The Examination of the Changes in the Magnetic Properties of the Poly(methyl methacrylate)

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Abstract. Poly(methyl methacrylate) PMMA was prepared by using Atom Transfer Radical Polymerization technique. The production of PMMA as thermoplastic polymer was executed as an effective way by using the living polymerization technique. The changes in magnetisation properties of PMMA were determined with the rise of the polymerisation temperature from 45°C in argon to the room temperature in air. Hence the excess oxygen effect on the magnetic properties was investigated to examine the changes of the magnetic properties depending on the air-sensitivity of the PMMA with the decrease of the temperature. The hysteresis loops indicated that the production ambient conditions of the PMMA has affected the magnetic properties and the magnetic properties varied from diamagnetic to paramagnetic ordering with the decrease of the polymerization temperature in the excess oxygen.

1. Introduction
There are several polymerization techniques such as radical polymerization, emulsion polymerization, solution polymerization, anionic polymerization, and bulk polymerization. Atom Transfer Radical Polymerization (ATRP) is the most versatile controlled/living radical polymerization method and ATRP is an effective method to prepare the polymers controlled the functionalities, topologies and compositions [1]. Recombination of chain ends is important at living polymerization. Foundation of living anionic polymerization followed by controlled/living polymerization made very large impact both on polymer and materials science, as it has opened new frontiers and capabilities in polymer science [2]. The main characteristics of the living polymerization technique are quick initiation of the reactive chain ends in the chain termination and the chain transfer at the polymer chain growing process. This process gives living polymerization specialty of growing macromolecular species [3]. Poly (methyl methacrylate) (PMMA) is a transparent thermoplastic polymer coming from the acrylate family. Methyl methacrylate (MMA) is the monomer of the PMMA. The method of polymerization of PMMA using MMA is radical polymerization technique. ATRP mechanism consists of six main components to synthesize the PMMA using monomer. These components are monomer, initiator, catalyst, ligand, solvent, temperature.

There was not available the detailed information about the magnetic properties of the PMMA prepared by living polymerization technique. In the present study it is reported the details on the structural characterization and the magnetic properties of PMMA produced by the living polymerisation technique. ATRP method provided to produce the well-defined air-sensitivity of the
PMMA. The magnetic properties were examined with the homogenous dispersion of metal ions in PMMA solution at the production step by using ATRP method.

2. Experiments

2.1. Material and Process
Tetra-n-buthylammonium bromide-Bu4NBr (C16H36BrN), 98+% (Alfa Aesar); Copper bromide (CuBr); Methyl methacry late-MMA (C5H8O2)n., 99% stab (Alfa Aesar); 1,1,4,7,7-Pentamethyldiethylenetriamine-PMDETA (C H N ), 98% (Alfa Aesar); Ethly 2-bromoisobutyrate-EBiB ( C6H11BrO2), 98+% (Alfa Aesar) were used in the experiments. Extra pure argon and regulator were received from Özvarış Co. The preparation and measurements were performed inside AtmosBag four-hand, size L, closure type, Tape-seal (Sigma-Aldrich) to fabricate the PMMA produced by using the living polymerisation technique.

2.2 Production of PMMA by using Living Polymerization Technique
Extra pure argon and regulator is obtained from obtained and chained to a concrete wall to meet the safety regulations. There was not external intervention requirement in this study. Before materials measurements AtmosBag four-hand, non-sterile, size L, closure type, Tape-seal (Sigma-Aldrich) completely vacuumed, followed by 10 min extra pure argon circulation into system. Bu4NBr (1.031 g, 3.2 mmol) and, PMDETA (0.069 g, 0.4 mmol) were added to tube (8 × 2.5 cm) equipped inside atmosbag. Inside the glove bag, the extra pure argon is applied to the tube.

2.3. The measurement of the magnetic properties of the PMMA
A Lake Skore Cryotronics 7410 Vibrating-Sample Magnetometer (VSM) was used to measure the magnetic properties of the PMMA at Universiti Teknologi PETRONAS Department of Fundamental and Applied Sciences, Faculty of Science and IT, Seri Iskandar, Perak, Malaysia in Figure 1.

Figure 1. The used Vibrating-Sample Magnetometer (VSM).

3. Results and Discussions

3.1. Raman Spectroscopy for Analysis of PMMA
The characteristics of Raman spectra of PMMA produced by ATRP method were determined by using a Horiba Raman Spektroscopy in Universiti Teknologi PETRONAS (UTP), Faculty of Science, Department of Fundamental and Applied Sciences, Seri Iskandar, Perak Malaysia.
Raman measurements were performed at room temperature. The characteristics of Raman spectra were presented for the PMMA produced in room temperature (in Figure 2 and Table 1) and for the PMMA produced at 45°C in argon (in Figure 3 and Table 2). Hence it was possible to evaluate the details on Raman spectra of the well-defined air-sensitivity of the PMMA. The detailed information about the reason of the Raman peak positions and their functional group/vibrations were presented in Horiba Jobin Yvon Raman Application Note. The similar Raman spectra results for PMMA optical fibres fabricated by a preform drawing process are available in the literature [4]. The increase of Raman intensity results is presented with the rise of the temperature for the nanomaterials and nanostructures [5]. The details on the increase of Raman intensity with the rise of the polymerization temperature at the production step of the PMMA were examined in Fig. 2-3 and Table 1-2. There was not a considerable change in Raman spectra with the temperature increase but the intensity values increased depending on the rise of the polymerization temperature of the PMMA at the production step.

![Figure 2. Raman spectra of PMMA produced in room temperature in air.](image)

| Raman Peak Positions (cm\(^{-1}\)) | Functional Group/Vibration                                      |
|-----------------------------------|---------------------------------------------------------------|
| 597.26                            | \(\nu(C-Br)\)                                                 |
| 668.49                            | \(\nu(C-Br)\)                                                 |
| 816.44                            | \(\nu(C-O-C)\)                                                |
| 1134.25                           | \(\nu(CC)\) alicyclic, aliphatic chain vibrations             |
| 1465.75                           | \(\delta(CH_3)\) asym                                         |
| 1898.63                           | \(\nu(C=C)\) strong bonds                                    |
| 2101.37                           | \(\nu(C\equiv C)\) strong bonds                               |
| 2167.12                           | \(\nu(C\equiv C)\) strong bonds                               |
| 2967.12                           | \(\nu(C-H)\) aliphatic                                       |
3016.44 \ u(=\text{C-H}) \text{ strong} \\
3252.05 \ u(O-H) \text{ weak}

**Figure 3.** Raman spectra of PMMA produced at 45°C in argon.

**Table 2:** Raman frequencies of the chemical functional groups/vibrations of PMMA produced at 45°C.

| Raman Peak Positions (cm\(^{-1}\)) | Functional Group/Vibration                      |
|-----------------------------------|------------------------------------------------|
| 561.64                            | \ u(\text{C-Br})                                 |
| 819.18                            | \ u(\text{C-O-C})                                |
| 1134.25                           | \ u(\text{CC}) alicyclic, aliphatic chain vibrations |
| 1465.75                           | \ \delta(\text{CH}_3) \text{ asym}               |
| 1745.21                           | \ u(\text{C=O})                                  |
| 2101.37                           | \ u(\text{C=C}) strong bonds                     |
| 2167.12                           | \ u(\text{C=C}) strong bonds                     |
| 2969.86                           | \ u(\text{C-H}) aliphatic                        |

3.2. **Energy Dispersive X-ray (EDX) analysis**

The changes in C and O amount at the PMMA matrix were determined to evaluate their effect on the magnetic properties. The results in Energy Dispersive X-ray analysis were performed for the PMMA samples produced in room temperature (Figure 4) and in 45 °C (Figure 5).
There was a slight difference in the EDX analysis results between the PMMA samples produced at room temperature in air and at 45 °C in argon. Hence it was possible to evaluate the excess oxygen effect on the magnetic properties of the PMMA and to examine the changes in the air-sensitivity of the polymer clearly. It was determined that there were the slight increases at C and O intensity when the polymer was produced in air.

### 3.3. X-ray Fluorescence (XRF) Analysis

XRF analysis was performed in Istanbul Technical University Energy Institute, Istanbul Turkey. XRF analysis has conducted to examine the copper amount in the PMMA and the purity of the polymer matrix produced by the living polymerization technique (Table 3).

| Detected | ppm  | +/-  |
|----------|------|------|
| Cu       | 4502 | 71   |

**Table 3. XRF results of produced living polymer PMMA.**
3.4. Variable Pressure Environmental Scanning Electron Microscopy (VP-ESEM) Analysis
The VP-ESEM Analysis was performed in Universiti Teknologi PETRONAS (UTP), Faculty of Science, Department of Fundamental and Applied Sciences, Seri Iskandar, Perak Malaysia. Ionizing radiation exposure and thermal effects depending on electron flux at SEM analysis can cause damage to polymeric materials. Besides, damages can occur in the form of breaking chemical bonds, mass loss and degradation of crystallinity in Figure 6-7 [6].

The PMMA samples were investigated under optimized conditions for topographic description using a Variable-Pressure Environmental Scanning Electron Microscope (VP-ESEM). Extensive VP-ESEM studies have been performed on the prepared samples and wide range of morphological information about the PMMA produced by living polymer. It was not possible to get SEM images directly without coating the material instead the samples have been processed with variable pressure environmental scanning electron microscope.

Varying the pressure makes it possible to obtain images without coating but radiation damage is expected with presence of oxygen at the chamber [6-7]. The VP-ESEM images were taken for PMMA samples produced at room temperature in air (at 100X magnifications in Figure 8 and at 1.00kX magnifications in Figure 9) by applying EHT 20 kV voltage in this study.

Figure 6. SEM images of a molded surface of Poly(oxymethylene) (POM) with holes and beam damage (Goldstein, 2003).

Figure 7. Damage resulting from focusing at higher magnification (Goldstein, 2003).

Figure 8. VP-ESEM images of the produced PMMA in air.

Figure 9. Focused VP-ESEM image of the produced PMMA in air.

3.5. The improvement in the magnetic properties of the PMMA
The magnetic types of the elements used in the production of the PMMA were determined as diamagnetism and paramagnetism. The magnetic properties of the used elements and the possible occurred oxygen species at the production of the PMMA were presented in Table 4 and Table 5 [8-9]. The production process of polymer in air can generate copper superoxides (CuOx, x = 2, 3, 4) which
can improve the magnetic properties of the polymer as the peroxides and superoxides are ionic compounds. Besides, O$_2$ is paramagnetic as it has two unpaired electrons. The superoxide ion (O$_2^-$) has an unpaired electron. Hence, the superoxide ion (O$_2^-$) is paramagnetic and has an intermediate O–O bond. The peroxide ion (O$_2^{2-}$) is diamagnetic and has an O–O single bond [8-9]. Magnetic Properties of Diatomic Oxygen Species are presented in Table 5.

Table 4. Magnetic types of the used elements for the production of the PMMA by using ATRP method.

| Element | Carbon (C) | Hydrogen (H) | Bromine (Br) | Nitrogen (N) | Copper (Cu) | Oxygen, O$_2$ |
|---------|------------|--------------|--------------|--------------|-------------|---------------|
|         | X          | X            | X            | X            | X           | X             |

Diamagnetic
Paramagnetic

Table 5. Magnetic properties of diatomic oxygen species.

| Species       | Unpaired Electrons | Magnetic Properties |
|---------------|--------------------|---------------------|
| Oxygen        | O$_2$              | 2                   | Paramagnetic   |
| Superoxide ion| O$_2^-$            | 1                   | Paramagnetic   |
| Peroxide ion  | O$_2^{2-}$         | 0                   | Diamagnetic    |

The changes in the magnetic moment of the metal ions at PMMA were determined with VSM analysis. The metal ions were presented their magnetic properties in the PMMA structure after the homogeneous dispersion of the metal ions at the polymerization process of PMMA. Magnetization curves were determined by using a vibrating sample magnetometer in Figure 10a for PMMA produced at room temperature and their details were presented in Fig. 10b. Besides, magnetization curves for PMMA produced at 45 °C in argon were examined in Figure 11.

Figure 10 a. Magnetization curves of the PMMA produced at room temperature in air.
Figure 10b. VSM profile of magnetic moment (emu) versus applied field (G) curve of PMMA.

Figure 11. Magnetization curves of the PMMA produced at 45 °C in argon.
The different magnetic properties such as magnetization \( M_s \), intrinsic coercive force \( H_{ci} \) (indicating its resistance to demagnetization), and retentivity \( (M_r) \) (indicating the residual magnetization at zero field) were examined by using VSM analysis and the results were presented in Table 6.

**Table 6. Magnetic Properties of the PMMA.**

| Magnetic Properties of PMMA Produced in different temperatures | \( M_s \) (emu) | \( H_{ci} \) (G) | \( M_r \) (emu) |
|---|---|---|---|
| room temperature | 526.090 E-6 | 4158.4 | 024.11 E-6 |
| 45°C | 017.975 E-6 | 0.0 | 810.42 E-9 |

The decrease of the temperature improves the magnetic properties of the material [10]. It was suggested that the copper superoxides formed more effectively than Copper(I) peroxide \( (Cu_2O_2) \) when the temperature of the PMMA solution decreased to the room temperature at excess oxygen in air. This result addressed to reason the increase in the magnetic moment with the decrease of the room temperature at excess oxygen in air. Hence, the excess oxygen in ambient led to the formation of the copper superoxides effectively and the magnetic moment increased with the presence of the excess oxygen in air.

The improvement in the magnetic properties was attributed to the rise of the paramagnetic Cu(II) ions as a result of the decrease of the production temperature of PMMA from 45 °C (in argon) to the room temperature (in air). It was assumed that the diatomic oxygen species such as \( O_2 \) and \( O_2^- \) have affected the magnetic properties of PMMA at room temperature in air as the excess oxygen diffusion accelerated on the surface of the PMMA at room ambient. But the decrease in the magnetic properties was attributed to the increase of the number of diamagnetic Cu(I) ions as a result of the decrease in the unpaired electrons of the diatomic oxygen (such as \( O_2^- \) ) depending on the increase in the temperature to 45 °C in argon. The increase in the magnetic properties of the PMMA was attributed to the increase in the number of the unpaired electrons of the diatomic oxygen resulted with the improvement in the magnetic properties of the PMMA at room temperature.

The results of the Raman spectra analysis supported to appear the \( (O-H) \) vibrations after the production of the PMMA at room temperature in air. It is explained that \( Cu_2(OH)_3 \) improve the magnetic properties of the material in the literature [11]. The improvement of the magnetic properties in the PMMA produced at room temperature indicated that the formation of \( Cu_2(OH)_3 \) according to the appearance of the Raman OH vibration of the PMMA.

### 4. Conclusions

In conclusion, the magnetic properties of the elements used in PMMA produced at 45 °C in argon referred to more non-magnetic properties than the magnetic properties of the PMMA produced at room temperature in air. The decrease of the polymerization temperature in air made the modification of the electronic structure of the PMMA resulted with the improvement in the magnetic properties.

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### References

[1] Müller, A. H., & Matyjaszewski, K. (2010). Controlled and Living Polymerizations: Wiley Online Library.
[2] Geckeler, K. E., & Nishide, H. (2009). Advanced nanomaterials: John Wiley & Sons.
[3] T. Bel, H. Cakar, N. Yahya, C. Arslan, N. Baydogan, Investigation of the Bubble Effect in Lightweight PMMA Polymer, Defect and Diffusion Forum, 2017, Volume 380, pp. 227-231
[4] K J Thomas, M Sheeba, V P N Nampoori, C P G Vallabhan and P Radhakrishnan, Raman spectra of polymethyl methacrylate optical fibres excited by a 532 nm diode pumped solid state laser, J. Opt. A: Pure Appl. Opt. 10 (2008) 055303(5pp).
[5] Ph. Colomban and A. Slodczyk, Raman Intensity: An Important Tool in the Study of Nanomaterials and Nanostructures Vol. 116 (2009) ACTA PHYSICA POLONICA A No. 1
[6] Goldstein, J. (2003). Scanning electron microscopy and x-ray microanalysis (3rd ed.). New York: Kluwer Academic/Plenum Publishers.
[7] Lyman, C. E. (1990). Scanning electron microscopy, X-ray microanalysis, and analytical electron microscopy : a laboratory workbook. New York: Plenum Press.
[8] Y.W. Zhu, A.M. Moo, T. Yu, X.J. Xu, X.Y. Gao, Y.J. Liu, C.T. Lim, Z.X. Shen, C.K. Ong, A.T.S. Wee, J.T.L. Thong, C.H. Sow, Enhanced field emission from O2 and CF4 plasma-treated CuO nanowires, Chemical Physics Letters 419 (2006) 458–463.
[9] Kenneth W Whitten, Raymond E. Davis, George G Stanley, Chemistry Solutions Manual, 10th Edition, Chegg Study, Publisher Mary Finch, 2014.
[10] Daopeng Zhang, Lingqian Kong, Ping Wang, Xia Chen Synthesis, Crystal Structures, and Magnetic Properties of Two [Cu(cyclm)]2+ - Based One-Dimensional Chain Complexes, 2016 Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, pp. 828-831, Volume 46, Issue 6.
[11] Wataru Fujita and Kunio Awaga, Magnetic Properties of Cu2(OH)3(alkanecarboxylate) Compounds: Drastic Modification with Extension of the Alkyl Chain, Inorg. Chem. 1996, 35, 1915-1917.