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Morphological and thickness analysis for PMMA spin coated films

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The present study shows the application of spin coating method in coating a thin layer of PMMA (Poly (methyl methacrylate)) from its solution in 1,2 Dichloroethane. The dependence of the polymeric film thickness h on concentration of polymer in the solvent c and the angular velocity ω is obtained experimentally as $h = 3.2c^{1.66}\omega^{-0.53}$. The reason of changes in the constant coefficients in different equations is distinct by comparing them with different solvents. This comparison shows that these constant coefficients in above equation depend on solvent type and the vaporization of solvent. The relationship between viscosity and concentration has been investigated and defined that viscosity can indirectly cause increasing the exponent of concentration or directly entered in equation without influencing in exponent of concentration that both of them cause the same result. Finally the surface morphology is related to the effective parameters in thickness and their effects on surface uniformity are discussed. It is shown that the factors which cause an increase in thickness may reduce the surface quality which limits the thickness of the layer produced by this method. Therefore, for a desired thickness, attention should be paid to the influence of different parameters on the surface uniformity; and optimum values should be chosen for controlling both thickness and surface morphology.

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Keywords: PMMA (Poly (methyl methacrylate)), 1,2 Dichloroethane, Morphology, Spin coating, Viscosity, Film thickness

1. Introduction

Spin coating is a method widely used in coating polymers. In many opto-electronic applications, such as Organic Light Emitting diodes (OLED) and photovoltaic cells, a thickness of less than 200 nm is desirable [1,2]. To produce a coating with such thickness, dilute solutions of polymer is used.

Because of its ability to produce uniform layers, transparency in visible wavelengths and ~~its~~ suitable glass transition temperature, PMMA (Poly (methyl methacrylate)) is used as host in many opto-electronic applications. In thin film coating applications, achieving the required thickness with desirable surface quality is very important. Generally, thickness of layer in this method is dependant on angular velocity, primary concentration, viscosity of solution and solvent vaporizability [3, 4]. The nature of this dependency varies across different materials and solutions. However, thickness generally depends on the weight percent of the polymer in solvent, c and angular velocity ω as indicated in the equation (1) below [5,16]:

$$h = Kc\omega^{-\alpha} \tag{1}$$

In this equation, α is a constant and the coefficient K depends on the solvent type, viscosity value and vaporizability rate. Since thickness generally depends on the angular velocity ω and concentration c, Walsh et al. in their study obtained the thickness of a layer coated by polymer PMMA with a molecular weight of *(M_W* =101300) as follows [6,7]:

$$h = Ac^n\omega^{-\alpha} \tag{2}$$

And experimentally achieved the following equations for two different solvents:

$$h = 0.92c^{1.56}\omega^{-0.51} \text{ Solvent: Toluene} \tag{3}$$

$$h = 4.3c^{1.33}\omega^{-0.5} \text{ Solvent: Chloroform} \tag{4}$$

In both equations (3 and 4), the exponent of ω is the same value; but they have not provided a precise justification for the power of c. Furthermore, coefficient A has been attributed to the vaporization of the solvent without any clarifications.

In this paper, a thin layer of polymer Poly methyl methacrylate (PMMA) with a molecular weight of 996000 coated by spin coating method has been investigated. By using Dichloroethane as solvent, the experimental equation 8 was obtained. Comparing this equation with the one for different solvents (3,4) we studied the reason of variation in exponent of concentration and related it to viscosity. Also the effect of participate factors that influence in both thickness and morphology of surface is studied. The manner of achieving a film with desired thickness in high uniformity explained.

2. Materials & procedure of experiment

2.1. Preparation of material and solvent

PMMA (M_W =996000), 1,2 Dichloroethane, Dichloromethane, and chloroform all from Aldrich were used in the experiments.

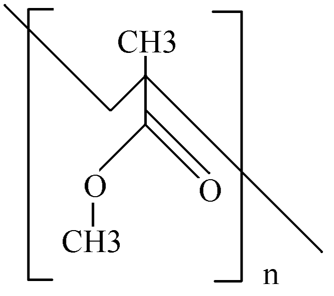


Fig. 1. Schematic Structure of PMMA polymer

PMMA, which weighed in ± 0.0001 gram accuracy, was dissolved in all of the three aforementioned solvents at given percents by means of an ultrasonic bath; the resultant solution was then filtered through a 0.7 μm filter.

2.2. Viscosity measurements

For viscosity measurement a simple method was used. The time necessary for the solution to pass through a capillary tube is measured and compared with that of the solvent. Viscosity of the solution is proportional to its density and flow time through the fine tube. Since our solutions are diluted, the densities of the solvent and solution are assumed to be approximately equal. Therefore, Equation 5 may be used to obtain the relative viscosity ν_r :

$$\nu_{\mathrm{r}} = \frac{\nu}{\nu_0} = \frac{\mathrm{t}}{\mathrm{t}_0} \tag{5}$$

Where ν and ν_0 are respectively the viscosity values for the solvent and the solution. By calculating the ν_r and with the solvent viscosity, we can obtain the solution viscosity**.**

2.3. Substrate preparation

Due to the low thickness of the polymeric thin layer, substrate cleaning is of great importance. At the beginning, the glass slides were cut out in given dimensions followed by washing by de-ionized water and soap. Afterward, they were successively put for 20 minuets in acetone, propanol and methanol in the ultrasonic bath and washed using de-ionized water. Finally, the substrate was dried in the oven at 80° C for 30 minutes to remove the excess water.

2.4. Spin coating and thickness measurement

A Novocontrol Technology spin coating system was used in this study. Spin coating was achieved by pouring the solution on a clean substrate to fully cover it. After selecting the velocity of the spin coater, it was switched on to start coating. The velocity used in the experiments was around 1500-3000 rpm. The spin coating duration for all samples was 30 seconds. To remove the extra solvent from the layer, the samples were placed in the oven at a temperature of 60°c for 30 minutes after spin coating. For measuring the thickness of the layer, the layer was removed partly to make a step suitable for surface profiling. Surface roughness of the polymer layer and also its thickness were measured using a profile meter (Dektak8000).

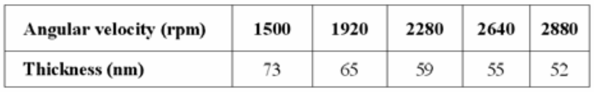
3. Results

In this section the results of the experiments on studying the effect of different parameters such as angular velocity, concentration and viscosity are presented.

3.1. The effect of angular velocity

To investigate the effect of angular velocity on the thickness of PMMA, the solutions formulated in 1% wt Dichloroethane were coated at different velocities. The thickness of each sample was then measured, as shown in Table 1.

Table 1. Effect of angular velocity on the thickness of polymer in dichloroethane.



Angular velocity (rpm)	**1500**	**1920**	**2280**	**2640**	**2880**
Thickness (nm)	73	65	59	55	52

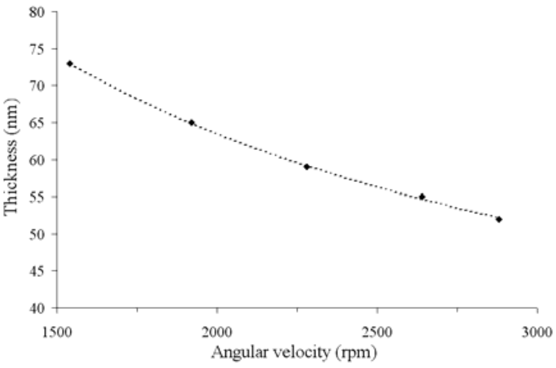


Fig. 2. Thickness of PMMA in Dichloroethane vs. coating velocity.

Fig. 2 shows the experimental results and the curve fitted with function $y = k\,\omega$“. The constants obtained in this function are presented in equation 6:

$$h = 3.76c^{0.53}\ \text{Solvent: Dichloroethane} \tag{6}$$

As the equation clearly suggests, thickness is partially proportional to angular velocity as reversed square, which is in line with theoretical results and also with the previous results obtained for PMMA.[4,5,7,9,10]

3.2. The effect of concentration

As expected, by increasing the concentration, thickness of layer increases as well. The changes in thickness observed at a velocity of 2100 rpm are shown in table 2 and plotted in Fig. 3.

Table 2. Effect of concentrations on thickness of polymer in dichloroethane.

Concentrations (wt%)	**1**	**1.5**	**2**	**3**
Thickness (in dichloroethane) (nm)	68	120	200	420

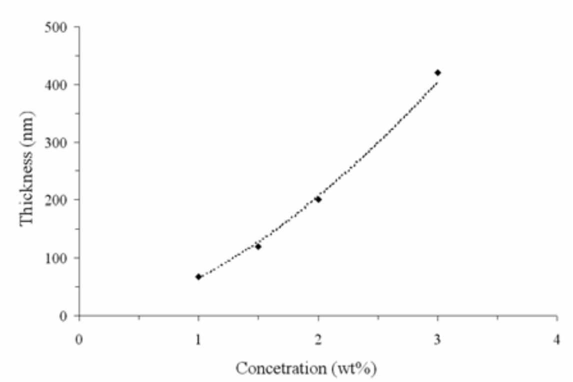


Fig. 3. Thickness of PMMA in dicholoroethane vs. coating concentration.

Fitting this curve with $y = kc^n$ produces equation (7) which shows relativity between thickness and concentration.

$$h = 0.064c^{1.66}\ \text{Solvent: Dichloroethane} \tag{7}$$

The obtained exponent (1.66) for concentration is larger than the one reported for toluene and chloroform [7,8]. Therefore, to find the rationale for this disparity, some viscosity measurements had to be performed.

Comparing equation 6 with 7 and also considering equation (2) reveals the dependence of thickness on both concentration and angular velocity:

$$h = 3.2c^{1.66}\omega^{-0.53} \tag{8}$$

3.3. The effect of viscosity

To investigate viscosity, we used the proportional viscosity method explained above. The dependence of viscosity on primary concentration was reported as a power-law function as assumed in equation (9) [5,11]:

$$\nu = \nu_0 + ac^n \tag{9}$$

In this equation, the first term is relative to solvent viscosity ν_0 and the second one to viscosity of polymeric solution, respectively; "c" is the primary concentration. Table 3 and figure 4 are showing the results obtained for three different solvents.

Table 3. Viscosity dependency on concentration

Concentration	**0.01**	**0.02**	**0.03**	**0.04**	**0.05**
Dichloromethane	0.54	0.64	0.88	1.11	1.34
Dichloroethane	1	1.26	1.58	2	2.37
Chloroform	0.63	0.8	1.04	1.3	1.56

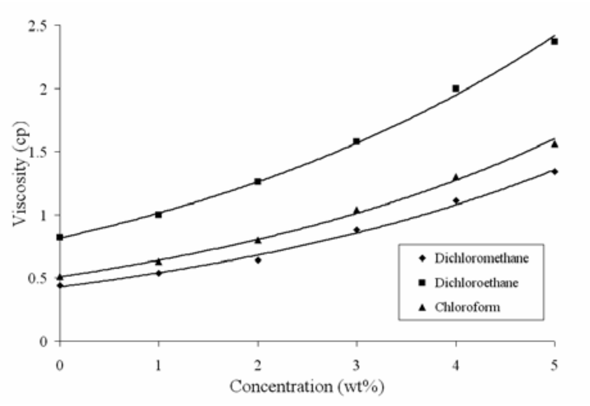


Fig. 4. Viscosity dependency on concentration for three different solvents.

By fitting the obtained results (for the dependence of viscosity on concentration) with equation 9, the following results will be obtained:

$$v = 0.12c^{1.3} + 0.51 \tag{10}$$

$$v = 0.17c^{1.37} + 0.82 \tag{11}$$

$$v = 0.08c^{1.49} + 0.44 \tag{12}$$

The value of altitude in these equations equals the viscosity of solvent. Table 4 shows the exact value for these parameters [12]

Table 4. Viscosity dependency on solvent.

Solvent	Chloroform	Dichloroethane	Dichloromethane
Viscosity (cp)	0.57	0.9	0.44

Values in Table 4 seem rather compatible with equations 10-12.

As said before, the second term in equations 10-12 refers to the polymeric solution viscosity. Although we used the same polymer in all of the three experiments, changing the solvent also varies the first terms.

Since the term of solvent viscosity is already separated (ν_0), the difference between first terms can be inferred to be just due to the polymer viscosity variation in different solutions.

4. Discussion

In the light of equation (8), the dependence of thickness on both concentration and angular velocity is obtained as an exponential term, and can be obtained through equation (2) with the thickness value given. To explain for the changes in the exponents of concentration in different solvents, equation (1) is selected as the primary equation. In this equation, K is dependent on viscosity and can be permuted into an exponential form [5,13,14].

$$h = Ac{\nu_0}^{m}\omega^{\alpha} \qquad (13)$$

Where A is a constant and v is the solution viscosity.

Comparing the results of dichloroethane concentration (Table 2) with equation (13) results in:

$$h = 0.064c(0.17c^{1.37} + 0.82)^{1.7} \qquad (14)$$

(Angular velocity has been a constant throughout the experiment, hence a constant coefficient in equation (14))

According to equation (14), direct effect of concentration is as order one.

By comparing the latter equation with equation 7, we can divide concentration effect into two parts: order one, which is deemed as the direct effect of concentration and the remaining order, which can be regarded as the viscosity effect.

Comparing the results obtained in this study with those reported by Walsh (equation 3 and 4) shows that the order of concentration calculated in our equation is greater than its corresponding value in toluene and chloroform because the viscosity of dichloromethane is greater than that of toluene and chloroform, and also because our polymer's viscosity proves to be greater due to its molecular weight,.

To explain for equations 3 and 4 one should say that, although the viscosity of toluene and chloroform are approximately equal, (toluene = 0.59 cp and chloroform = 0.57cp), polymer viscosity in different solvents can be different, for the reasons explained in equations 10-12. The same fact even applies in where viscosity values of solvents are equal. Therefore, any changes in solvent viscosity cause changes in order of concentration.

The constant indices in equations 3, 4 and 9 increase (which is explained by changes in solvent's vapor pressure) with concurrent increase in the amount of vaporization. Vapor pressure amounts for the three different solvents used in the study are shown in table 5 [12].

Table 5. Vapor pressure dependency on solvent.

Solvent	Dichloromethane	Chloroform	Dichloroethane
Vapor pressure (mmHg)	356	169	71

Any increase in the solvent's vapor pressure causes the solvent to vaporize faster and for the polymer's layer to freeze more quickly, which lead to an increase in layer's thickness.

5. Investigation the uniformity of layer

5.1 Effect of concentration

Table (6) shows surface fluctuation values (from peak to valley) for different concentrations of PMMA in dichloroethane. Coating rate was set at 2280 rpm.

Table 6. Fluctuation of surfaces for different PMMA concentration.

Concentration (wt %)	1	1.5	2	5
Ratio of fluctuations to thickness	0.17	0.16	0.27	0.35
Fluctuations of surface	10	20	55	150-250

The changes observed in the roughness of surface suggest that as the thickness increases [15], so does the fluctuation-thickness ratio to the extent that at 5% concentration, this fluctuation is too variable to be measured properly. Therefore, it can be concluded that increasing concentration is not an appropriate way to increase thickness; rather, to obtain a uniform thickness we have to find the optimal concentration and modify other factors to achieve the desirable thickness.

5.2 Effect of coating rate

Surface fluctuation changes at 1% concentration of dichloroethane are shown in table (7).

Table 7. Fluctuation dependency on angular velocity.

Angular velocity (rpm)	1500	1920	2280	2640	2880
Fluctuations (nm)	10	10	14	14	15

At these rates and ranges of concentration, surface fluctuations do not change considerably by increasing the coating rate.

5.3. Effect of solvent

Changes in surface fluctuations at 2280 rpm and at 1% concentration are shown in table8.

Table 8. Fluctuation dependency on solvent

Solvent	**Dichloroethane**	**Chloroform**	**Dichloromethane**
Fluctuation (nm)	10	17	65

As it can be seen in table 8, as solvent vaporizability increases (Table 5), fluctuations increase as well. This is not unexpected because the polymer loses the solvent and freezes without having enough time to become thin and spread uniformly; therefore, surface quality decreases [17].

Figs. (5) and (6) show the wavy surface fluctuations for the polymers in dichloroethane and chloroform.

This wavy form is known as the striation form, which is created as a result of variations in the adhesion of solvent at different points caused by changes in evaporations of solvent. This form is often seen in solvents which have high evaporation rate.

The images in Figs. (5) and (6), which were produced by a microscope at 550X, illustratively compare this form in two thin layers coated by PMMA solved in different solvents.

The observed fluctuations in the sample produced in dichloroethane solution are fewer in comparison to the ones observed in the chloroform solution.

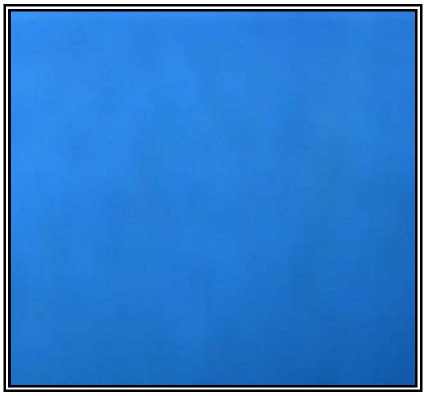


Fig. 5. PMMA solved in dichloroethane (2%wt).

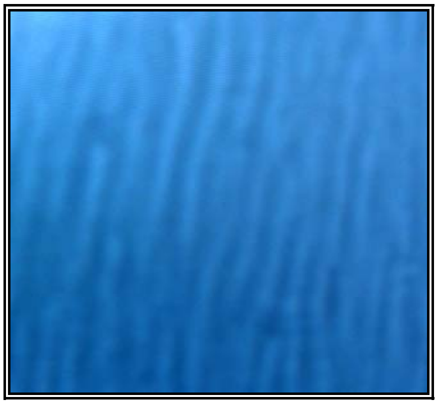


Fig. 6. PMMA solved in chloroform (2%wt).

5. Results and discussions

Thickness of PMMA can be controlled by changing the concentration, spinning rate and the solvent type. In our experiments, angular velocity affected the thickness approximately in reverse square. The effect of concentration depends on the solution’s viscosity, which in turn depends on the molecular mass of the given polymer and the viscosity of the solvent. Furthermore, vaporizability of the solvent also affects the ultimate thickness as a constant index.

To obtain the desirable thickness with appropriate quality in low thickness cases, we have to achieve optimality in concentration, spin velocity and the type of solvent. Increasing the concentration of solution will rapidly decrease the uniformity of the layer. Therefore, lower concentrations are highly recommended. By changing the angular velocity, we can change the thickness without incurring any loss in the uniformity of the surface. Furthermore, the type of solvent selected plays an effective role in uniformity of surface and in the ultimate thickness as well. A solvent with low vaporizability brings about better uniformity of surface and also produces lower thickness. Therefore, the solvent should be selected on the bases of the desirable thickness and uniformity.

Acknowledgments

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References

[1] C. J. Tonzola, M. M. Alam, S. A. Jenekhe, J. Adv. Mater. **14**, 1086 (2002).
[2] S. A. Jenekhe, S. Yi, Appl. Phys. Lett **77**, 2635 (2000).
[3] W. W. Flack, D. S. Soong, A. T. Bell, D. W. Hess, J. Appl. Phys. **56**, 1199 (1984).

[4] A. G. Emslie, F. T. Bonner, L. G. Peck, J. Appl. Phys. **29**, 858 (1957).

[5] D. J. Meyerhofer, Appl. Phys. **49**, 3993 (1978).

[6] C. Walsh, E. I. Franses, Thin Solid Films **347**, 167 (1999).

[7] C. Walsh, E. I. Franses, Thin Solid Films **429**, 71 (2003).

[8] C. J. Lawrence, Phys. Fluids, **2**, 453, 1990.

[9] D. E. Bornside, C. W. Macosco, L. E. Scriven, J. Appl. Phys. **66**, 5185 (1989).

[10] D. E. Bornside, R. A. Brown, P. W. Ackmann, J. R. Frank, A. A. Tryb, F. T. Geyling, J .Appl. Phys. **73**, 585 (1993).

[11] C. C. Chang, C. Pai, W. Chen, S. A. Jenekh, Thin Solid films **479**, 254 (2005).

[12] I. M. Smallwood, Handbook of organic solvent properties, Elsevier, 1996.

[13] W. J. Daughton, F. L. Givens, J. Electrochem. **129**, 173 (1982).

[14] B. T. Chen, Polymer Eng. Sci. **23**, 399 (1983).

[15] C. Liang, L. Xue, H. Y. Chun, Appl. surface Sci **7252**, 8156 (2006).

[16] J. Paul, H. Lima, A. M. Andrade, J. Mater. Sci-Mater Electron. **17**, 593 (2006).

[17] S. Zeno, W. Wicks, F. N. Jones, S. P. Pappas, D. A. Wicks, Wiley Inter Science, New York, Ch. **18**, 349 (2007).

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