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Determination of the intrinsic viscosity and molecular weight of Poly(methyl methacrylate) blends

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Abstract: PMMA blends were synthesized through Atom Transfer Radical Polymerization (ATRP) method under at different concentration ratios. The viscosity characteristics of the structure were investigated to determine the behavior of macromolecules in blends. The viscosity characterization of the nanoparticles was determined to explain the molecular structure and interactions. The intrinsic viscosity of the blend was calculated with three different models including Huggins, Kraemer, and Rao. All blends were performed to understand the effect of additives concentration on molecular conformations and the intrinsic viscosity of the polymers. The voluminosity (V_E) and the shape factor (υ) were calculated for the blends to understand the miscibility behavior. From experimental results, it was observed that the intrinsic viscosity was increased with the increase in the amount of substance and the solubility of the system in solution.

1. Introduction

The controlled /living radical polymerization is a radical polymerization that can be stopped and re-initiated under external control. There are three types methods used for the controlled /living radical polymerization and they are applied to a large number of monomers. The applied methods are nitroxide mediated polymerization (NMP), metal-catalyzed atom transfer radical polymerization (ATRP), and reversible addition-fragmentation chain transfer (RAFT) [1]. The chain transfer and the termination reactions can be eliminated in controlled radical polymerization. The molecular weight and polydispersibility are adjustable to produce polymers without being affected by chain transfer processes. The use of the living radical polymerization presents some advances in compare to conventional free radical polymerization. The main advantages of the living polymerization are predetermined molar mass and control over end-groups. Besides, the use of ATRP technique has several advantages: catalytic amounts of transition metal complexes are used; many initiators are commercially available, including multifunctional and hybridsystems; a large range of monomers can bepolymerized (with the exception of unprotectedacids); end-functionalization is very simple; a large range of temperatures can be employed [2].

1.1 Molecular weight

Poly (methyl methacrylate) (PMMA) recognized as plexiglass or acrylic glass [3]. The trade names of PMMA are plexiglas, acrylite and lucite. PMMA has the transparent and thermoplastic properties and generally utilized in sheet form [4]. It is a lightweight choice among the glassy materials [5]. Whereas molecules or atoms in crystalline materials are linked to one another in a certain order polymer materials which can be formed by more than one chain have a random sequence. Polymer materials consist of chains, and these chains may vary in number in terms of the monomer which is the building block of polymers. Therefore, it is not possible to mention a single molecular weight in most of polymer materials. [6-7].

There are 4 kinds of molecular weight in polymers:

a) Number Average Molecular Weight (M_n) which can be expressed briefly in Eq-1: it is obtained by dividing the total molecular weight by the total number of molecules. It is obtained by methods based on the measurement of colligative properties such as freezing point descent, boiling point rise, osmotic pressure, vapor pressure drop.

$$M_n = \frac{\sum_i N_i M_i}{\sum_i N_i} \quad (1)$$

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b) Weight Average Molecular Weight (Mw), the higher the molecular weight of the molecule, the greater the effect of the molecule on the Weight Average Molecular Weight of the polymer. Unlike first kind of molecular weight molecules forming polymers do not have the same effect in calculating of molecular weight. It can be calculated in Eq-2:

$$M_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} \quad (2)$$

where M_i is the molecular weight of a chain, N_i is the number of chains of that molecular weight, and i is the number of polymer molecules [8].

c) Z-Average Molecular Weight (M_z), it is an uncommon type of molecular weight .It is obtained by ultracentrifugation method. It is used to determine mechanical properties such as toughness. It can be calculated in Eq-3:

$$M_z = \frac{\sum_i N_i M_i^3}{\sum_i N_i M_i^2} \quad (3)$$

where M_i is the molecular weight of a chain, N_i is the number of chains of that molecular weight, and i is the number of polymer molecules [9].

d) Viscosity Average Molecular Weight (M_v), Viscosity is the measure of resistance to flow and the viscosity of the solid materials is calculated by dissolving in a suitable solvent. M_v is briefly calculated in this way: the polymer material is diluted in a suitable solvent in different proportions. So, solutions are obtained at different concentrations. The viscosities of these diluted solutions are calculated, and then the molecular weight of the polymer material is calculated. The relationship between viscosity and molecular weight can be explained as follows. Flowing of large chain polymers is difficult due to entanglement and friction between the chains. That makes the solution ticker and these exhibit higher viscosities.

The intrinsic viscosity, η as function of average molecular weight, M is represented by Mark-Houwink Sakurada equation (in Eq-4).

$$[\eta] = KM^{\alpha} \quad (4)$$

: where K and α are empirically determined constants for a given polymer solvent temperature system.
As it can be seen in equation 1-2-3, the distribution of molecular weights in a heterogeneous polymer is that $M_z > M_w > M_v > M_n$. This can be easily applied in Figure 1 [10].

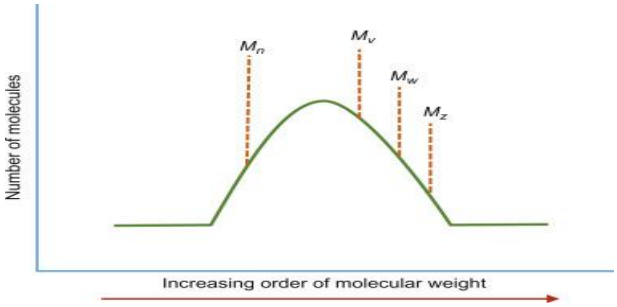

Figure 1. Demonstration of molecular weights in a heterogeneous polymer [10].

1.2 Polydispersity

Monodisperse (some natural polymer) molecular weights of all polymer molecules are same. Polydisperse pronounces for synthetic polymers and the distributed molecules and it is named as Polydispersity Index (PI). It is a measure of heterogeneity within the structure. If PI is 1, then $M_w=M_n$ like some natural polymers molecular weight is identical in all structure. If PI is more than 1, $M_n>M_w$ and there is heterogeneity within the structure.

One of the most desirable properties of materials used in engineering is the homogeneous structure. As the polydispersity increases, heterogeneity in the structure will increase, and especially mechanical differences will occur within the structure. It must be reduced the heterogeneity of the structure to eliminate these unwanted mechanical differences. In recent years, polymers have been started to produce between 1.0 and 1.2 PI and this rate of heterogeneity has been gradually reduced as molecular weight differences in the structure are requested to be reduced to the minimum level (Figure 2) [11].

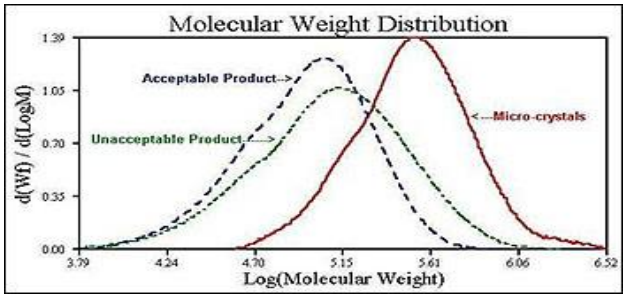

Figure 2. Molecular Weight Distribution [11].

1.3 Relationship between viscosity and mechanical properties

High mechanical values are desirable, however it is observed that it crawl after an approximate value of

molecular weight whereas the viscosity exhibits a continuous increase with increasing molecular weight [12-17]. Since the high viscosity means difficult molding of the material, an optimization is needed between these values. This value of molecular weight is 10000-1000000 g/mol. The above mentioned information is clearly seen in the Figure 3 [12].

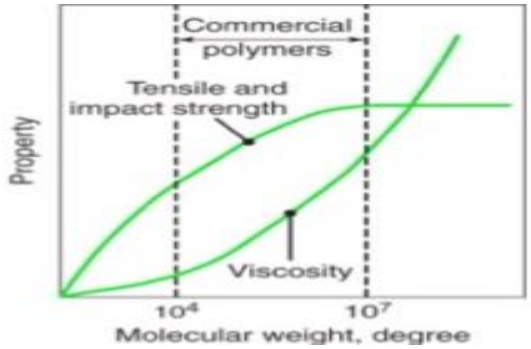

Figure 3. Relationship between viscosity and mechanical properties [12].

2. Experiments

The used chemicals for the synthesis of PMMA produced by ATRP method:

- MMA($C_5H_8O_2$)=50 mL, d=0.939 g/cm^3, 0.4695 mol
- EBİB($C_6H_{11}BrO_2$) =0.7826 mmol (density=1.329 g/cm^3, Vebib= 115.987µL)
- PMDETA($C_9H_{23}N_3$)=0.0004 mol (denstiy =0.830 g/cm^3,Vpmdata=164.290 µL)
- Bu_4NBr=2.00920 g
- CuBr=0.11176 g

Bu_4NBr (Tetra-n-butylammonium Bromide) was used as solvent at the production of PMMA. Bu_4NBr concentration was increased double amount in PMMA solution to evaluate the molecular weight variations of PMMA by using the maximum amount of the solvent in PMMA solution.

2.1 Measurement of Viscosity for the Determination of Average Molecular Weight

Viscosity average molecular weight test belonging base PMMA by ATRP was performed in the following order to obtain homogeneous solution

Weighing of Polymer Samples by using Sensitive Balance to be Measured Viscosity: The samples (0.1g, 0.3 g, 0.5 g and 0.8 g) belonging base PMMA by ATRP was weighed respectively on the precision scale, whose brand is Radwag AS 220 / C / 2 and whose accuracy is 10^{-4} g .

Preparation of Solvent: 50 mL of toluene was used as solvent in each sample and the used toluene was measured in the measuring cylinder. Solution Preparation and Measures Taken to Maintain the Amount of Solvent: Measured toluene, PMMAs and magnetic stir bar making the mixture homogeneous are placed in the conical flask. Since toluene is a volatile material, this flask was sealed to be airtight. Any loss in toluene results in a difference between the target concentration and the concentration obtained. This also leads to erroneous results.

The flask was placed on a magnetic stirrer set at 250 revolutions per minute at room temperature to obtain homogeneous solution.

Measuring the Viscosity of the Solution: When the solutions became homogeneous, the flasks were taken from the magnetic stirrer and the viscosities of the mixtures were measured by means of a viscometer. The measurements were carried out with AND-SV-10 viscometer. This viscometer has anaccuracy with 0.01 cP for the measurements.

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Table 1. Equation constants for various polymer-solvent pairs [17].

Polymer-solvent system	K x 10^3 mL/g	α (Equation constant)
PMMA-Acetone	7.70	0.700
PMMA-Benzene	5.20	0.760
PMMA-Toluene	***7.00***	***0.710***
Poly vinyl acetate-Acetone	10.20	0.720
Poly vinyl acetate-Benzene	56.30	0.620
Poly vinyl acetate-Acetonitrile	41.50	0.620
Poly vinyl alcohol-Water	45.30	0.640
Poly styrene-Benzene	10.60	0.735
Poly styrene-Toluene	11.00	0.725

Equations and expressions used to measure the viscosity molecular weight of solution: the results were used to obtain relative viscosity and specific viscosity, reduced viscosity, inherent viscosity, intrinsic viscosity. Finally, calculated intrinsic viscosity used in the Mark-Houwink equation. Where η (the intrinsic viscosity), M (Molecular weight) and α, K constants for the particular polymer solvent system. The appropriate solvent for the produce PMMA in this study was toluene and its fixed value was presented in Table 1. The result with viscosimetric molecular weight test was determined and Mark-Houwink equation (Eq-4). η was

determined ascut-off point of y axes, k was constant for toluene (0.007 mL/g), α was constant for toluen (0.71) as solvent, M=Avarage Molecular Weight (in Eq-4).

The molecular weight of the polymer was measured by using viscometer and the molecular weight called viscosity average molecular weight obtained by this technique. The mechanical properties of the polymers which are anisotropic materials can be modified according to the directions, as PMMA molecular weight is livingpolymer. The molecular weight and chain uniformity of the structure will be determined according to $[\eta] = KM^{\alpha}$ (in Eq-4). $[\eta]$: intrinsic viscosity, M: molecular weight, K and α are empirically determined constants for a given polymer solvent temperature system. After intrinsic viscosity value was determined by viscometer method, molecular weight was determined [13]. Assessment of intrinsic viscosity [η] was evaluated. For this purpose, the relative viscosity (η_{rel}) (Eq-5) was calculated from the ratio between the flow time of the polymer solution (t) and the flow time of the pure solvent (t_0). Relative viscosity (η_{sp}), [η] and inherent viscosity (η_{inh}) were determined by using Eq. 5-8 [12-14].

Relative viscosity:

$$\eta_{rel} = \frac{t}{t_0} \quad (5)$$

Specificviscosity:

$$\eta_{sp} = \frac{t}{t_0} - 1 = \eta_{rel} - 1 \quad (6)$$

Intrinsic viscosity:

$$[\eta] = \frac{t - t_0}{t_0 * C} = \frac{\eta_{sp}}{C} \quad (7)$$

Inherent viscosity:

$$\eta_{inh} = In\frac{t/t_0}{C} = In\frac{\eta_{rel}}{C} \quad (8)$$

3. Results

Table 2 presents the values to determine the viscosity of the solvent and the solutions at different concentrations. Table 3 shows the viscosities of the solutions at different concentrations used to calculate the instristic viscosity value.

Table 2. Information about base PMMA.

Amount of PMMA (g)	Solvent (Touluen) Amount (ml)	Concentration of Solution (g/ml)	Solvent Touluen Viscosity (cP)	Solution Viscosity (cP)
0.1	50	0.002	0.58	0.64
0.3	50	0.006	0.58	0.68
0.5	50	0.01	0.58	0.78
0.8	50	0.016	0.58	0.88

Table 3. Changes in the inherent viscosity of the solutions at different concentrations for base PMMA.

Relative Viscosity (η_r)	Specific Viscosity (η_{sp})	Reduced Viscosity (η_{red})	Inherent Viscosity (η_{inh})
1.103448276	0.103448276	51.72413793	49.22003641
1.172413793	0.172413793	28.73563218	26.51078244
1.344827586	0.344827586	34.48275862	29.62658161
1.517241379	0.517241379	32.32758621	26.05586275

The assessment of intrinsic viscosity for base PMMA was presented in Figure 4. Hence, average molecular weight is determined by using Eq-4. A result of the calculations, the average molecular weight of base PMMA was found to be 274.042 g / mol.

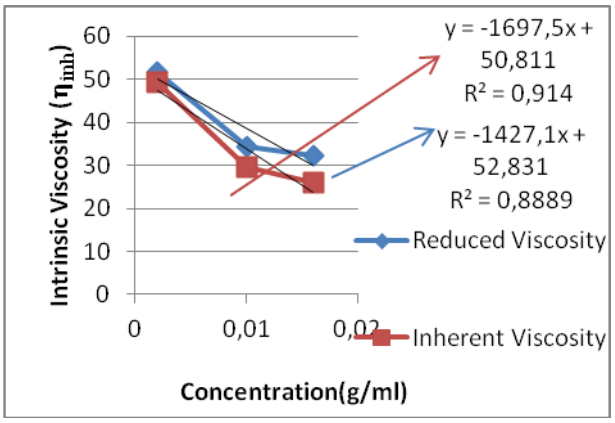

Figure 4. The assessment of intrinsic viscosity of base PMMA.

4. Discussions

Synthetic polymers do not consist of the same chains as crystalline atoms or molecules and in them cannot be mentioned a constant molecular weight [16-19]. In addition to that, the obtained molecular weight values can be influenced by many parameters of production [20-22]. The molecular weight values of polymer materials are available in a range for several materials in Table 4 [18].

Table 4. Molecular Weight of Various Molecules [18].

Molecules	Molecular weight (g/mol)
Water	18
Alcohol	46
Stearic Acid	384
Polistiren	60.000-100.000
Low Density Polyethylene (LDPE)	30.000-60.000
High Density Polyethylene (HDPE)	30.000-150.000

PMMA synthesized by using different techniques has an average molecular weight in the range of 42.000-130.000. Since, the increase of the value in a controlled manner means improvement of mechanical properties, the average molecular weight was increased by several methods (such as, ATRP, ARGET ATRP). The effect of ATP on molecular weight was clearly examined in Table 5. The average molecular weight of the base PMMA was determined as ~ 270.000 g/mol. The results indicate that the molecular weight has higher than that of industrial PMMAs.

Table 5. Average Molecular Weight of base PMMA.

Material	Avarage Molecular Weight (g/mol)
PMMA [17] (by GPC)	120.000
PMMA [18] (PMMA prepared from the block copolymer micelle/homopolymer)	90.000
PMMA [19] (PMMA synthesed by the catalyzed recyclable Ni–Co alloy nanoparticle)	129.500 (Mw/Mn=1,300)
PMMA [20] (ARGET ATRP)	42.500 (PDI=1.36)
PMMA (produced by ATRP method in this study)	274.043

PDI: Polydispersity index.

GPC: A gel permeation chromatography.

ARGET: Activators regenerated by electron transfer.

5. Conclusions

The results of this study indicated that PMMA produced by ATRP method was suitable technique to improve the average molecular weight in this study. PMMA produced by ATRP method named the living polymerization technique has higher the average molecular weight than the molecular weight of the PMMA produced by different techniques in the literature. The molecular weight for the PMMA produced by ATRP method was determined ~270.000 g/mol.

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