

Characterization and Solution Properties of Poly(Methyl Metha-Acrylate) – Poly(Ethylene Glycol) Blends

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ABSTRACT

Measurements of viscosity of poly methyl methacrylate (PMMA)/poly ethylene glycol (PEG) blends in tetra hydro furan (THF) as a common solvent, were carried out for different blend compositions at 30, 40 and 50°C. Using the viscosity data, interaction parameters μ were computed to determine miscibility. These values revealed that the blend was miscible when the PMMA content was more than 30% of the blend. Further, the results revealed that the change in temperature has significant effect on the miscibility of PMMA/PEG polymer blends. The simple of (PMMA/PEG) blends were characterized by using (FTIR).

1. INTRODUCTION

During the last two decades, the phenomenon of inter-diffusion in miscible polymer blends has been the subject of many investigations and is of interest for several applications such as welding and blending of polymers [1]. When two miscible polymers come into contact with each other, mutual diffusion across the interface between the two polymers may occur.

In general, polymer-polymer interactions are small and the polymer coil volume is determined by polymer-solvent thermodynamic interactions [2]. viscosity probes the interaction of molecular structure with the solution. Several theories in polymer physics literature[4] The viscometric method used successfully in compatibility characterization of poly blends. It is the low cost, and rapid techniques to study the miscibility of polymer blends. [6,7] by this techniques was studied thermodynamics and interaction to alt of mixed of polymer blends [3,8,9] in order to make two mixed polymers. we make them have less energy when mixed than they would be separated.

In this study, we measured the viscosity of poly methyl methacrylate (PMMA)/poly ethylene glycol (PEG) blends in tetra hydro furan (THF) as a common solvent, for different blend compositions at 30, 40 and 50°C. with



the help of viscosity data available to us, interaction parameters μ were computed to determine miscibility. The simple of (PMMA/PEG) blend and unblends were characterized by using (FTIR).

2. Experimental section

2.1. Materials and solution preparation.

Poly(ethylene glycol) (PEG) with an average molecular weight of 3500-4500 and melting point ($m_p=58-64^\circ\text{C}$) was supplied by Scharlu, Poly (methyl methacrylate) (PMMA) of molecular weight 35×10^4 by Aldrich. Tetra hydro furan (THF) by Aldrich with purity 99.9% HPLC grade was used as reagent grades and used without further purification. The polymer solutions were prepared by dissolving 0.5g of each polymer separately in 100 ml THF from these solutions were prepared different concentration for each polymer in within the range from 0.2 to 0.5 (g/dl) of polymer. The polymer blends were prepared by solution casting using THF as solvent. (PMMA/PEG) were blended in several weight percent ratios and dissolved in THF. The solutions were stirred overnight and then poured into glass dishes and allowed to evaporate slowly at room temperature.

2.2. Viscosity measurements [4,8,12].

The viscosity measurements were carried out using a conventional Ubbelohde viscometer that was placed in a thermostatically controlled bath with a precision of 0.01°C . Measurements were initiated after approximately 5–10 minute equilibrium time. The flow times were determined from an average of several readings (more than 3 readings). All the viscosity measurements were performed according to the following specially designed experimental procedures.

The efflux time t_0 minute of pure solvent THF recording at different temperatures 30, 40 and 50°C , with repeated the t_0 minute (3 times).

Then 15 ml from 0.5 (g/dl) of the polymer solution (PEG in THF) was transferred into viscometer and the flow time (t) minute for solution recorder in temperature water-bath (30, 40 and 50°C). The experiments were repeated by 15 ml with PEG (0.4, 0.3 and 0.2) (g/dl) separately as the same 0.5 (g/dl) solution. The flow time (t) of PMMA solutions were measured as the same way.

15 ml of this solution [70/30] concentration 0.5 (g/dl) was transferred into viscometer in constant temperature water-bath (30°C). The flow time minute blend recorder with repeated this process (3 times). The experiments were repeated (4 times) by diluting blend solutions by adding (5 ml of solvent THF each time to obtained the flow time of dilute blend solutions (0.4, 0.3 and 0.2) (g/dl) for [70/30] at the same temperature degree. The experiments were repeated at (40 and 50°C) by the same way. Then the other ratios with different concentration and different temperatures (30, 40 and 50°C) carried out such as first ratio.

2.3. FTIR Analysis.

Fourier Transform Infrared Spectroscopy (FTIR) method applies to characterize vibrations in molecules by measuring the absorption of light of certain energies that correspond to the vibration of the molecules from low to high frequency. FTIR spectra of polymer blends carried out by (Varian 800 FT-IR Spectrometer, Scimitar) with KBr pellets at room temperature .

3. RESULTS AD DISSECTIONS

Solution Properties.

Thermodynamic quantity of polymer concentration be obtained by intrinsic viscosities, $[\eta]$ by plotting the reduced viscosity (dl/g) of polymer solutions against concentration (g/dl). The measured values of reduced viscosity data for PMMA, PEG in THF and their blend ratios (70/30, 60/40, 50/50, 40/60 and 30/70) at 30, 40 and 50°C, are given in tables 1, 2 and 3 respectively.

The plots of reduced viscosity versus concentration (g/dl) for the pure components and their blends solutions at 30, 40 and 50°C, refer to figures 1, 2, 3.

Intrinsic viscosity $[\eta]$ and Huggins Coefficient KH are determined from taking intercept and slope these values show in table 4. The values of KH take range 0.024-0.37 their according to literature [5].

Table (1): Reduced viscosity data for PMMA, PEG and their blends in solution at 30°C.

Conc. g/dL	(PMMA/PEG) composition ratios in solutions at 30°C.						
	PMMA	PEG	70/30	60/40	50/50	40/60	30/70
0.5	0.926	0.122	0.68	0.62	0.54	0.46	0.35
0.4	0.919	0.121	0.65	0.59	0.52	0.44	0.33
0.3	0.909	0.118	0.62	0.55	0.49	0.41	0.31
0.2	0.899	0.115	0.58	0.52	0.47	0.39	0.29

Table (2): Reduced viscosity data for PMMA, PEG and their blends in solution at 40°C.

Conc. g/dL	(PMMA/PEG) composition ratios in solutions at 40°C.						
	PMMA	PEG	70/30	60/40	50/50	40/60	30/70
0.5	0.910	0.108	0.64	0.58	0.52	0.44	0.32
0.4	0.897	0.107	0.61	0.55	0.49	0.42	0.31
0.3	0.879	0.102	0.58	0.52	0.48	0.40	0.30
0.2	0.838	0.099	0.53	0.48	0.46	0.37	0.28

Table (3): Reduced viscosity data for PMMA, PEG and their blends in solution at 50°C.

Conc. g/dL	(PMMA/PEG) composition ratios in solutions at 50°C.						
	PMMA	PEG	70/30	60/40	50/50	40/60	30/70
0.5	0.894	0.098	0.60	0.54	0.46	0.40	0.30
0.4	0.879	0.092	0.57	0.50	0.44	0.38	0.29
0.3	0.849	0.084	0.54	0.47	0.41	0.35	0.28
0.2	0.804	0.079	0.49	0.43	0.39	0.32	0.26

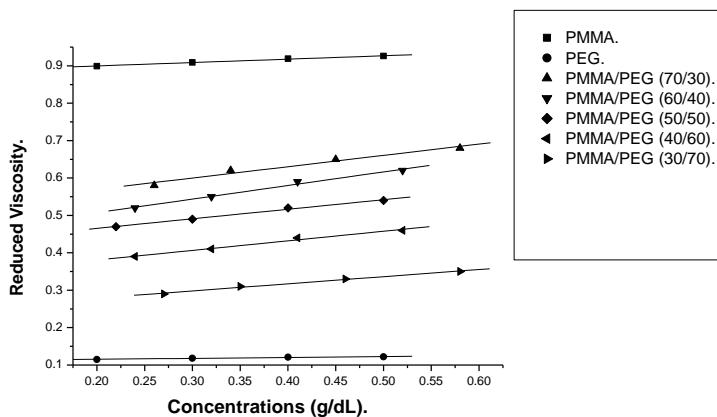


Figure (1): Reduced viscosity versus concentration (g/dL) for PMMA/PEG blend solutions at 30°C.

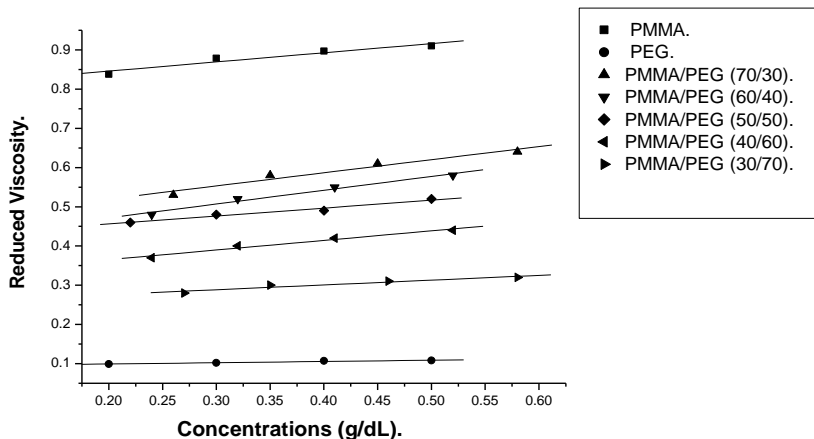


Figure (2): Reduced viscosity versus concentration.(g/dL) for(PMMA/PEG) blend solutions at 40°C.

Table (4): The Huggins constant K_H and Intrinsic viscosity $[\eta]$ at different temperatures.

Conc. g/dL	(PMMA/PEG) composition ratios in solutions at 50°C.					
	K_H	$[\eta]$	K_H	$[\eta]$	K_H	$[\eta]$
100/0	0.091	0.8814	0.234	0.7991	0.3000	0.7515
70/30	0.308	0.5123	0.329	0.4595	0.3044	0.4319
60/40	0.355	0.4449	0.338	0.4106	0.3763	0.3528
50/50	0.227	0.4275	0.173	0.4303	0.2441	0.3420
40/60	0.245	0.3349	0.240	0.3215	0.2849	0.2581
30/70	0.180	0.2469	0.126	0.2536	0.1310	0.2351
0/100	0.024	0.1106	0.032	0.0928	0.0650	0.0655

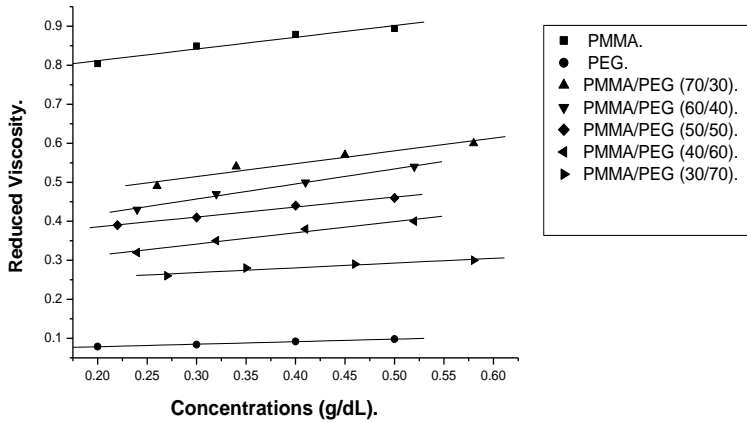


Figure (3): Reduced viscosity versus concentration (g/dL) for (PMMA/PEG) blend solutions at 50°C.

values of intrinsic viscosity and Huggins constant were obtained in this way illustrated in table 4. From this data, it can be observed the intrinsic viscosity for PMMA,PEG,PMMA/PEG decreases for all the three systems with temperatures and that the intrinsic viscosity remains less than PMMA and higher than PEG throughout the investigated temperature.

A general decrease in intrinsic viscosity with temperature observed in both,(table and figure 2), is due to decrease in interactions of polymer with solvent as the quality of solvent deteriorates at this temperature.

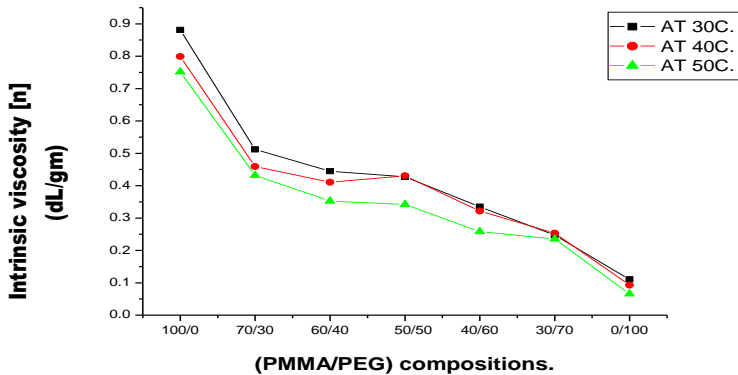


Figure (4): Intrinsic viscosity versus composition ratios at different temperatures.

Using these values, Chee[6] defined a more effective interaction parameter, as follows:

$$\mu = \frac{\Delta B}{\{[\eta]_2 - [\eta]_1\}^2} \dots\dots\dots (1)$$

where $[\eta]_1$ and $[\eta]_2$ are the intrinsic viscosities for the pure component solutions.

The blend is miscible when ($\mu \geq 0$) and immiscible [12] when ($\mu < 0$). The values of μ calculated with the preceding expression at 30, 40 and 50 °C are represented in table4.

Table (5): Interaction parameters μ of PMMA/PEG blends at 30, 40 and 50°C.

Compositions PMMA/PEG	Interaction parameter (μ) .		
	At 30 °C	At 40 °C	At 50 °C
70/30	0.422329	0.394599	0.259139
60/40	0.502328	0.394599	0.259139
50/50	0.285626	0.081806	0.130961
40/60	0.316882	0.214769	0.217660
30/70	0.207731	-0.0135509	-0.1094144

The relation between the interaction parameters (μ) and intrinsic viscosity $[\eta]$ are inverses according to equation(1), which explained why the value of(μ)to ratios (50/50) and(30/70) decreases with small arise for intrinsic viscosity $[\eta]$ at (40°C) which can also be observed in table 4.

In general, the results of interaction parameters (μ) in table5 enhancing and confirm that (PMMA/PEG)blend in solutions may be miscible for all ratios which were investigated.

Fourier Transform Infrared Spectroscopy (FT-IR).

Comparing figure 5 , and with figure(6 a,b,c) we are observed in region (C=O) of blend splits into two separate modes at (1734-1730)cm-1 and (1637)cm-1. As the similar in the region of O-H where small peak arise in the wide bands at (3517)cm-1 and (3440)cm-1. As its clear that the two regions in C=O stretch may be assigned to the native and loosely associated states. The carbonyl group, which is absolutely free from association, can have an absorption peak at 1730cm-1 [10]. The shoulder at 1637cm-1 corresponds, most likely to the hydrogen bond between oxygen atoms in PMMA units and PEG hydroxyl groups. The oxygen atoms in ester groups can also associate with PEG terminal -OH groups [10]. The most energetically favorable of hydrogen bonding through the oxygen atoms and C=O with OH groups of PEG in the blend PEG / PMAA-co-EA and PEG/PVP system has been explained with more details in previous literature[10]. In the spectrum of PMMA/PEG blend (1:3) the bands at the same region 1637 cm-1 possess low intensities compared with that (1:1 and 3:1).

That was maybe attributed to increased intra H-bonding between PEG chains with increased the amount of PEG in blend.

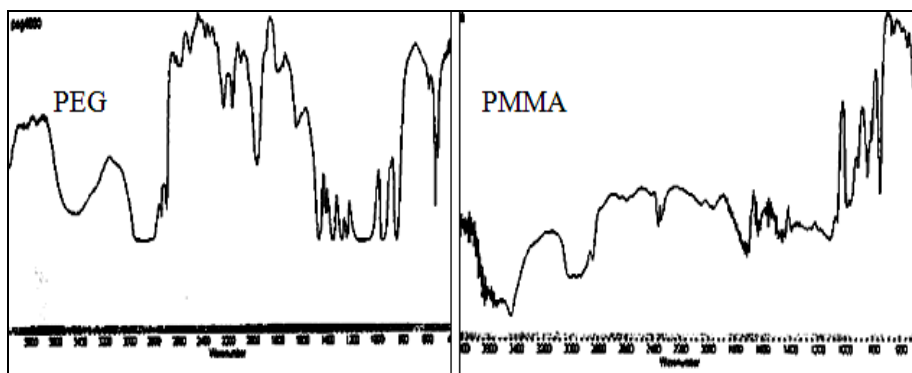


Figure5 FTIR spectrum for both the pure PEG,PMMA.

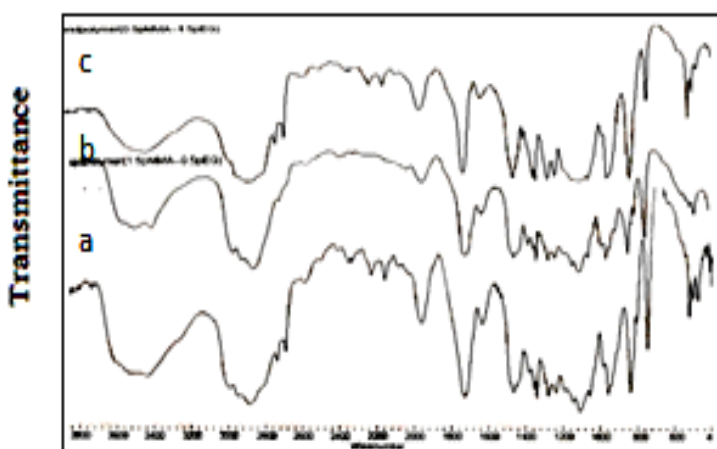


Figure 6 FTIR spectrum of (a, b, c)(1:1, 3:1 and 1:3)ratios of (PMMA/PEG)blends.

CONCLUSION

From the experimental data by Using viscosity, it has been shown that the thermodynamic affinity(similarity - suitable)of the solvent for the polymer affect the flexibility of the polymer chains, degree of aggregation of chains and the structure of the solutions effect the viscosity of solutions. The shape of the reduced viscosity versus concentrations curves is similar to those for the homo polymers and it is possible to predict the intrinsic viscosity of blends from those of the constituent polymers. In the case of blending, it is concluded that various ratios and concentrations of polymer blend systems has been found ,in generally, miscible or compatible mixtures as judged from the linear behavior of the reduced viscosity versus concentrations plots and from the absence of crossover over the whole range of ratios and concentrations at temperature has been confirmed. Observed Interaction parameters(μ) confirmed the polymer blend compatibility. It is also concluded

that the viscometry is simple technique determine the miscibility or compatibility of the polymer blend.

The different size of spheres indicating to still interaction effect with PMMA. That's confirmed by appeared newly peak and shifted the wave numbers for other peaks in FT-IR spectrum

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تشخيص ودراسة خصائص المحاليل لخليط من بولي اثلين جليكول وبولي ميثيل ميثاكريلات

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ملخص

تم في هذا البحث قياس اللزوجة لمخلوط بوليمري لكل من بولي اثلين جليكول (PEG) وبولي ميثيل ميثا اكريلات/(PMMA) في مذيب رابع فيوران الهيدروجين (THF) وبنسب مختلفة وعند درجة حرارة 30 و 40 و 50 درجة مئوية ومن خلال بيانات اللزوجة المختلفة , ومقياس التداخل μ بين البوليمرين ثم حساب مدى قابليتهما للامتزاج, وقد وجد ان قابلية الامتزاج للبوليمرين تزداد بارتفاع نسبة بولي ميثيل ميثا اكريلات عن 30% وان التغيرات في درجة الحرارة تؤثر تأثيرا واضحا على قابلية امتزاج البوليمرين , ايضا تم تميز هذه المحاليل ومدى تداخلها باستخدام جهاز (FTIR).