IMPACT OF HUMIDITY ON CHEMICAL BONDING, POROSITY AND MICROSTRUCTURE OF 3D PRINTED PLA

R.A. Hamid[1,*], D. Sindam[1], S. Akmal[2], L. Abdullah[1] and T. Ito[3]

[1]Faculty of Industrial and Manufacturing Technology and Engineering, Universiti Teknikal Malaysia Melaka, 76100 Durian Tunggal, Melaka, Malaysia.

[2]Faculty of Mechanical Technology and Engineering Technology, Universiti Teknikal Malaysia Melaka, 76100 Durian Tunggal, Melaka, Malaysia.

[3]Graduate School of Computer Science and Systems Engineering, Okayama Prefectural University, Kabuki 111, Soja-shi, Okayama 719-1197, Japan.

*Corresponding Author's Email: rahimah.hamid@utem.edu.my

Article History: Received 8 July 2023; Revised 1 September 2023; Accepted 15 November 2023

ABSTRACT: Commonly used 3D printing material, such as polylactic acid (PLA), degrades when exposed to high temperatures and humidity. Moisture in the filament causes material degradation due to interactions with polymer molecules, particularly in hygroscopic filaments. This study aimed to investigate the impact of humidity on the chemical composition and porosity of 3D-printed PLA specimens. Four conditions were examined: a new PLA as a reference, used PLA stored in a vacuumed bag with 50g desiccant, used PLA stored without desiccant, and used PLA exposed to humidity for 48h, 96h, and 150h. Filament porosity was determined using the Archimedes Principle, while Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM) were employed to analyze the chemical composition and structural changes, respectively. The findings revealed that humidity influences the chemical bonding of 3D-printed filaments, increasing the intensity of the O-H bond. More prolonged humidity exposure decreased density and increased porosity in the printed parts. Filaments stored with desiccant exhibited lower O-H bond intensity and porosity than those without desiccant. Additionally, prolonged humidity exposure, like 150h, caused more significant structural changes and larger surface morphology gaps, approximately 28.37%, than the control group, indicating lower density in the printed filaments. Therefore, the used filament must be stored properly to avoid moisture and produce porous and lower-strength 3D-printed parts.

KEYWORDS: *3D Printing; Humidity; PLA; Chemical Bonding; Porosity*

1.0 INTRODUCTION

Humidity is one of the key factors influencing the filament's properties. PLA is an organic substance that quickly absorbs moisture and is particularly sensitive to trace water levels [1]. Excessive humidity can cause the PLA filaments to degrade [2]. When the filament absorbs water, and the 3D printer heats it for extrusion, the water and heat combine to form steam, which causes the filament to bubble as it exits the hot end, resulting in an uneven surface on the print. The rapid expansion of steam within the filament can create bubbles or voids in the printed part, resulting in porosity. These voids interrupt the printed layers' continuity and compromise the part's structural integrity. If the PLA filament has been subjected to heavy moisture for an extended period, the filament has lost tensile strength at printing, allowing bubbles to emerge on the product's surface [3].

Mitchell et al. [4] stated that the elongation ratio, degradation rate, and average molecular weight increase when humidity increases. As a result, the mechanical properties of the 3D printed parts will decrease due to the changes in the chemical structure of the polymer with exposure to water [5]. Due to the principle of 3D printing, thermal deformation generated during the printing operation is affected by moisture [6]. A chemical analysis of the moisture-exposed filament is significant for ascertaining the chemical bonding modifications between the humidity-exposed and original filaments [7]. According to Liao et al. [8], the porosity and crystallinity of the printed parts are two characteristics that can influence the structural change of the printed parts. While the impact of moisture on the 3D printing process is widely acknowledged, there remains a notable research gap in the precise characterization of moisture levels during prolonged exposure and its correlation with the effects. Specifically, no studies have employed FTIR analysis to identify the extent of moisture absorption and its associated chemical changes in the filament over varying exposure durations. Therefore, the present study aims to identify the effect of moisture on the polymeric chemical chain bonding, porosity, and microstructural changes of the humidity-exposed 3D-printed PLA at different humidity level conditions. The finding of this study may demonstrate the correlation between the duration of moisture exposure and its effect on the porosity and intensity level of hydrogen bonds.

2.0 METHODOLOGY

In this study, a humidifier was employed to introduce controlled moisture conditions to the specimens for durations of 48, 96, and 150 hours. The time intervals were set using a digital timer to ensure precise and consistent exposure. Specific humidity levels were maintained consistently throughout the designated durations. Initially, the PLA filament was categorized into four groups:

a. A new PLA filament as a reference;
b. Used PLA filament stored in the vacuum bag with 50g of desiccant,
c. Used PLA filament stored in the vacuum bag without desiccant,
d. Filament stored in an open atmosphere and subjected to a humidifier for a period of 48, 96, and 150 hours.

Since the primary performance of the additive production process relies on the appropriate set of process parameters [9], the process parameters for 3D printing were set constant for all groups, as shown in Table 1. The number of replications is set to three for all groups, and the dimension of the sample is depicted in Figure 1. Ender 3 V2 was used for printing the additively manufactured samples.

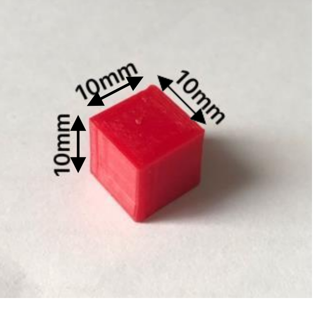


Figure 1: Dimension of the FTIR sample (10mmx10mmx10mm) (WxLxH)

Table 1: 3D printing process parameters

Factor	Level
Printing temperature	220 °C
Bed temperature	60 °C
Printing speed	60 mm/s
Filling percentage	100%
Layer thickness	0.10 mm

Then, an FTIR machine (JASCO FT/IR 6100), as displayed in Figure 2 was used to analyze the polymeric chain bonding, particularly in the O-H group, to identify the influence of moisture on the filament.

(a) (b) (c)

Figure 2: (a) FTIR machine, (b) specimens and (c) measurement chamber

For the porosity analysis, Archimedes's Principle was adopted. The analytical balancing scale measuring method with distilled water is employed to limit the occurrence of air bubbles. Using this equipment, as shown in Figure 3a, it is possible to obtain precise mass measurements of samples in water and air. Each sample was tested in the atmosphere and water three times. Measuring was done once the scale had been re-calibrated. Each measurement result was recorded once the scale had reached equilibrium.

(a) (b)

Figure 3: (a) Analytical balancing scale and (b) SC 7620 mini sputter coater

The 3D printed components' surface was sputter-coated with 10nm of 20% palladium and 80% gold using SC 7620 mini sputter coater, as indicated in Figure 3b. The microstructural study is essential to determine how the structural change occurs after exposing the filaments to moisture. The microstructural study was examined at magnifications of 50x and 100x using a Carl Zeiss Evo 50 scanning electron microscope (SEM) equipped with a 15 kV acceleration voltage, as shown in Figure 4. ImageJ analyzer was used to measure the interlayer gap lengths in the SEM images for comparison.

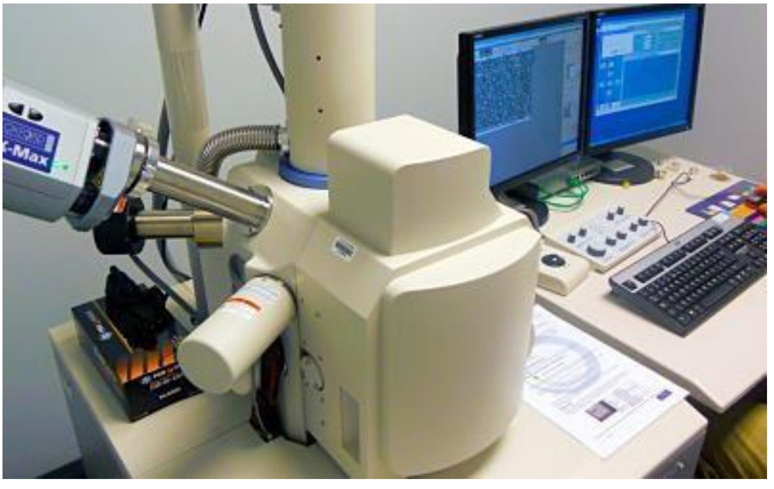


Figure 4: SEM machine (Carl Zeiss Evo 50)

3.0 RESULTS AND DISCUSSION

3.1 FTIR Analysis

Figure 5 displays the transmittance vs. wavelength graph obtained from the FTIR spectra analysis to identify the influence of moisture in the polymeric chemical chain bonding of the 3D-printed PLA. There are three different bonds in the graph, which are identified as hydroxide ion bond (O-H), carbon-hydrogen bond (C=H), and carbon monoxide bond (C-O). The IR (Infrared Radiation) peaks or stretching bands that were analyzed on this graph according to the O-H region that has been marked. The O-H bond is expected to be found in the range of wavenumbers from around 2800 cm^{-1} to 3000 cm^{-1}, as suggested by [10].

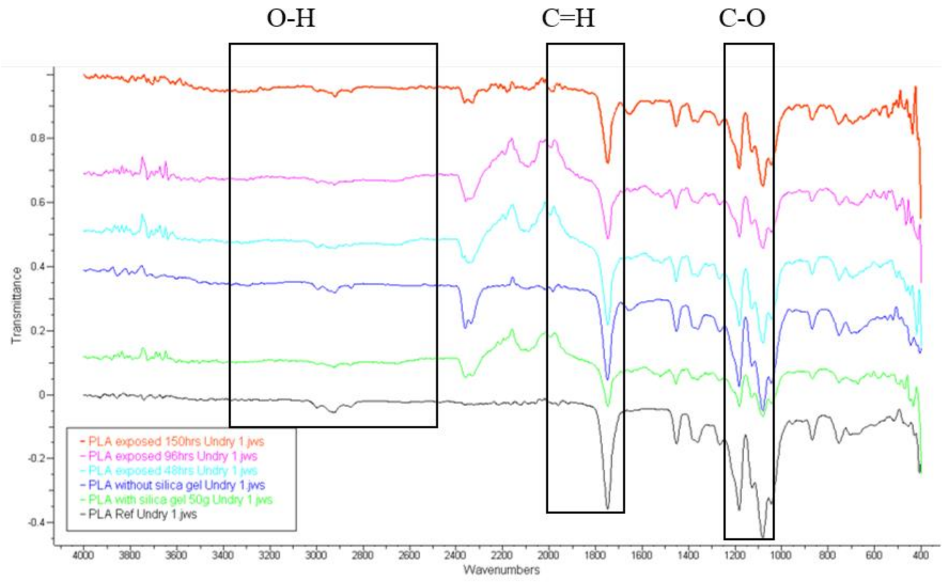


Figure 5: Intensity level of the hydrogen bonds (O-H) for different groups

The finding shows that the duration of humidity exposure (hours) proportionally contributes to the increase in transmittance of the O-H bond. According to Figure 5, the highest O-H peak was spotted in the group stored in an open atmosphere and subjected to moisture. The exposure duration is also significant; the longer the exposure time, the higher the O-H peak was. 150 hours of exposure has the highest O-H peak, followed by 96 and 48 hours, respectively. Next, the PLA that was stored in a vacuum bag with desiccant exhibited a low intensity of the O-H bond compared to the PLA filament that was stored without desiccant, which showed a slightly higher intensity of the O-H bond. The findings indicate that the desiccants can effectively control the humidity during storage. As expected, the reference filament demonstrates the lowest intensity of the O-H bond. The results supported the findings from Pagnin et al. [11], who suggested that the influence of gases in the ambient atmosphere might cause a morphological changes in the polymeric film structure. In this study, however, the influence of moisture, on the other hand, has resulted in the polymeric structural changes in the chemical bonding, which is proven using the FTIR analysis. Figure 6 shows the chemical structure of pure PLA. When polymers are broken down into smaller units called monomers, the molecule of water (H_2O) is used to break the original bond of the polymer caused by a hydrolysis reaction. Since both water (H_2O) and polymers are polar molecules, they are naturally attracted to one another. As a result of this reaction, long polymer chains will be cut into shorter segments. Shorter polymer chains cause the filament to become more brittle than flexible.

If hydrolysis continues, the filament might disintegrate into tiny fragments before it can be fed into a 3D printer. Unfortunately, once the effects of hydrolysis have begun to manifest, they cannot be stopped by simply drying the filament. All macromolecules undergo the same hydrolysis and dehydration reactions, but each monomer and polymer reaction is unique to its group. The polymerization, or more specifically, the level of polymerization, is influenced by moisture in the filament. This theory supported the findings of this study, which indicated a high transmittance level for the longer moisture exposure time. Therefore, the finding confirms that moisture has caused the filament to go through a chemical reaction that permanently alters the structure of the polymer.

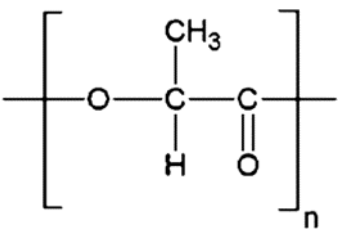


Figure 6: Chemical structure of PLA [12]

3.2 Density

The density test of the printed PLA was performed using analytical balancing scale. The Archimedes Principle, which is the water immersion technique, was applied in this test to determine the relative density of the PLA using Equation 1. The theoretical density of pure water is 1 g/cm^3.

$$\rho = \left(\frac{W_a}{W_a - W_w}\right)\rho_W \tag{1}$$

Where ρ is relative density of sample in (g/cm^3), W_a is the weight of the sample in the air, W_w is the weight of the sample in water, and ρ_W is the density of distilled water which is 0.1g/cm^3.

Figure 7 exhibits the density measurement for all groups. The graph shows a continuous change in density measurement with a declining trend if the filament is exposed to humidity. The reference filament illustrates the maximum density, followed closely by the used filament stored in the vacuum bag with a 50g desiccant. The filament stored in a vacuum bag but without a desiccant has a slightly lower density than that stored with a desiccant. The density gradually dropped when the filament was exposed to a humidifier for 48 hours. Then, a steep decline in density was measured when the filament was exposed to humidity for 96 hours and continued to fall for 150 hours. Table 2 tabulates the weight measurement in air and water in all groups.

From this finding, it can be concluded that exposure to humidity changes the material's chemical chain bonding, and the presence of water during printing can also affect the printed parts' porosity. Specimens that have been exposed to humidity show a low, dense measurement, which also indicates a high porosity in the microstructure. If the printed parts are porous, it will simultaneously affect the mechanical strength of the part [13].

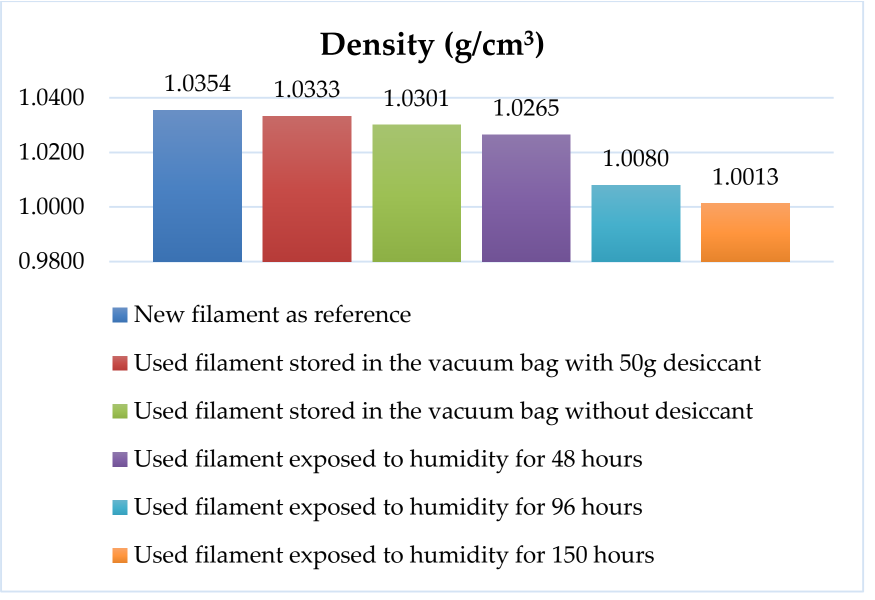


Figure 7: Density level at different condition

Table 2: Weight of sample and its density

Group		Weight in air (g)	Weight in water (g)	Density (g/cm^3)
A new PLA filament as a reference		1.16	1.14	1.0354
Used PLA filament stored in the vacuum bag with 50g of desiccant		1.19	1.16	1.0333
Used PLA filament stored in the vacuum bag without desiccant		1.17	1.16	1.0301
Filament stored in an open atmosphere and subjected to a moisture-exposed for a period of 48, 96, and 150 hours.	48	1.17	1.15	1.0265
	96	1.16	1.15	1.0080
	150	1.17	1.15	1.0013

3.3 Microstructure Analysis

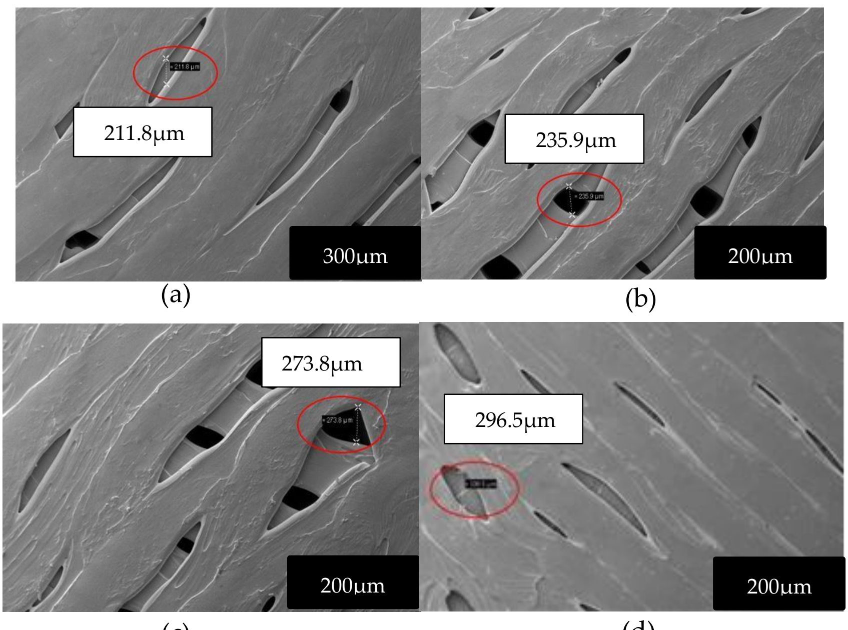
Table 3 shows the structural length measurement in the SEM images of the specimens. The longest surface morphology was found on the sample exposed for 150 hours, as indicated in Figure 8, with an increment of 28.37% than the reference group.

The structural change of each filament varies according to the condition or storage of the filament before printing. The finding supported the density analysis result, where with a high level of porosity in the specimen with 150 hours' duration with moisture, the analysis of its microstructure shows bigger gaps compared to the other group.

Table 3: The structural length measurement

Type of sample	Length 1	Length 2	Length 3	Average
	Micrometer (µm)			
New filament as a reference	211.80	216.90	220.90	216.53
Used filament stored in the vacuum bag with 50g desiccant	235.20	227.50	214.30	225.67
Used filament stored in the vacuum bag without desiccant	273.80	218.30	221.40	237.83
Used filament exposed to humidity for 48h	235.90	258.00	221.70	238.53
Used filament exposed to humidity for 96h	260.50	283.40	254.30	266.07
Used filament exposed to humidity for 150h	296.50	280.10	257.30	277.97

Moisture can affect the extrusion process, subsequently expanding the surface gap. Moisture-absorbed filaments exhibit poor material flow and may experience uneven melting, leading to inconsistent layer bonding. This uneven bonding and reduced interlayer adhesion contribute to the formation of voids and porosity in the printed part. Therefore, the finding concludes that the longer the surface morphology gaps, the wider the structural gap in the microstructure, indicating increased porosity.



(c) (d)

Figure 8: Cross-sectional microstructure of the PLA (a) reference specimen, (b) vacuumed with 50 g desiccant, (c) vacuumed with no desiccant, (d) exposed to moisture for 150 hours

4.0 CONCL U S ION

To conclude, moisture affects the polymeric chemical chain bonding, porosity, and microstructural changes of the PLA, and the duration of exposure is proportionate to the impacts. The longer the filament was exposed to the humidity, the more intense the O-H transmittance was recorded, and the more porous the 3D-printed part became.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the facilities provided by Universiti Teknikal Malaysia Melaka for this research work. This research was funded by the research grant PJP/2022/FKP/KP/S01902.

AUTHOR CONTRIBUTIONS

D. Sindam: Conceptualization, Methodology, Software, Writing-Original Draft Preparation; R.A. Hamid; S. Akmal: Data Curation, Validation, Supervision; L. Abdullah; T. Ito: Software, Validation, Writing-Reviewing and Editing.

CONFLICTS OF INTEREST

The article has not been published elsewhere and is not under consideration by other journals. All authors have approved the review, agree with its submission and declare no conflict of interest on the article.

REFERENCES

[1] R. J. Zaldivar, T. D. Mclouth, G. L. Ferrelli, D. N. Patel, A. R. Hopkins, and D. Witkin, "Effect of initial filament moisture content on the microstructure and mechanical performance ULTEM ® 9085 3D printed parts", *Additive Manufacturing*, vol. 24, pp. 457–466, 2018.

[2] N. Elmrabet and P. Siegkas, "Dimensional considerations on the mechanical properties of 3D printed polymer parts", *Polymer Testing*, vol. 90, no. 106656, pp. 1-15, 2020.

[3] A. P. Valerga, M. Batista, J. Salguero, and F. Girot, "Influence of PLA filament conditions on characteristics of FDM parts", *Materials (Basel).*, vol. 11, no. 8, pp. 1-13, 2018.

[4] M. K. Mitchell and D. E. Hirt, "Degradation of PLA fibers at elevated

temperature and humidity", *Polymer Engineering Science*, vol. 55, no. 7, pp. 1652–1660, 2015.

[5] K. M. Z. Hossain, A. J. Parsons, C. D. Rudd, I. Ahmed, and W. Thielemans, "Mechanical, crystallisation and moisture absorption properties of melt drawn polylactic acid fibres", *European Polymer Journal*, vol. 53, no. 1, pp. 270–281, 2014.

[6] T. Kobayashi, J. Nishii, M. Ishida, H. Furumoto, Y. Utsumi, H. Kanematsu, C. Gruescu, "Experimental study of thermal deformation in a 3D-printing process with polymer filament", *Journal of Advanced Manufturing Technology*, vol. 13, no. 1, pp. 61–70, 2019.

[7] M. R. Shahmirzadi, A. Gholampour, A. Kashani, and T. D. Ngo, "Shrinkage behavior of cementitious 3D printing materials: effect of temperature and relative humidity", *Cement and. Concrete. Composites*, vol. 124, no. 104238, pp. 1-17, 2021.

[8] Y. Liao, C. Liu, B. Coppola, G. Barra, L. Maio, L. Incarnato, and K. Lafdi, "Effect of porosity and crystallinity on 3D printed PLA properties", *Polymers (Basel).*, vol. 11, no. 9, pp. 1–14, 2019.

[9] O. A. Mohamed, S. H. Masood, and J. L. Bhowmik, "Modeling, analysis, and optimization of dimensional accuracy of FDM-fabricated parts using definitive screening design and deep learning feedforward artificial neural network", *Advanced Manufacturing*, vol. 9, no. 1, pp. 115–129, 2021.

[10] M. Olam and N. Tosun, "3D-printed polylactide/hydroxyapatite/titania composite filaments", *Material Chemistry and Physics*, vol. 276, no. 125267, pp. 1-11, 2022.

[11] L. Pagnin, R. Calvini, R. Wiesinger, and M. Schreiner, "SO2- and NOx-initiated atmospheric degradation of polymeric films: Morphological and chemical changes, influence of relative humidity and inorganic pigments", *Microchemiical Journal*, vol. 164, no. 106087, pp. 1-11, 2021.

[12] X. Montané, J.M. Montornes, A. Nogalska, M. Olkiewicz, M. Giamberini, R. Garcia- Valls, M. Badia-Fabregat, L. Jubany, and B. Tylkowski, "Synthesis and synthetic mechanism of polylactic acid", *Physical. Sciences Reviews.*, vol. 5, no. 12, pp. 1–11, 2020.

[13] R. A. Hamid, F. H. Hamezah, and J. Abd Razak, "Influence of humidity on the tensile strength of 3d printed PLA filament", *Lecture Notes in Mechanical Engineering*, vol. 25, pp. 497–502, 2022.