



MECHANICAL DEGRADATION OF HIGH MOLECULAR WEIGHT POLYMER WITH SURFACTANT ADDITION IN A ROTATING DISK APPARATUS

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ABSTARCT

Mechanical degradation hampers the practical usage of polymers for turbulent drag reduction application. Mechanical degradation refers to the chemical process in which the activation energy of polymer chain scission is exceeded by mechanical action on the polymer chain, and bond rupture occurs. When a water-soluble polymer and surfactant are mixed in water solution, the specific structures (aggregates) are formed, in which polymer film is formed around micelle. In this work, Xanthan gum (XG) – Sodium lauryl ether sulfate (SELS) complex formation and its effect on percentage viscosity reduction (%VR) was studied. It was found that SELS surfactant reduced the mechanical degradation of XG much more efficiently than this polymer alone. Xanthan Gum (XG) has been tested for its shear stability and degradability. 0.5% and 1.0 % by weight concentration solutions were exposed to shear stirring at different speeds and time; also 0.5% through 1.5% by weight concentration solutions of SELS were added to XG solutions to determine the ability of SELS to reduce the mechanical degradation of XG. It has been noticed by measuring the percentage viscosity reduction (%VR) of the mixture of XG-SELS that the % VR decreases when added this surfactant to XG polymer.

الخلاصة

يحد الانحلال الميكانيكي للسلاسل البوليمرية من الاستخدامات العملية في تطبيقات تقليل الاعاقة في الجريان المضطرب. كما أن الانحلال الميكانيكي يعمل على تقليل الطاقة الموجودة في سلاسل البوليمر الطويلة عن طريق تكسير وتحطيم هذه السلاسل. أن إضافة المواد النشطة سطحيا إلى محاليل البوليمر في وسط مائي يعمل على تكوين جزيئات تسمى التجمعات أو (الاركييت) بحيث أن سلاسل البوليمر تحيط بجزيئات المواد النشطة سطحيا المسماة بالمذيلات في هذه التجمعات أو (الاركييت) وان هذه التجمعات أو (الاركييت) هي التي تعمل على تقليل الاعاقة أو تقليل الانحلال الميكانيكي في الجريان المضطرب. في هذا البحث تم حساب تأثير إضافة المواد النشطة سطحيا المسمى (صوديوم ليورال أثير سلفيت) على بوليمر (صمغ الزانثان) عن طريق حساب النسبة المئوية لنقصان اللزوجة، حيث تم استخدام تركيزين من بوليمر (صمغ الزانثان) وهما 0.5 و 1.0 نسبة وزنيه ومعاملتهما مع تركيزين آخرين من المواد النشطة سطحيا وهما 0.5 و 1.5 نسبة وزنيه لمعرفة مدى تأثير المواد النشطة سطحيا على تقليل الانحلال الميكانيكي للبوليمر (صمغ الزانثان)، فقد تم ملاحظة أن إضافة المواد النشطة سطحيا يعمل على تقليل الانحلال الميكانيكي للبوليمر المستخدم.

Keywords: Mechanical degradation, Polymer–surfactant aggregates, Viscosity reduction

INTRADUCTION

The phenomenon in which drag of a dilute polymer solution is drastically reduced in turbulent flow by minute amounts of suitable additives has been well documented (**C.A. Kim et.al. 2001**). This implies that fluid containing these additives requires a lower pressure drop than pure solvent to maintain the same flow rate in a pipe. Although the mechanism for drag reduction has been the subject of extensive research, a complete and satisfactory explanation has not been reported. Nonetheless, drag reduction applications can be found in various engineering areas including the transportation of crude oil, increasing speed of boats and water supply and irrigation systems (**H.J. Choi et.al. 1999**), (**H. J. Choi et.al 2000**).

Among various additives such as polymers, surfactant solutions, and fiber particles, polymers are considered the most effective drag reducing agent. High-molecular-weight poly (ethylene oxide) (PEO) and polyisobutylene have been widely used as drag reducers. However, the use of these polymers in practical applications has been severely limited due to their poor mechanical stability in turbulent flow. The search for shear-stable drag reducing polymers continues to be a challenging task (**J.I. Sohn et.al. 2001**).

Drag-reducing polymers are found to lose their effectiveness when subjected to an intense turbulence field for sufficient amounts of time. These losses are usually associated with chain scission. However, if aggregation enhances drag reduction, it follows that degradation should also occur because of the breakup of agglomerates. Several studies used intrinsic viscosity measurements to infer that changes in the average molecular weight accompanies changes in the effectiveness of a polymer. However, the use of intrinsic viscosity to measure molecular weight when entanglements or aggregates are present has been questioned (**Matthew W. Liberatore et.al. 2004**).

Origins and mechanisms of degradation discussed in the literature depend on an insight into the nature of polymeric liquids. In modern polymer

science, it is widely believed that attractive forces of cohesion between macromolecules in polymeric liquids and possibilities for the occurrence of supermolecular structures owing to these forces may be neglected. When considering concentrated systems, as a rule the attention is focused on the geometrical entanglements of chains. It is assumed that destruction is determined by high stress concentrations and, hence, an increased probability of breaking chemical bonds at sites of the entanglements. For dilute solutions, within the framework of this concept destruction is associated with deformations and stresses in a separate polymer chain. It is assumed that destruction occurs even for an arbitrarily small polymer concentration. Theories of destruction considering a behaviour of single chain in flow were proposed in works. Neglecting the cohesive forces which exist between the molecular chains results in an inadequate description of structure of the polymeric liquids. As a result, inferences which follow from this simplified consideration are in contradiction with experimental data (**V.N. Kalashnikov 2002**).

As has been shown in recent investigations (**V.N. Kalashnikov 2002**), for an understanding of the behaviour of polymeric liquids taking into account the forces of cohesion between the chains and study of self-assembly formations arising due to these forces are essential. It was shown that degradation is directly connected with specific supermolecular structures and does not occur in solutions with discrete macromolecules. As it turned out, even for very small concentrations the polymer solutions may represent two phase fluids. When, at a constant concentration, the molecular weight of the dissolved polymer increases, one of the two phases—namely, the phase rich in polymer—separates out in the form of dispersed globules. It then forms a three-dimensional network whose elements are liquid-crystalline fibrils. Abicontinuous structure is formed in which each phase occupies a connected space. With the appearance of the fibrillar network there arises the possibility for destruction of polymer molecules in response to shear flow, under



ultrasonic action, freezing, molecular fluctuations (V.N. Kalashnikov 2002).

The objective of the present work is concerned with the ability of Sodium lauryl ether sulfate (SELS) to reduce the mechanical degradation of high molecular weight Xanthan gum in water turbulent flow using a rotating disk apparatus. Therefore, dilute solutions of Xanthan gum with different concentrations in addition to different concentrations of Sodium lauryl ether sulfate (SELS) were exposed to shear degradation of a mechanical stirrer with blades. Furthermore, the relations between the increasing in percentage viscosity reduction with shearing time in a rotating disk apparatus were also studied.

EXPERIMENTAL WORK

The water soluble Xanthan Gum (technical grade) of molecular weight about 5.0×10^6 g/mole was supplied from local market in Baghdad and Sodium lauryl ether sulfate (SLES) which were supplied by the general company of vegetable oil industries, Baghdad. SELS of general formula $(CH_3(CH_2)_{10}CH_2(OCH_2CH_2)_3OSO_3^-Na)$ is a white gel material with a molecular weight of 372 g/gmol with an active material of 76%. Tap water was used for dissolving of Xanthan gum polymer and Sodium lauryl ether sulfate (SLES) surfactant. The total dissolved salts of tap water was 394 mg/l as tested in laboratory of Environmental ministry, Baghdad. The method of solution preparation adapted here was to make 0.5 %, 1 % and 1.5 % g/ml concentrations in a separate container. Thus 2.5, 5 and 7.5 gram of corresponding polymer or surfactant was placed in a one litter conical flask and mixed with 500 ml of the corresponding solvent (tap water).

The polymeric solutions of different concentrations were exposed to high speed stirred at different time. The viscosity of the solutions was measured as function of time and stirring speed, to evaluate the degree of polymeric degradation. The stirrer used has a sharp edge and rotating speed range 250–5000 rpm. Solutions of concentrations, 0.5 and 1.0 g/ml percent for Xanthan gum and 0.5 and 1.5 g/ml percent for Sodium lauryl ether sulfate were exposed to such shear degradation at 1000, 2000 and 3000 rpm

stirring for different time up to 1h (15, 30, 45 and 60 min).

The apparatus for shear degradation experiments consists of a 1000 ml beaker. The operated procedure was carried out by placing 300 ml of corresponding polymeric-surfactant solution (150 ml polymer + 150 ml surfactant) in the beaker. The stirring device was started at a fixed rotation speed. After each time period, the stirring was stopped, and raise the container from stirring device. Samples were taken to measure the viscosity of the solution. After that, the stirring was continued for further time period at the fixed rotation speed. All experiments were taken place at room temperature, 20–25°C.

The viscosity was measured by using Fungi lab viscometer, which measures fluid viscosity at a given shear rate. The principle of operation of the Fungi lab viscometer is to rotate a spindle, which is immersed in the test fluid until the fluid is at the immersion groove on the spindles shaft through calibrated spring. The viscous drag of fluid against the spindle is measured by the spindle deflection. The viscosity measurements of Fungi lab viscometer is in centipoises or milli Pascal seconds.

The percentage viscosity reduction %RV was calculated using the solution viscosity before and after degradation as in eq. (1):

$$\%RV = \frac{\mu_b - \mu_a}{\mu_b} * 100 \quad (1)$$

Where:

μ_b = viscosity of solution before degradation

μ_a = viscosity of solution after degradation

RESULTS AND DISCUSSION

Due to a broad range of applications of surfactants and polymers, enormous amount of work has been done on the characterization and properties of surfactant and polymer solutions. Due to a wide variety of molecular structures, polymer and surfactant when mixed together in aqueous solution display a wide variety and sometimes even very strange pattern of properties (Ketan Prajapati 2009).

Xanthan Gum (XG) as a water soluble polysaccharide polymer is considered to be an effective drag-reducer agent in turbulence flow of hydrocarbons and water solvents (Marwa F. Abdul Jabbar 2008). Hence, it was worthy to investigate the shear stability of XG toward mechanical forces and its effect on drag reduction performance. Therefore, XG water solutions of 0.5% and 1.0 % concentrations were exposed to shear degradation by mechanical stirring at 1000, 2000 and 3000rpm. The results of time dependence of viscosity changes at different conditions are illustrated in figures 1, 2. Figure 1 shows a gradual decrease of the viscosity with exposure time and stirring speed due to degradation of XG polymers.

While, figure 2 indicates the combined effect of exposure time and stirring rate on percentage lowering of the viscosity. The original viscosity of 1 % solution was 401.3 cp decrease to 385.8, 353.8 and 300.9 cp at shearing with 1000, 2000 and 3000 rpm stirring rate respectively at 1hr exposure time. These are equal around 3.86, 11.91 and 25.0186% decrease respectively. These indicate that the degradation increases as exposure time and stirring speed increases.

A gradual decrease of viscosity was observed at time progress due to the degradation of polymer molecules under turbulent flow (high turbulent flow means high stirring speed). The viscosity behaviour in turbulent flow is appeared to be related to shearing force (stirring speed) in which these cause the breakage of main chain of the polymer by the mechanical energy. Therefore viscosity decrease with time as a consequence of scission of polymeric chain caused by turbulence flow (Marwa F. Abdul Jabbar 2008).

The polymeric solutions of different concentrations were exposed to high speed stirred at different time. The viscosity of the solutions was measured as function of time and stirring speed, to evaluate the degree of polymeric degradation. The stirrer used has a sharp edge and rotating speed range 250–5000 rpm. Solutions of concentrations, 0.5 and 1.0 g/ml percent for Xanthan gum and 0.5 and 1.5 g/ml percent for Sodium lauryl ether sulfate were exposed to such shear degradation at 1000 , 2000 and 3000 rpm stirring for different time up to 1h.

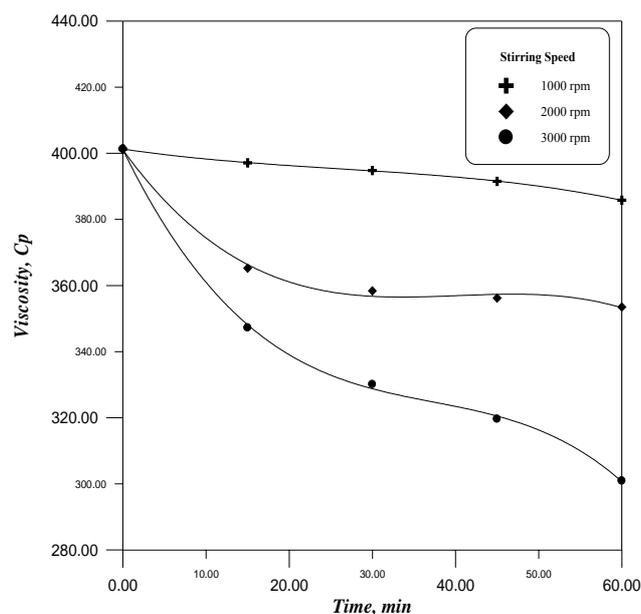


Fig. 1 Effect of exposure time and stirring speed on the viscosity of 1 % XG solution

Figures 3, 4 and 5 show the effect of concentration of SLES surfactant to modify the percentage of degradation (percentage viscosity reduction) for 0.5 % concentration XG polymer for different stirring speed and up to 1h exposure time.

For an absolute quantity of SLES surfactant, it was found that the percentage viscosity reduction of 0.5 % concentration XG polymer was found to be within the range of (0 to 2.7), (0 to 2.89) and (0 to 4.5) for 1000, 2000 and 3000 stirring speed respectively, while the percentage viscosity reduction of 0.5 % concentration of SLES surfactant added to 0.5 % concentration of XG polymer was found to be within the range of (0 to 0.90), (0 to 2.37) and (0 to 4.01) for 1000, 2000 and 3000 stirring speed respectively. It was found that the percentage viscosity reduction for the addition of 0.5 % concentration of SLES surfactant reduced the %RV within the range of (2.7 to 0.91), (2.89 to 2.37) and (4.5 to 4.01) for 1000, 2000 and 3000 stirring speed respectively, and up to 1h exposure time. Therefore, it can be concluded that surfactant additives substantially prevent the degradation of XG polymer, also helped to slow down the degradation effect (Nam-Jin Kim et.al. 2000).

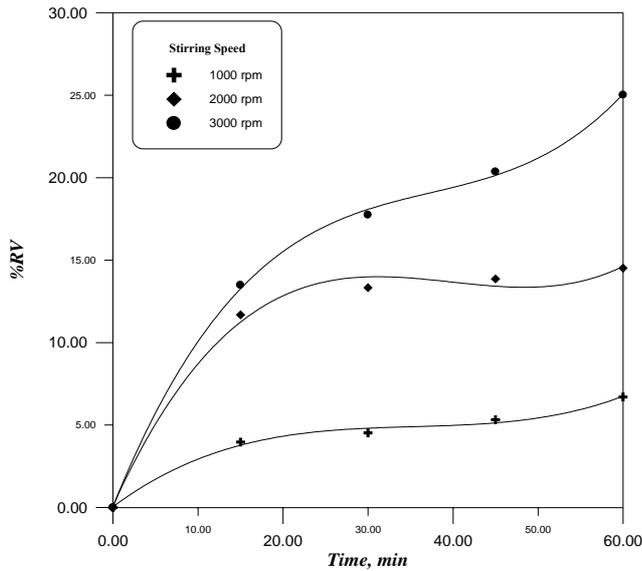


Fig. 2 Effect of exposure time stirring speed on Percentage viscosity reduction for 1 % XG solution

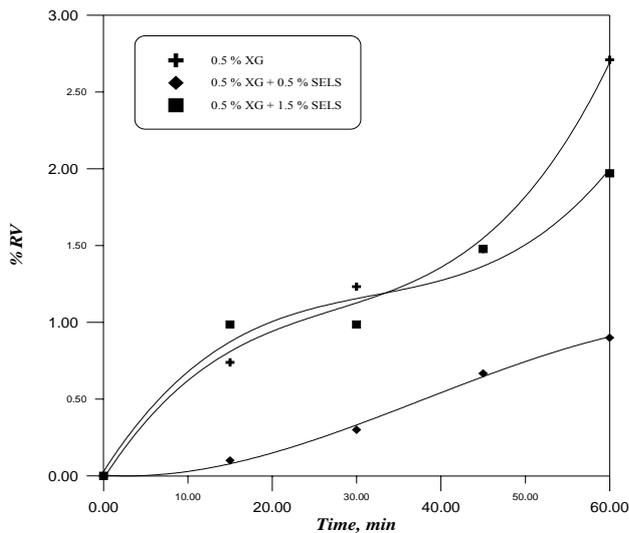


Fig. 3 Percentage viscosity reduction Vs. time for the system of 0.5 % XG solution and SELS for 1000 rpm stirring speed

Also it was found that the percentage viscosity reduction of 1.5 % concentration of SELS surfactant added to 0.5 % concentration of XG polymer to be within the range of (0 to 1.97), (0 to 2.75) and (0 to 4.617) for (1000, 2000 and 3000) rpm stirring speed respectively. Therefore, the addition of 1.5 % concentration of SELS surfactant decrease the %RV within the range of (2.7 to 1.97), (2.89 to 2.75) and (4.5 to 4.317) for (1000, 2000 and 3000) rpm stirring speed respectively, and up to 1h exposure time.

Also when the concentration of SELS added to 0.5 % concentration XG polymer increase from 0.5 to 1.5 the percentage viscosity reduction increase from (0.90 to 1.97), (2.37 to 2.75) and (4.01 to 4.317) for (1000, 2000 and 3000) rpm respectively, stirring speed and up to 1h exposure time.

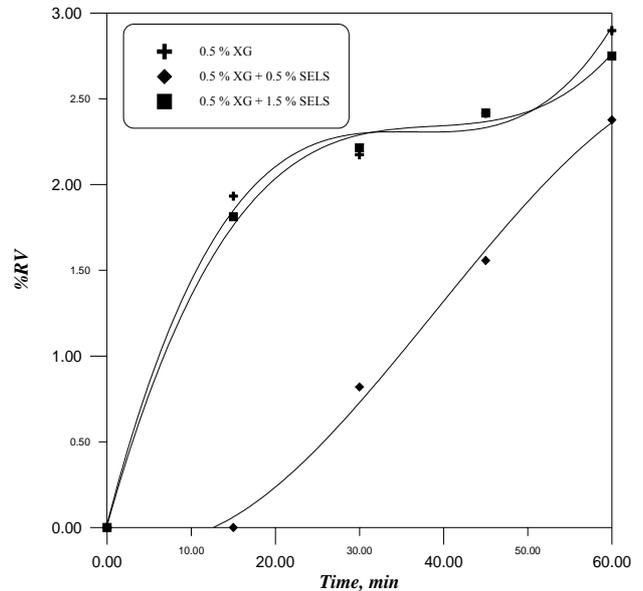


Fig. 4 Percentage viscosity reduction Vs. time for the system of 0.5 % XG solution and SELS for 2000 rpm stirring speed

It is generally concluded from figures (3, 4 and 5) and the data included in these figures, that the addition of 1.5 % concentration of SELS surfactant to 0.5 % concentration of XG polymer for different stirring speed, approximately don't effect of the rate of degradation of XG polymer or reduce the rate of degradation with small amount.

This because the amount of surfactant in the solution higher than the amount of polymer, this large amount of SELS compare with the amount of XG mean that the amount of micelles in the solution is higher than the amount of chains of the polymer (the amount of free micelles is high). In other words, after the solution of polymer – surfactant formed aggregation structure the free micelles come from the excess concentration of surfactant that not formed aggregation form making the degradation more rapid. Because this free micelles broke down the advantage of aggregation form (increase the degradation) by broken its.

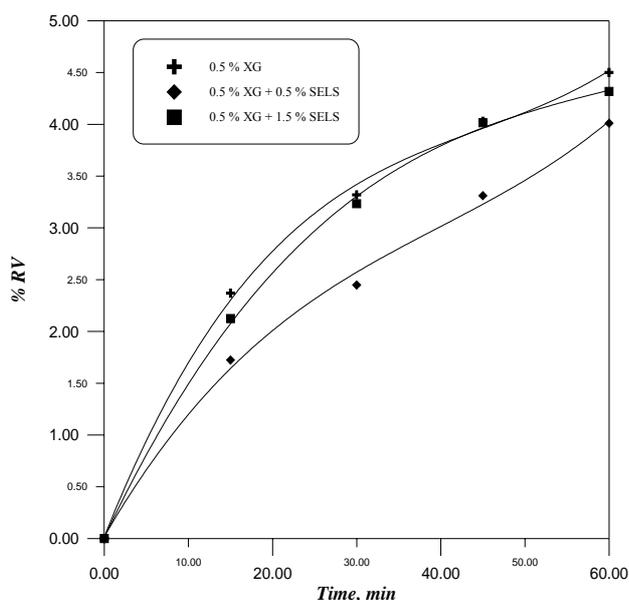


Fig. 5 Percentage viscosity reduction Vs. time for the system of 0.5 % XG solution and SELS for 3000 rpm stirring speed

Also, It is generally concluded from figures (3, 4 and 5) and the data included in these figures, that the addition of 0.5 % concentration of SELS surfactant to 0.5 % concentration of XG polymer for different stirring speed, decrease the rate of degradation of the polymer, but this degradation decrease with increase the stirring speed (shearing rate), as shown in figures 4 and 5 for 2000 and 3000 stirring speed. Therefore, the percentage viscosity reduction for an absolute amount of SELS is 0.91 for 0.5 % XG at 1000 rpm stirring speed and up to 1 hr exposure time, reduce to 0.91 when added 0.5 % SELS, while the percentage viscosity reduction decrease within the range (2.89 to 2.37) and (4.5 to 4.01) for 2000 and 3000 stirring speed respectively, for the same concentration of SELS added and exposure time.

Figures 6, 7 and 8 show the effect of concentration of SELS surfactant to modify the percentage of degradation (percentage viscosity reduction) for 1 % concentration XG polymer for different stirring speed and up to 1h exposure time.

For an absolute quantity of SLES surfactant, it was found that the percentage viscosity reduction of 1 % concentration XG polymer was found to be within the range of (0 to 6.69), (0 to 14.5102) and (0 to 25.0186) for 1000, 2000 and 3000 stirring speed respectively, while the percentage viscosity

reduction of 0.5 % concentration of SELS surfactant added to 1 % concentration of XG polymer was found to be within the range of (0 to 2.83), (0 to 4.24) and (0 to 3.84) for 1000, 2000 and 3000 stirring speed respectively. It was found that the percentage viscosity reduction for the addition of 0.5 % concentration of SELS surfactant reduced the %RV within the range of (6.69 to 2.83), (14.5102 to 4.24) and (25.01 to 3.84) for 1000, 2000 and 3000 stirring speed respectively, and up to 1h exposure time. Therefore, it can be concluded that the addition of 0.5 % concentration SELS to 1 % concentration polymer reduce the rate of degradation higher than that the reduction of degradation come from the addition of 0.5 % concentration SELS to 0.5 % concentration polymer for different speed and exposure time.

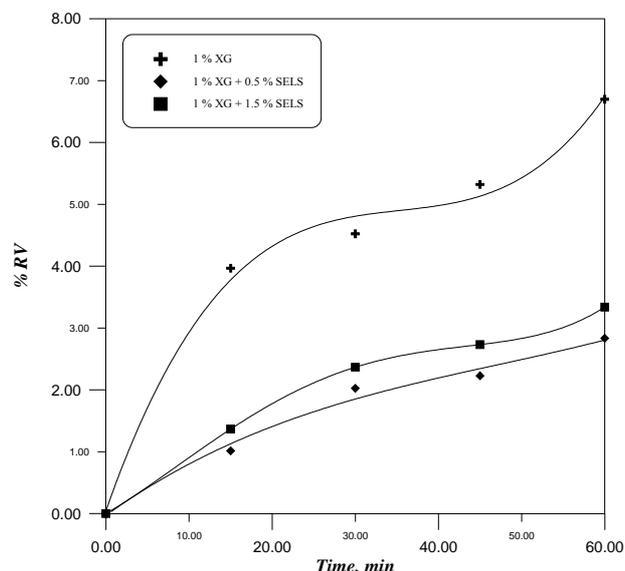


Fig. 6 Percentage viscosity reduction Vs. time for the system of 1 % XG solution and SELS for 1000 rpm stirring speed

Also it was found that the percentage viscosity reduction of 1.5 % concentration of SELS surfactant added to 1 % concentration of XG polymer was found to be within the range of (0 to 3.33), (0 to 11.342) and (0 to 5.55) for (1000, 2000 and 3000) rpm stirring speed respectively. Therefore, the addition of 1.5 % concentration of SELS surfactant decrease the %RV within the range of (6.69 to 3.33), (14.51 to 11.34) and (25.0186 to 5.55) for (1000, 2000 and 3000) rpm stirring speed respectively, and up to 1h exposure time. Also when the concentration of SELS added to 0.5 % concentration XG polymer increase from



0.5 to 1.5 the percentage viscosity reduction increase from (2.834 to 3.33), (4.241 to 11.342) and (3.846 to 5.55) for (1000, 2000 and 3000) rpm respectively, stirring speed and up to 1h exposure time.

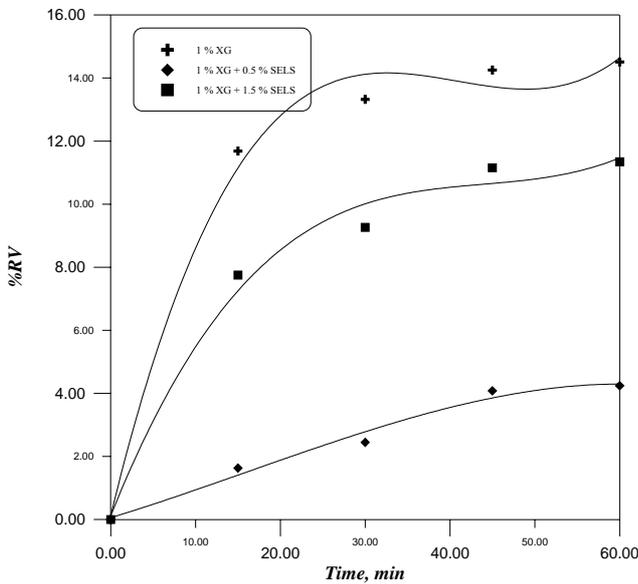


Fig. 7 Percentage viscosity reduction Vs. time for the system of 1 % XG solution and SELS for 2000 rpm stirring speed

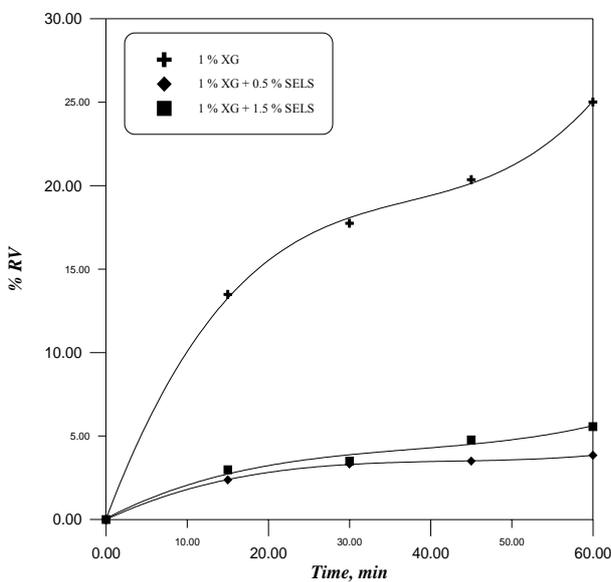


Fig. 8 Percentage viscosity reduction Vs. time for the system of 1 % XG solution and SELS for 3000 rpm stirring speed

It is generally concluded from figures (6, 7 and 8) and the data included in these figures, that the addition of 0.5 % or 1.5 % concentration of SELS

surfactant to 1 % concentration of XG polymer for different stirring speed and exposure time, reduce the rate of degradation more than the addition of 0.5 % or 1.5 % concentration of SELS to 0.5 % concentration of polymer and this return to the effect of the amount of aggregation form in each case. In other words, the equilibrium amount between the micelles of surfactant and the chains (coiled or straight) of the polymer that's has the ability to form aggregation structure.

Figures 9 and 10 show the effect of stirring speed on the rate of degradation (percentage viscosity reduction) for different concentration of polymer and surfactant and up to 1 hr exposure time. It was shown that the mechanical degradation increased with increase the stirring speed. Therefore, Form figure 10 and at 1000 rpm, the percentage viscosity reduction for pure XG, 0.5 % SLES and 1.5 % SELS are (2.7, 0.9 and 1.97) while the percentage viscosity reduction at 3000 rpm become (4.5, 4.01 and 4.31). Therefore, increase the stirring speed mean that the rate of shear force increase and the polymer or surfactant is degraded more rapid than low stirring speed.

Also, from figure 9 and at 1000 rpm, the percentage viscosity reduction for pure XG, 0.5 % SLES and 1.5 % SELS were (6.69, 2.83 and 3.33) while the percentage viscosity reduction at 3000 rpm become (25.01, 3.846 and 5.55).

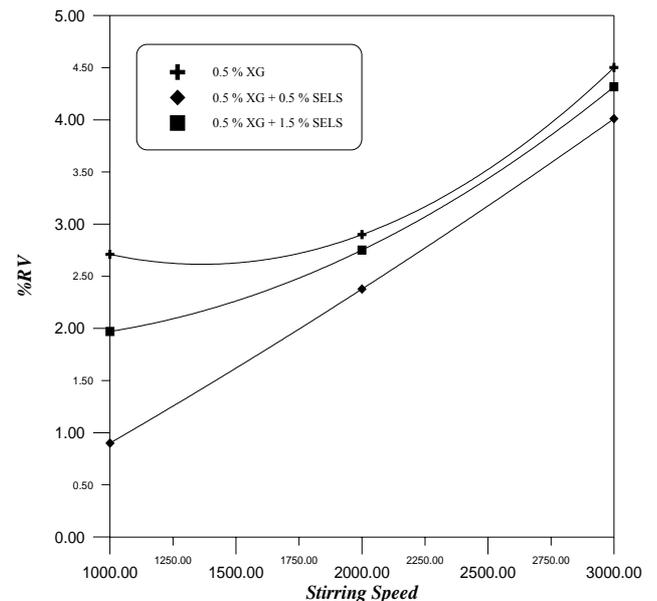


Fig. 9 Effect of stirring speed on Percentage viscosity reduction of 0.5 % XG solution and SELS for 1 hr exposure time

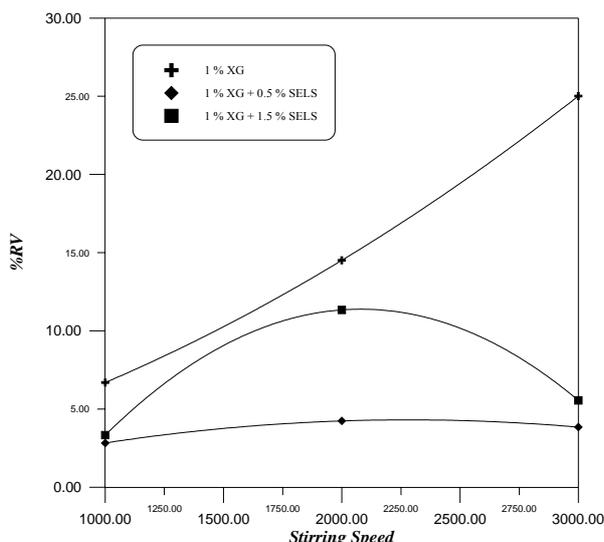


Fig. 10 Effect of stirring speed on Percentage viscosity reduction of 1 % XG solution and SELS for 1 hr exposure time

But also from figure 10 it was found that the rate of degradation (percentage viscosity reduction) for 3000 rpm is smaller than that for 2000 rpm for both (0.5 % and 1.5 %) concentration of SELS added to XG. This may be explained by the fact that the formation of aggregation (polymer + surfactant) is become better at high Reynolds number (high rate of stirring speed).

CONCLUSIONS

The results of the present investigation on the mechanical degradation effect in a synthetic polymer solution with surfactant additives can be summarized as follows;

- 1- When SELS is added to a XG, the mixture would appear to be more effective in the preventing the effect of mechanical degradation.
- 2- The addition of 0.5 % concentration of SELS surfactant to both (0.5 % and 1 %) concentration of polymer is considered the best concentration of surfactant that added to polymer at different stirring speed and exposure time.
- 3- Degradation at high stirring speed occurs more rapidly than that at low stirring speed, thereby indicating that when the

stirring speed increases, mechanical degradation plays an important role.

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cac: critical aggregation concentration

SDS : sodium dodecyl sulfate

SELS : Sodium lauryl ether sulfate

PEO : poly ethylene oxide

psp : polymer saturation point

XG : Xanthan gum

% VR : Percentage viscosity reduction

NOMENCLATURE