethyl ethers (A) and PEO diols (B) on cement particles. Polymer and particles not to scale.

mechanism]. A similar lubrication effect is observed with commercial superplasticisers, which use PEO chains grafted to poly(acrylic acid) to lower the viscosity of cement paste.^{24,25} However, such an effect is not possible for the dimethyl ether due to the lack of hydroxyl groups.

In contrast, the sample based on the diol starts with a very high-initial viscosity at low-shear rates and shows pronounced shear thinning of approximately two orders of magnitude. This observation can again be explained by the formation of H-bonds between the polymer and the surface of the cement particles. With OH groups at both ends of the polymer, the chains can bridge cement particles and one cement particle can host multiple hydrogen bonds, which results in the formation of a hydrogen-bonded network [Fig. 5(B)]. A related phenomenon in the solution chemistry of colloids is known as "bridging-type flocculation."^{26,27} Upon shearing, the network of hydrogen bonds is stressed, and with increasing shear stress, the bridges gradually collapse leading to the observed shear-thinning behavior. Extrapolation of the curves in Figure 4 appears to indicate that they would intersect in one point, which is in agreement with the investigations of Brown et al. saying that the viscosity at high-shear rates is rather unaffected by particle interactions.¹³ However, this point is beyond the limits of the used rheometer.

To further investigate the lubricating effect observed for samples based on the monomethyl ether at higher shear rates, a series of mixtures at constant $\phi = 0.45$ but increasing molecular weights was prepared. Through the use of η_R , the curves in Figure 6 are directly comparable and the differences are related to the interactions between cement particles and the polymer chains. An increase in the molecular weight from 1000 g mol^{-1} to 2000 g mol^{-1} amplifies the lubricating effect in such a way that no significant friction or jamming is observed in the form of shear thickening. However, it should be noted that the absolute viscosity of the mixture based on the 2000 g mol^{-1} PEO MME are $\sim 55\%$ higher than those of the 1000 g mol^{-1} at high-shear stresses and $\sim 160\%$ higher at low-shear stresses.

Samples based on the 5000 g mol^{-1} PEO MME show a significantly different behavior. At low-shear rates, the reduced viscosities are considerably higher than for samples based on the 1000 and 2000 g mol^{-1} , and slight shear thickening is observed. However, with increasing shear rates, a plateau is reached. Both observations indicate differences in the interfacial structure compared with the samples based on the 1000 and 2000 g mol^{-1} PEO MME. Careful observation of Figure 2(B) reveals that the pure 5000 g mol^{-1} PEO MME is already more entangled than the 2000 g mol^{-1} (slope at 5000 is ~ 2). It is thus assumed that in the case of the 5000 g mol^{-1} PEO MME, the chains on the cement surface are at least partially entangled with chains in the continuous phase or on the surface of other particles, resulting in the observed higher initial value of the reduced viscosity. The fact that with the 5000 g mol^{-1} PEO MME shear thickening is observed at low-shear stresses as opposed to the 1000 and 2000 g mol^{-1} PEO MME additionally supports the assumption of entanglement being responsible for the different behavior. Although the pure polymer does not show shear-thickening behavior, the entanglement of chains on the particle surface can contribute to jamming and effect shear-thickening behavior. With increasing shear rate, the chains on the particle surface are increasingly disentangled until a plateau is reached, where the particles move freely. Because of the steric repulsion of the longer chains, the reduced viscosity becomes more or less shear-rate independent.

The effect of the cement content on the rheological behavior of the polymer melts was studied using the 1000 g mol^{-1} PEO MME (Fig. 7). Upon increasing the volume fraction of the fine-grained cement in the polymer, the behavior gradually changes from Newtonian for the pure PEO-polymer (Fig. 2) to shear

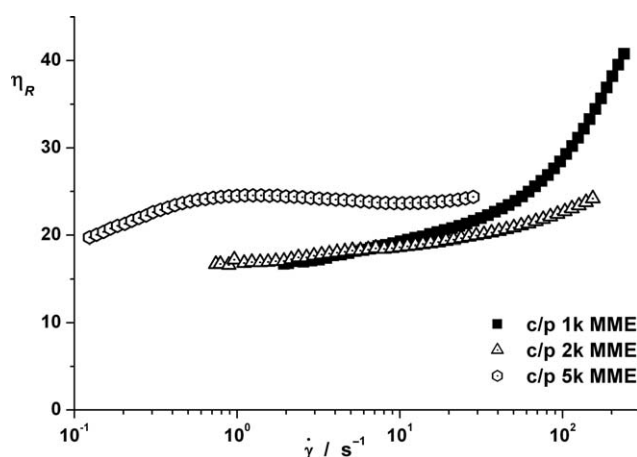


Figure 6 Influence of the molecular weight on the reduced viscosity η_R of c/PEO monomethyl ether dispersions at $T = 70^\circ\text{C}$.

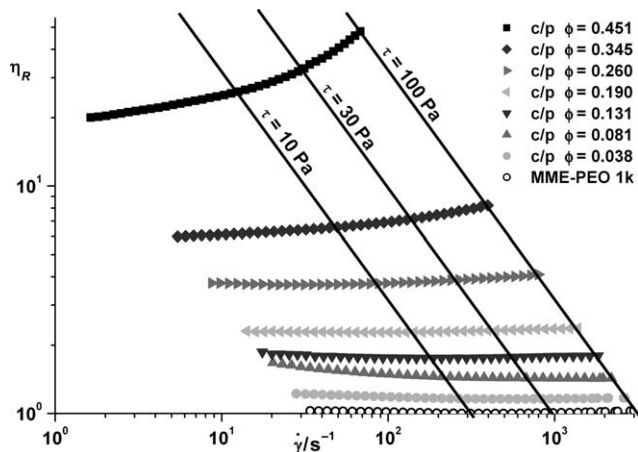


Figure 7 Influence of the cement content in cement-in-polymer dispersions prepared from the 1000 g mol^{-1} PEO monomethyl ether on the reduced viscosity η_R at 70°C .

thickening for highly filled dispersions. The deviation from Newtonian behavior starts approximately at $\phi = 0.26$ (50 wt %). It should be noted that the apparent shear-thinning behavior at low-strain rates for $\phi = 0.081$ might be due to insufficient dispersion of the cement grains during preparation.

The solid lines in Figure 7 connect measurements of equal shear stress τ . It appears that with increasing cement content, η_R does not increase linearly. To corroborate this, the reduced viscosity was plotted against the cement content ϕ at $\tau = 10, 30,$ and 100 Pa (Fig. 8) and fitted using eq. (2). For nonideal systems, the maximum volume fraction ϕ_M is influenced by two factors, namely, the anisodiametricity^{28,29} and the polydispersity.²⁹ With increasing deviation from monodispersity, ϕ_M increases due to smaller particles moving into the gaps between the

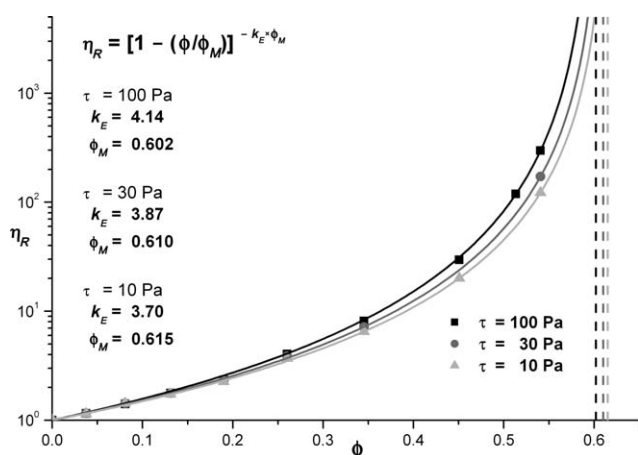


Figure 8 Results of the fit according to eq. (2) using the η_R and ϕ values from Figure 6. The dashed vertical lines indicate the calculated maximum volume fractions ϕ_M .

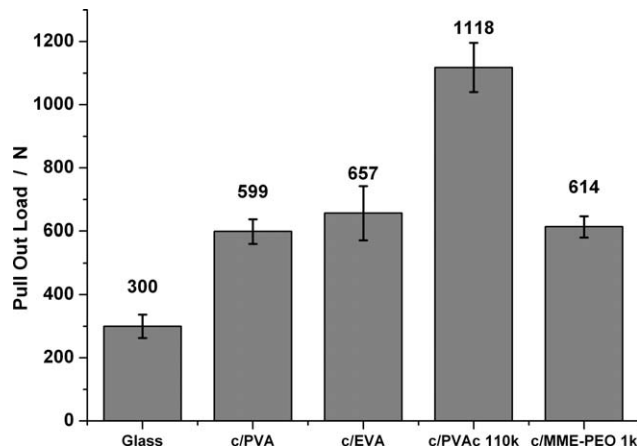


Figure 9 The pull-out load of 2400 tex alkali-resistant glass rovings coated with $c/\text{PEO MME } 1000 \text{ g mol}^{-1}$ from the melt in comparison with reference materials.

larger particles. Increasing anisodiametricity on the other hand decreases ϕ_M , as the packing of irregular formed particles is less perfect.

Figure 8 shows the fit of the data extracted from Figure 7 according to eq. (2) together with the calculated values for k_E and ϕ_M . The following observations can be extracted from the fit: (i) all k_E values are larger than 3.1, the value for cubes, indicating a high irregularity of the cement particles in accordance with the SEM image (Fig. 2); (ii) all ϕ_M values are close to the lower limit of the random packing density of $\sim 0.61\text{--}0.65$,¹⁸ which is in accordance with high k_E values; (iii) upon decreasing shear stress τ , k_E decreases whereas ϕ_M increases. The decrease of k_E is most notable because it indicates the particles behaving more “sphere-like” at lower shear stresses and implies that, at lower shear stresses, the particles can pass each other more easily; in other words, less jamming occurs. A direct consequence of this lower amount of jamming is the observed increase in ϕ_M albeit this being only 1.3 vol % (0.8 wt %).

To test the reinforcing performance of these mixtures, 2400 tex alkali-resistant glass rovings were coated with a mixture based on the 1000 g mol^{-1} PEO MME ($w = 0.7$) in a pultrusion process from the melt. The mixture proved to be easy to handle and fully penetrated the multifilament (data not shown). Double-sided pull-out tests were run as described previously.³⁰ The c/PEO mixture is less efficient in improving the fiber-matrix adhesion than the best solvent-based mixture (c/PVAc , $w = 0.8$) partly because of the lower cement content—a constraint of the melt-based process. However, it matches the c/PVA and c/EVA (both $w = 0.8$) despite the lower cement content and exceeds the pull-out load of the uncoated glass by a factor of 2.

CONCLUSIONS

The rheological properties of cement-in-poly(ethylene oxide) dispersions depend on the polymer properties such as molecular weight and end-groups as well as the cement content. The influence of the polymer properties is not straight forward. Increasing molecular weight provides for increased lubrication and a reduction of the interparticle friction, but at the same time gives rise to entanglement. Changing the end-groups from dimethyl ether to monomethyl ether and diol increases the extent of hydrogen bonding, and in the case of the diols, hydrogen-bonded networks with high viscosities are obtained. As a result, the PEO diols are unsuitable for preparing coating formulations, and the PEO monomethyl ethers with 1000 or 2000 g mol⁻¹ seem optimal in the present system. Increasing cement content causes a disproportionate rise in the viscosities. Using a literature-known model to fit the correlation showed that at lower shear forces, the cement particles behave in a more sphere-like way and as a result, the maximum volume fraction of cement can be increased. Thus, during preparation and application, lower shear forces are recommended which facilitate the processes (lower viscosity) or allow the use of higher cement contents (at a given viscosity).

In contrast to similar, previously published cement-in-polymer dispersions, which required a solvent-based preparation and application process, these mixtures can be prepared and applied from the melt using established equipment and match as coating for glass rovings the performance of the solvent-based systems despite lower cement content. This is an enormous advantage in terms of a potential scale-up and industrial application as coating for continuous glass-fiber reinforcements in concrete.

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