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Rheological properties of cement pastes admixed with some alkanolamines

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Abstract

The influence of addition of some alkanolamines, namely, monoethanolamine (MEA), triethanolamine (TEA) and polytriethanolamine (PTEA) on the rheological properties of the fresh pastes made of sulfate resisting cement (SRC) and ordinary Portland cement (OPC) was investigated. Different cement pastes made with and without these alkanolamines were prepared at a water/cement (w/c) ratio of 0.40. The shear rate–shear stress relationship was established by a co-axial cylindrical Rheotest. It was found that the rheological properties of the various cement pastes were affected by (i) the type and amount of alkanolamine, (ii) the type of cement and (iii) the applied shear rate. The alkanolamines were found to possess a significant retarding effect on the hydration of SRC in the order: TEA>PTEA>MEA.

Keywords: Ethanolamines; Cement; Shear stress; Apparent viscosity

1. Introduction

The rheological properties of fresh cement pastes are very interesting because of their influence on the consistency, workability and setting characteristics of the cement. Understanding how to control the rheological properties of the fresh cement paste is very important for the economical proportioning of concrete and proper mixing and placement methods.

Admixtures are generally used to improve the quality of plastic concrete, such as increased workability or water reduction and quality of hardened concrete [1]. Triethanolamine (TEA) is used as a grinding aid in cement manufacture and as a constituent in certain admixture formulations in concrete practice. Addition of TEA in cement hydration is thought to reduce the excessive retarding action of water reducing agents. Partial or complete replacement of $CaCl_2$ by TEA is favored because of TEA action as a corrosion inhibitor of embedded metals in reinforced concrete [2].

The exact action of TEA on cement pastes is very complex, poorly understood and depends mainly on type of cement. All addition rates of 0.02%, 0.25% and 0.5% of TEA to type I Portland cement acts as a set accelerator, mild retarder and a severe retarder, respectively. At 1%, however, it is a very strong accelerator [3–5].

Heren and Olmez [6] studied the effect of mono-, di- and triethanolamine on the hydration and mechanical properties of white Portland cement. They found a retardation effect on the hydration of white Portland cement in the order: TEA>DEA>MEA.

In this study, the effect of MEA, TEA and PTEA on the rheological properties of two types of cement has been investigated using a coaxial Rheotest. New parameters were obtained to give us more information about the effect of addition of these alkanolamines on the hydration characteristics of the fresh cement pastes.

2. Experimental

Ordinary Portland cement (OPC) and sulfate resistance cement (SRC), supplied by Helwan Portland cement company, were used in this investigation.

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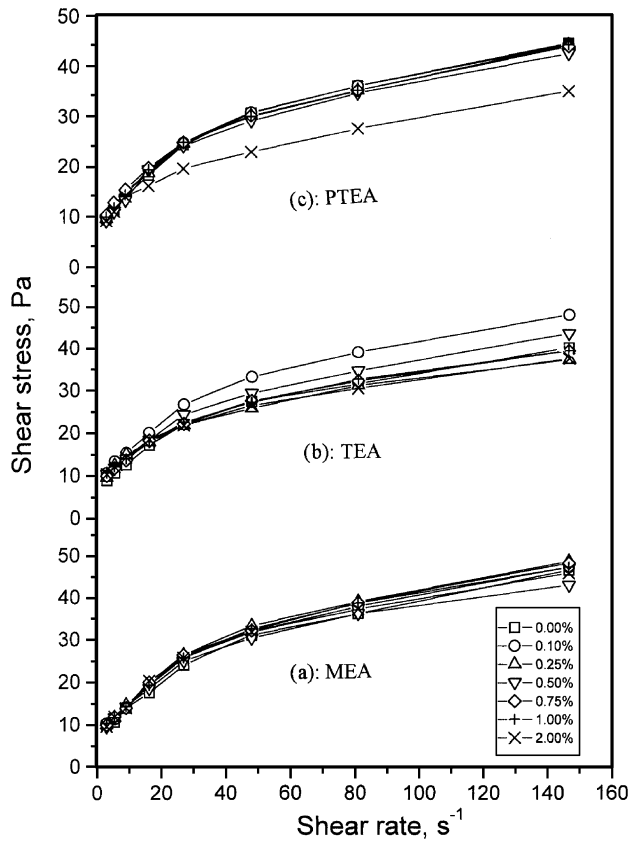

Fig. 1. Shear stress–shear rate of OPC pastes admixed with different doses of MEA, TEA and PTEA.

Merck supplies MEA and TEA. TEA had been condensated in the presence of sodium hydroxide to give poly-triethanolamine (PTEA) [7].

PTEA has a density of 1.2 gm/ml, a pH value of 12.0 and an average molecular weight of 804 g/mol as determined from mass spectroscopy [8].

The chemical composition of OPC was found to be: CaO, 64.5%; SiO_2, 20.08%; Al_2O_3, 5.27%; Fe_2O_3, 2.86%; MgO, 2.24%; SO_3, 2.13% and (Na_2O+K_2O), 0.036%, respectively; its Blaine surface area is 3045 cm^2/g. The calculated phase composition of OPC was found to be: C_3S, 64.38%; β-C_2S, 9.01%; C_3A, 9.13% and C_4AF, 8.69%, respectively. The chemical composition of SRC was found to be: CaO, 62.18%; SiO_2, 21.22%; Al_2O_3, 4.29%; Fe_2O_3, 5.19%; MgO, 2.19%; SO_3, 2.75% and (Na_2O+K_2O), 0.032%, respectively; its Blaine surface area is 3760 cm^2/g. The C_3A content of SRC was found to be 2.57%.

The pastes were prepared by mixing exactly 50 g cement in a porcelain dish together with various additions of the different admixtures. The water/cement ratio was 0.40 and the admixture contents were 0.0%, 0.10%, 0.25%, 0.50%, 0.75%, 1.0% and 2.0% by weight of cement. Mixing was done according to Roy and Asaga method [9]. The shear rates were ranging from 3 to 146.8 S^{-1}.

3. Results and discussion

The rheological properties of the different OPC and SRC pastes made with and without ethanolamines were studied using Rheotest 2.1 recording shear stress–shear rate relationships.

3.1. Effect of ethanolamines on the rheological properties of OPC pastes

Figs. 1 and 2 show the effect of addition of MEA, TEA and PTEA on the shear stress and apparent viscosity values of OPC pastes.

The results of Fig. 1 indicate that the shear stress increases with increasing the applied shear rate for all pastes investigated. In addition, the apparent viscosity–shear rate relationships are represented in Fig. 2 for the admixed OPC pastes.

The pastes admixed with MEA possess higher values of shear stress than those of control (OPC) at low values of shear rate while at higher shear rate values the dose rate of 0.5% has the lowest values of shear stress (Fig. 1a). In addition, Fig. 2a shows the apparent viscosity of OPC pastes admixed with MEA, which indicates that the viscosity of the pastes decreases with increasing the applied shear rate; this is due

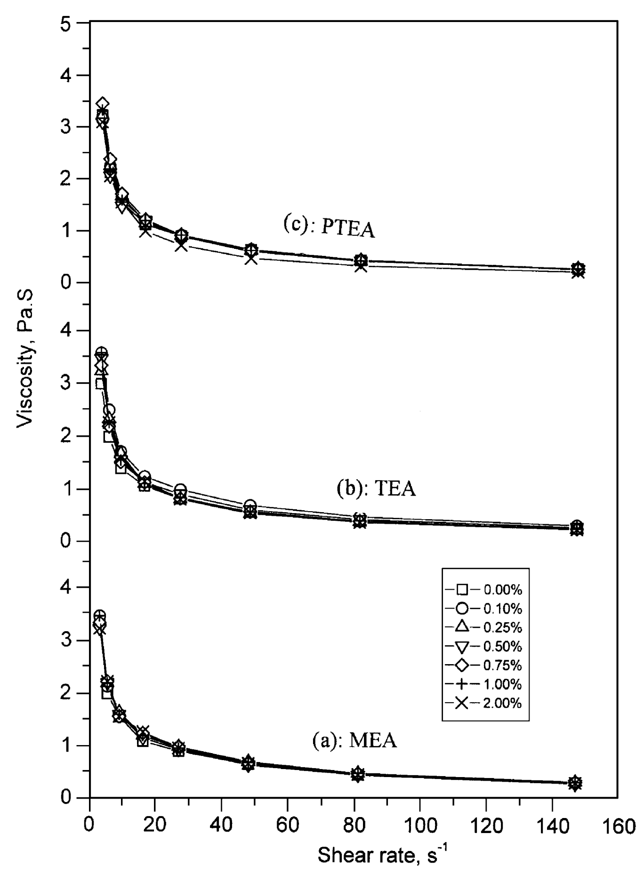

Fig. 2. Viscosity–shear rate of OPC pastes admixed with different doses of MEA, TEA and PTEA.

to the breakdown of the cement particle agglomerates. The viscosity values of the pastes, admixed with MEA, are higher than those of the (neat cement paste) control sample. The differences in paste viscosities decrease with increasing the shear rate. In general, the results of Figs. 1a and 2a indicate that MEA may be has some accelerating effect on the hydration of OPC pastes.

Figs. 1b and 2b show the effect of TEA on the rheological properties of OPC pastes. Evidently, OPC pastes admixed with all doses of TEA have higher shear stresses than those of control paste (OPC) at low values of shear rate (< 16.2 S^{-1}), as shown in Fig. 1b. This may be due to the increase of the contact of water with cement particle, which increases the hydration of the pastes. At higher shear rate values (>16.2 S^{-1}), the pastes containing of 0.25% and 2.0% TEA possess lower shear stresses than those of control; while the pastes containing 0.10 and 0.5%TEA have shear stress values higher than those of control. The maximum shear stresses at maximum shear rate are 40.04, 47.9, 37.8, 43.5, 39.3, 39.2 and 37.5 Pa for the pastes containing 0.00%, 0.1%, 0.25%, 0.50%, 0.75%, 1.00% and 2.0% doses of TEA, respectively. Fig. 2b shows the apparent viscosity of OPC pastes admixed with different doses of TEA, obviously all of the admixed pastes have higher viscosity values than those of control at lower values of shear rate; while at high shear rate values the pastes containing 0.25% and 2.0% dose have lower viscosity values than those of control. The pastes containing 0.1% and 0.5% TEA have higher viscosity values than those of control. In general all paste viscosities are reduced with increasing shear rate due to the breakdown of cement agglomerates. The minimum apparent viscosities (at the maximum shear rate) are 0.27, 0.25, 0.30, 0.27, 0.27 and 0.25 Pa S for the pastes containing 0.00%, 0.1%, 0.25%, 0.50%, 0.75%, 1.00% and 2.0% TEA additions, respectively. From the results of Figs. 1b and 2b, the effect of TEA additions on the properties of OPC pastes depends on: (i) the addition rate, where the addition of 0.25% and 2.0%TEA has a strong retarding effect while 0.1% TEA has a strong accelerating effect and 0.50% addition results in a mild accelerating effect; (ii) the applied shear rate, where at lower shear rates TEA has an accelerating effect whereas at higher shear rates only the doses of 0.25% and 2.0% TEA possess a retarding effect.

Figs. 1c and 2c show the effect of PTEA addition on the rheological properties of OPC pastes. Evidently, the dose rate of the paste containing 2.0% PTEA has lower shear stress values than those of all pastes having the other different dose rates as shown in Fig. 1c. The maximum shear stresses values are 44.3, 44.3, 42.6, 44.0, 44.3 and 35.0 Pa for the addition rates of 0.00%, 0.1%, 0.25%, 0.5%, 0.75%, 1.0% and 2.0%, respectively. Fig. 2c shows the effect of PTEA additions on the apparent viscosity of OPC pastes. It was found that the apparent viscosities are markedly reduced by the shear rates up to 81.0 S^{-1} then slightly decreased; the dose rates of 2.0% and 0.5% have lower viscosity values than those of the control.

Obviously, the results of Figs. 1c and 2c indicate that effect of PTEA addition on the properties of OPC pastes depends on the dose rate where 2.0% PTEA addition has a significant retarding effect while 0.5% PTEA has a small retarding effect.

Therefore, the results of Figs. 1 and 2 indicate that the effect of ethanolamines on the rheological properties of OPC pastes varies according to the type of ethanolamine and its dose rate as well as the applied shear rate. From the work of previous researchers, TEA retards the hydration of C_3S and β-C_2S [2] due to the formation a complex on the hydrating surface of the grains [6,10]. In the presence of TEA, the hydration of C_3S and β-C_2S occurs with some changes in the morphology and microstructure of the hydration products [2,4]; whereas C_3A hydration is accelerated in presence of TEA [4,11] due to the accelerated formation of hexagonal aluminate hydrate and its transformation to the cubic form. Consequently, the effect of TEA depends mainly on the phase composition of OPC.

3.2. Effect of ethanolamines on the rheological properties of SRC pastes

Figs. 3 and 4 show the effect of MEA, TEA, and PTEA addition on shear stress and apparent viscosity of SRC pastes obtained at different shear rate values.

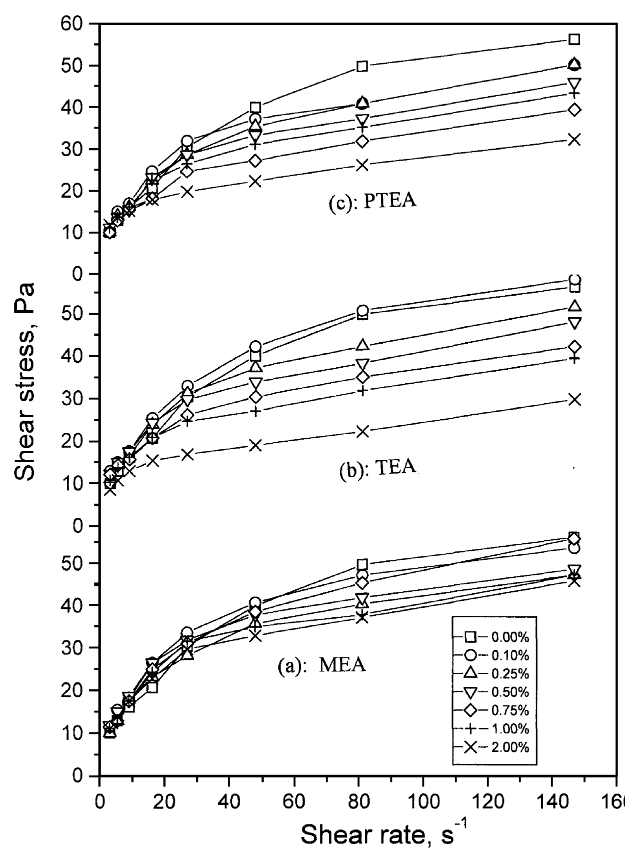

Fig. 3. Shear stress–shear rate of SRC pastes admixed with different doses of MEA, TEA and PTEA.

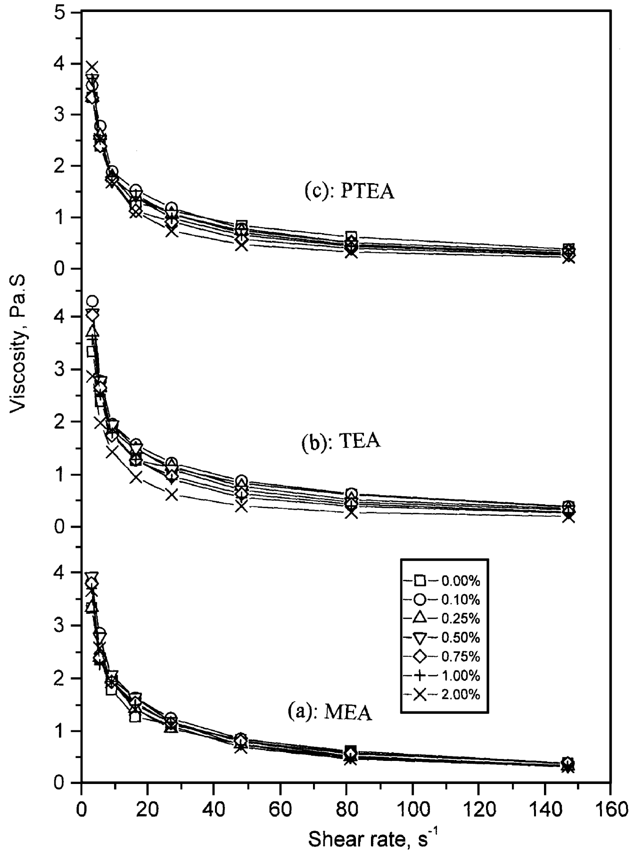

Fig. 4. Viscosity–shear rate of SRC pastes admixed with different doses of MEA, TEA and PTEA.

From the results of Fig. 3a, it is clear that all MEA addition possess higher shear stress values than those of the control at lower values of shear rate; while lower shear stress values are obtained at the higher shear rates. The maximum shear stresses are 56.1, 53.6, 47.2, 48.6, 55.8, 47.2 and 45.8 Pa for the pastes containing 0.00%, 0.1%, 0.25%, 0.50%, 0.75%, 1.0% and 2.0% doses, respectively. From the results of Fig. 4a, it is clear that the apparent viscosity values of all SRC pastes admixed with various doses of MEA are reduced with increasing shear rate up to 81.0 S^{-1} then tend to have a constant value, the viscosity values of all MEA admixed pastes are higher than those of the control at lower values of shear rate; at higher values of shear rate, however, lower values than those of control are observed. Therefore, MEA acts as an accelerating agent at low shear rates; while at higher shear rates it has a retarding effect. This is because the cement particle agglomerates has breakdown at higher shear rates, so the lubricating effect of MEA increases.

As shown in Fig. 3b, all of TEA-admixed SRC pastes possess higher values of shear stress than those of the control except those of the paste containing a TEA addition of 2.0%, at low shear rates. With the exception of the TEA dosage at 0.1%, the shear stress decreases with increasing TEA dosage. The most effective retarding action was found for the SRC paste containing 2.0% that reduced the maximum shear stress from 56.1 to 29.7 Pa.

Fig. 4b shows the effect of TEA addition on the apparent viscosity of SRC pastes. Evidently, at the lower shear rates all of the admixed pastes have higher viscosity values than those of the control except those of the paste admixed with TEA at 2.0%; while at higher shear rates increasing additions of TEA lead to a decrease in the apparent viscosity values except those of the paste containing 0.1% TEA. In general, TEA acts as a retarding agent except for the paste containing TEA addition of 0.1%, which acts as an accelerating agent.

Fig. 3c shows the effect of PTEA on the obtained shear stress of SRC pastes at different dose rates. It is clear that all pastes have lower shear stresses than those of the control (SRC alone) at high values of shear rate; the extent of reduction is in the order: in 2.0%>0.75%>1.0%>0.5%> 0.25%>0.1%. On other hand, at low shear rates, all of admixed cement pastes have higher values of shear stress than those of the control. The maximum values shear stresses were 56.1, 50, 50, 45.8, 39.3, 43.2 and 32.2 Pa for PTEA addition of 0.00%, 0.1%, 0.25%, 0.50%, 0.75%, 1.0% and 2.0%, respectively. Fig. 4c shows the effect of PTEA addition on the apparent viscosity of SRC pastes with different dose rates. All of PTEA admixed pastes have lower viscosity values than those of the control at high shear rates, while the neat SRC paste (control) has lower viscosity values at lower shear rates. Therefore, PTEA has some retarding effect at higher shear rates, while at low shear rates all PTEA additions cause an accelerating effect except the paste containing dose rate of 0.75%.

Fig. 5 shows the effect of shear rate on the variations of the apparent viscosity of SRC pastes with different dose rates of TEA. It is clear that the apparent viscosity decreases with increasing the shear rate. At highest shear rates (>48 S^{-1}), all dose rates provide slightly more or less the same apparent viscosity; this means that apparent viscosity is almost the same for all dose rates, due to the highly breakdown of the

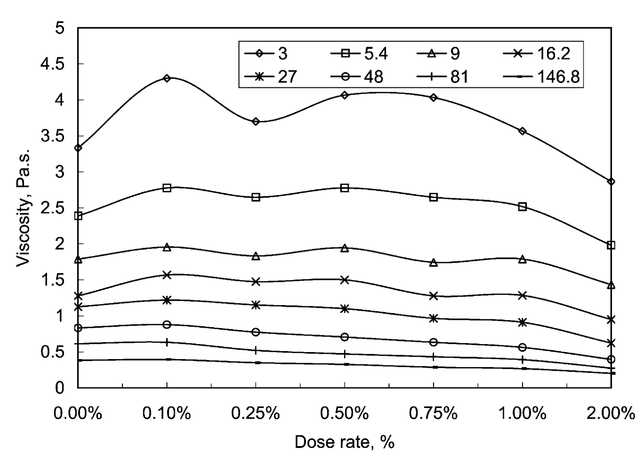

Fig. 5. Viscosity of SRC pastes as a function of dose rate of TEA at various shear rates.

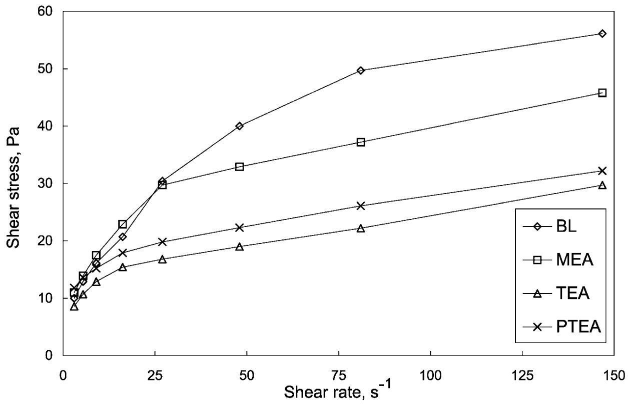

Fig. 6. Effect of admixture on the shear stress–shear rate relationship SRC pastes at a dose rate of 2%.

formed aggregates at the maximum shear rate (146.8 S^{-1}). At lower shear rates, there appeared an increase in the apparent viscosity for all dose rates except that of the paste made with TEA addition of 2.0%. Therefore, low apparent viscosity pastes could be obtained by increasing the shear rate that explains the effect of admixtures.

Fig. 6 shows the effect of type of ethanolamine on the rheological properties of SRC pastes at dose rate of 2.0%. It was found that, the retarding effect of alkanolamines follows the sequence: TEA>PTEA>MEA. This result might be related to the number of OH groups in the ethanolamine molecule, which can be adsorbed on the surface of cement particles causing a notable repulsive effect between the grains leading to more fluidity of the paste or may be due to their action as lubricating the cement particles, which also increase the fluidity of the paste.

HO-C_2H_4-N-C_2H_4-OH > HO-[-C_2H_4-N-C_2H_4-O-]$_6$-H
C_2H_4-OH C_2H_4-OH
TEA **PTEA**

> H-N-C_2H_4-OH
H
MEA

4. Conclusions

1. The effect of ethanolamines additions on the rheological properties of fresh cement pastes depends on three factors, namely, the addition rate, the applied shear rate and the cement type.
2. The viscosity of cement paste has been found to depend upon the shear rate. Thus, even at low concentrations of ethanolamines, it is possible to achieve lower values of viscosity at higher shear rates.
3. Ethanolamines affect on the rheological properties of SRC pastes in the order: TEA>PTEA>MEA.

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