Study OF Rheological Properties Of (PEO-PMMA)) Blends.

Raheem G. Kadhim
University of Babylon,
College of Science,
Department of Physics.
-

Ahmed S. Hussein
University of Babylon,
College of Science,
Department of Physics.
ahmed.aldulami67@gmail.com

Abstract:

This study includes measurement of some rheological properties of polyethylene oxide (PEO) , (polyethylene oxide + Polymethyl methacrylate((PEO + PMMA) polymers by using solvent Dimethylformamide (DMF) at room temperature such as density and shear viscosity. Other types of viscosities , viscosity average molecular weight and effective molecular radius were theoretically calculated. These samples were prepared in different concentrations (0.1,0.2,0.3,0.4,0.5,0.6,0.7,0.8 g/ml) % as solutions then the additive (PMMA) as (0.25 g) and (0.5 g) respectively , where the samples were prepared by liquids mixture . Results show that there are an increases in the density values , shear viscosity , relative viscosity and intrinsic viscosity , with increasing concentration of (PEO) before and after adding (PMMA) polymer. However it was found that the reduced viscosity of (PEO) and its additive are inversely proportional with concentrations.

Keywords: (PEO),(PEO- PMMA), rheological properties.

دراسة الخصائص الريولوجية لمزيج من بوليمري بولي اثيلين اوكسايد مع بولي ميتاكريليت المثيل (PEO-PMMA)

رحيم كعيد كاظم
جامعة بابل / كلية العلوم / قسم الفيزياء

أحمد شاكر حسين
جامعة بابل / كلية العلوم / قسم الفيزياء

الخلاصة:

أن هذه الدراسة تتضمن تسجيل الخواص الريولوجية للبوليمر بولي اثيلين اوكسايد (PEO) و بولي اثيلين اوكسايد مع بولي ميتاكريليت المثيل (PEO + PMMA) باستعمال المذيب ثنائي ميثيل الفورماميد (DMF) و التي تم قياسها في درجة حرارة الغرفة. وتشمل الكثافة واللزوجة القصية .ومنها تم قياس الأنواع الأخرى من اللزوجة أما المعدل أللزوجي للوزن الجزيئي وتأثير نصف القطر المولاري الفعال فتم حسابه نظريا ، حضرت عينات بوليمر (PEO) بتراكيز مختلفة (٠,١- ٠,٢ - ٠,٣ - ٠,٤ - ٠,٥ - ٠,٦ - ٠,٧ و ٠,٨ ٪ غم / مل) كمحلول ثم إضافة (PMMA) بمقدار (٠.٢٥ غرام) و (٠.٥ غرام) على التوالي.العينات أعدت بطريقة مزج السوائل . بينت النتائج حصول زيادة في قيم الكثافة ، اللزوجة القصية ، اللزوجة النسبية و اللزوجة الذاتية عند زيادة التراكيز للبوليمر (PEO) قبل وبعد إضافة بوليمر (PMMA) بينما نلاحظ التناسب العكسي للزوجة المختزلة للبوليمر (PEO)) قبل وبعد إضافة (PMMA) مع زيادة التركيز.

الكلمات المفتاحية: (بولي اثيلين اوكسايد)، (بولي اثيلين اوكسايد مع بولي ميتاكريليت المثيل)، الخواص الريولوجية.

1. Introduction

Rheology is a branch of physics that deals with the deformation and flow of matter under stress. It is particularly concerned with the properties of matter that determine its behaviour when a mechanical force is exerted on it. Rheology is distinguished from fluid dynamics because it is concerned with the three traditional states of matters rather than only liquid and gases [1]. Since the polymer blending technique can offer versatile and useful routes for improving polymeric material properties, it has been employed and applied for many polymeric systems . A broad range of studies on miscibility , crystallization , structure , and dynamics , for poly(ethylene oxide) (PEO)/ poly(methyl methacrylate) (PMMA) system have been investigated. PEO/PMMA blends have been reported as marginally miscible **[2].** The linear and nonlinear viscoelastic behaviors of poly(ethylene oxide) (PEO) in aqueous media have been investigated as a function of concentration and molecular weight. A particular interest has been paid to study the effect of turbulent flow under stirring, inducing both shear and elongational stresses, on the rheological behavior of the polymer solutions [3]. Rheology is also used to indicate the properties of a given fluid, as in mud rheology. Rheology is important property of drilling mud, drill-in fluids, work over and completion fluids, cements and specialty fluids and pills. Mud rheology is measured on a continual basis while drilling and adjusted with additives or dilution to meet the needs of the operation [4].

2. Experiment

2-1 Materials and Method

The materials used in the study divided into two categories (PEO) and its additives (PEO-PMMA) blends ,they were prepared by liquids mixture method ,the appropriate concentrations of blends (0.1 ,0.2 ,0.3 ,0.4 ,0.5 ,0.6 ,0.7 ,0.8 % g/ml) were dissolved in (250 ml) of Dimethylformamide (DMF) under stirring with a heat of 30 ^{o}C for 120 min. Rheological properties have important implications in many and diverse applications .

2-2 Density and Rheological measurements:

The density of the solution (ρ) for (PEO) was determined by the density bottle method and the viscosity was measured before and after adding (PMMA) for all concentrations using computerized viscometer type (Brookfield, DV- III Ultra Programmable Rheometer) fabricated by Japan. Elsewhere using different types of viscosity for (PEO) were determined before and after the adding (PMMA) by equations (1, 2, 3 and 4) [5]. The shear viscosity had been calculated by the following equation [5 ,6 , 7]:

$$\eta_{sh.} / \eta_o = (t\ \rho) / (t_o\ \rho_o) \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where (ρ.) and ($\eta_{sh.}$) are the polymer density and the shear viscosity respectively, (ρ_o) and (η_o) are density and viscosity of any solvent respectively, Relative viscosity ($\eta_{rel.}$) was calculated by the following equation.

$$\eta_{rel.} = (t / t_o) = (\eta_{sh.} / \eta_o) \quad \ldots\ldots\ldots\ldots\ldots (2)$$

The specific viscosity (η_{sp}) and reduced viscosity (η_{red}) were calculated by the equations where (C) is the concentration:

$$\eta_{spe.} = (\eta_{sh.} - \eta_o)/ \eta_o = (\eta_{rel.} - 1) \quad \ldots\ldots (3)$$

$$\eta_{red.} = \eta_{spe.} /C \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

The relative viscosity was calculated theoretically by using :

$$\eta_{rel} = \left[1 + [\eta]\frac{C}{8}\right]^8 \quad \text{..... (5)}$$

Philippoff equation

$$\ln \eta_{rel} = [\eta]C \quad \text{..... (6)}$$

.Arrhenius equation

Where [η] is the intrinsic viscosity.

And draw a graph between the relative viscosity and concentration Molar (Cm) we get [7]:

$$slope = 6.3\times10^{24}\, r_o^{\,3} \quad \text{.....(7)}$$

$$r_o = \sqrt[3]{slope/6.3\times10^{24}} \quad \text{..... (8)}$$

Intrinsic viscosity measured in specific solvent is related to molecular weight M , by the Mark – Houwink equation [6,7].

$$[\eta] = k_o M_v^a \quad \text{..... (9)}$$

Where (k) and (a) represent Mark-Houwink constants that depend on the polymer, solvent, and the temperature of the viscosity determinations.The unit of intrinsic viscosity is inverse concentration . For a particular polymer solvent system at a known temperature, (a) equal to (0.8) for good solvent [7,8] and (k_o) can be calculated by using the equation [5,6,7]:

$$b_m = k_o \quad \text{..... (10)}$$

$[\eta_m]$

Where (b_m) represent the slope of the curve for polymer blends that drawing between the intrinsic viscosity and concentration, so (η_m) is specific viscosity of polymer blend and calculated practically by above equation [6].

3. Result and Discussion:

3-1 Density

Density of all solutions of polymer (PEO) before and after addition of other polymer (PMMA) was measured at room temperature and the results are given in figure (1), which shows that increase the density values with increasing concentration of (PEO) and this is because the increased in the mass of the solution and the swelling made in the polymer chains as a result of soluble in dimathyelformmamide and in particular polymers of higher molecular weight and this is agree with reference [8].

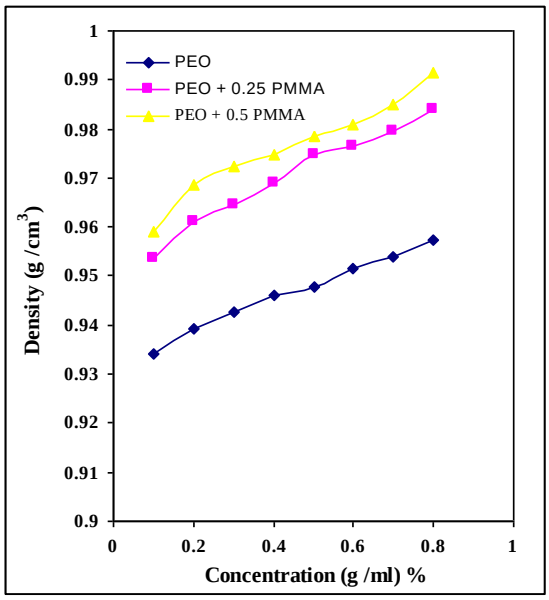

Fig. (1): Density Vs concentrations of (PEO) solutions before and after addition of (PMMA)

3-2 Shear Viscosity

From figure (2) , note that the values of the shear viscosity increases before and after the addition of (PMMA), the reason is due to the attractive forces between molecules of the solution after the addition is less than that before addition , so this leads to diverging of particles in mixing and it occupy a greater volume. This is leading to increase the values of shear

viscosities and this comes in a good agreement with reference [6,7].

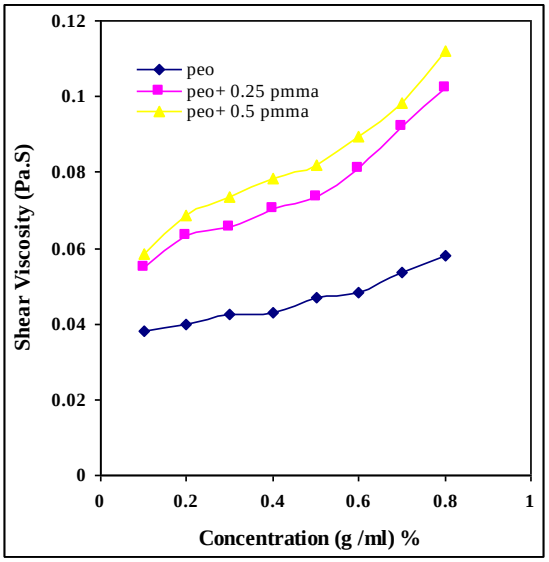

Fig. (2): Shear viscosity Vs concentrations of PEO before and after adding (PMMA)

3-3 Relative Viscosity

A nearly perfect linearity of the variation of relative viscosity with molar concentration can be seen in figure (3) which illustrates the relative viscosity change with a molar concentration before and after adding of (PMMA) polymers. It is shown to have the same behavior of shear viscosity and this is in agreement with references [8,9].

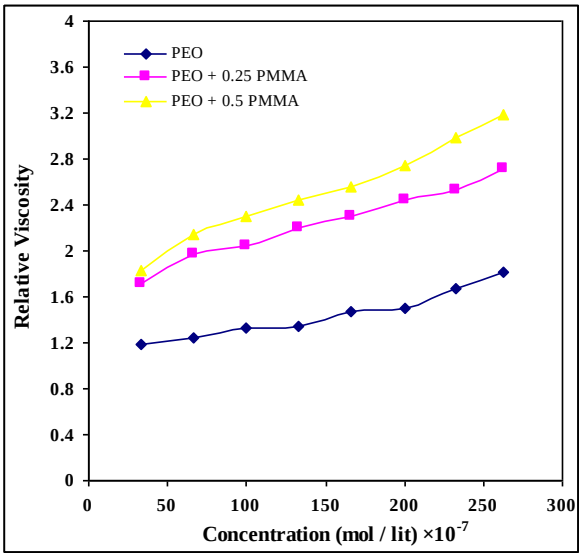

Fig. (3): Relative viscosity Vs molar concentrations of PEO before and after adding PMMA

3-4 Specific Viscosity

The results of qualitative change in viscosity with solutions of (PEO) polymer concentration values before and after the addition of (PMMA) are illustrated in figure (4) and this is in agreement with reference [9].

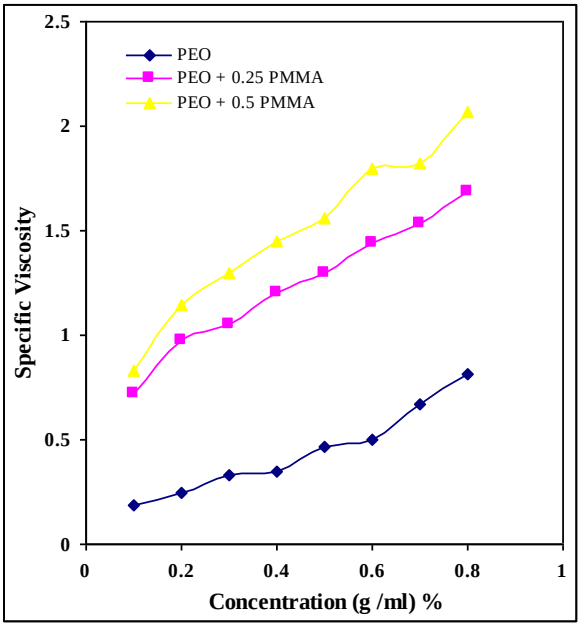

Fig. (4): Specific viscosity Vs concentrations of PEO before and after adding (PMMA).

3- 5 Reduced Viscosity

From figure (5) shows the plot of reduced viscosity against concentration. The curves showed upward turns at extremely dilute concentration region for all the samples, also figure (5) showed that the reduced viscosity of (PEO) and all its additives are inversely proportional to concentrations and this result is a normal fact, because the variation of specific viscosity is very small, so the reduced viscosity depends on the

specific viscosity and concentration and this is agreement with reference [9,10].

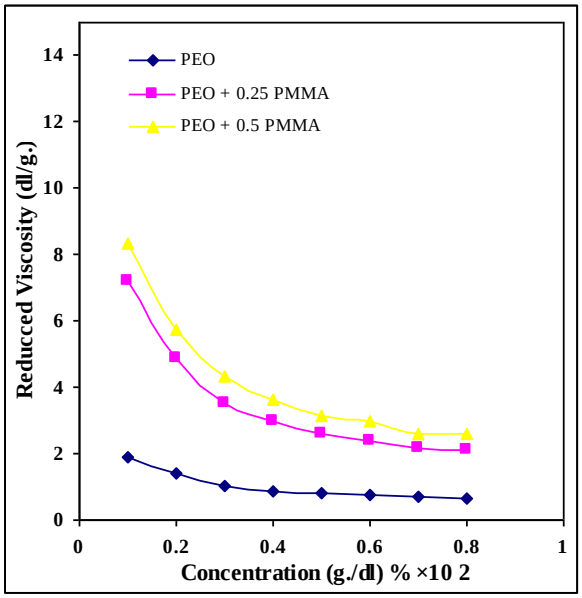

Fig. (5): Reduced viscosity Vs concentrations of PEO before and after adding (PMMA) .

3-6 Intrinsic Viscosity

The intrinsic viscosities of the samples were calculated by plotting a graph between reduced viscosities against the concentration of the solutions for (0.25 and 0.5g) weight additive from PMMA. The extrapolation of the slope as concentration goes to zero equal to the intrinsic viscosity values, as shown in Figure (5). The intercept values of these curves are shown in table (1). and this is agreement with reference [8,9, 10 ,11].

Table (1): Theoretical and experimental values of intrinsic viscosity of (PEO) before and after adding (PMMA) polymer.

Polymer Type	Effective Moleules Radius r (cm)	
	Low Concentration ×10 -7	High Concentration ×10 -7
PEO	1.5	1.9
PEO -0.25 PMMA	1.98	2.28
PEO -0.5 PMMA	2.2	2.3

3-8 Viscosity Average Molecular Weights

We show from table (3) an increase in viscosity average molecular weights after the addition of (PMMA) , the reason is that the molecular weight is defined as the product of the molecular weight of the monomer by the degree of polymerization, Since the addition increased the size of the polymeric chains (increasing the degree of polymerization) and therefore viscosity rate increased accordingly and this is agreement with reference [8.9.10].

Table (3): Theoretical and experimental viscosity average molecular weight of (PEO) before and after adding (PMMA) polymer.

Viscosity Average Molecular Weight (M_v)				
Polymer Type	$K_0 \times 10^{-4}$	Theoretical		Experimental
		Philippoff	Arrhenius	
PEO	2.4	301995	336995	319366
PEO – 0.25 PMMA	2.1	778956	801456	792440
PEO – 0.5 PMMA	2.0	871085	900080	890399

4. Conclusions

The summarized results from this work are the following:

1) It is found through the study that these polymers show a continuous change in their physical properties (rheological) as a result of adding (PMMA) to (PEO)which accordingly led to the

improvement of these rheological properties.

2) results show that increase the density values , shear viscosity , relative viscosity , intrinsic viscosity , with increasing concentration of (PEO) before and after adding (PMMA) polymer, while showed that the reduced viscosity of (PMMA) and all its additives are inversely proportional with concentrations.

5. Reference

[1] Oluranti S. A. , Emmauel R. S., Adesola T. A.and Olusesan F. B. ," Rheological Properties of Polymers: Structure and Morphology of Molten Polymer Blends " , Materials Sciences and Applications, (2011).

[2] Hee B. Kim a, Joon S. Choi a, Chung H. Lee a, Sung T. Lim a, Myung S. Jhon b. and Hyoung Jin Choi a. , "Polymer blend/organoclay nanocomposite with poly(ethylene oxide) and poly(methyl methacrylate " , European Polymer Journal , (2005) .

[3] Frédéric B. , Nadia E. , Alessandra D. A. , Fannie A. , Jean Y. S. and Alain D. , "Influence of dispersion procedure on rheological properties of aqueous solutions of high molecular weight PEO " , Springer-Verlag , (2009) .

[4] Huda R. H. , "Studying The Effect Of Adding CMC On Rheological Properites Of Non – Newtonian Fluids " , Al-Qadisiya Journal For Engineering Sciences ,(2010).

[5] Abdul-K. Al-B., Burak Y. K., Rawaa M. O. and Lamis F. N. , " Study of some mechanical and rheological properties of PVA/FeCl3 by ultrasonic " , International journal of Advanced Scientific and Technical Research , (2011).

[6] Karrar A. A. O. , " Enhancement of Some Physical Properties of Polyethylene Glycol by Adding Some Polymeric Cellulose Derivatives and its Applications " , University of Babylon / College of Science Department of Physics , Ph.D.Thesis, (2015) .

[7] Abdul K. J. Al-B. , Rawaa M. O. ," Structural Study Of Rheological And Mechanical Properties Of Polyvinyl Alcohol By Ultrasonic " , Journal of Babylon University, Pure and Applied Sciences, (2013) .

[8] Pedro G. T., Fernando C., and Gabriel B. , " Density and Viscosity of Concentrated Aqueous Solutions of Polyethylene Glycol " , Journal of Chemical and Engineering Data is published by the American Chemical Society. (1994).

[9] Talib O. K. and Estabraq S. K. , " Structure Rheology of Polyethylene Oxide Solution " , Iraqi Journal of Chemical and Petroleum Engineering , (1997).

[10] Ajaya B. , " Determination Of The Average Molecular Weight Of Sodium Polystyrenesulphonate From Viscosity Measurement." , Tribhuvan University, Nepal. , Scientific World, (2012) .

[11] Irina-E. L. , Maria B. And Simona M. ." Intrinsic Viscosity Of Aqueous Polyvinyl Alcohol Solutions " , Revue Roumaine De Chimie, (2009).