BIODEGRADABILITY OF POLYVINYL ALCOHOL IN SAND FOR RESIN BONDED SAND CASTING PROCESS

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ABSTRACT: Resin bonded sand casting is widely used for manufacturing automotive parts, especially those made of aluminium alloys. In general, resin bonded sand casting use alkaline resin as binding agent. Typically, they are from non-biodegradable materials that have issues on reclamation and disposal of the sand as well as cause hazard to the environment. Therefore, a biodegradable resin consisting of Polyvinyl Alcohol (PVA) as one of the solution contents was developed to substitute the non-environmental friendly resin. The purpose of this investigation is to attest that PVA is a biodegradable material under natural environment. Weight loss quantification was used as a method to study the biodegradability of PVA and Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy were used to examine the molecular bonding as well as the morphological structure of the resin after biodegradation. The degradation process was evaluated by the weight loss and molecular structure of the PVA. At the end of this study, the weight loss of PVA is insignificant to show the biodegradation process. However, further investigation using FTIR and Raman spectroscopy methods; it is observed that there is a significant change in molecular and morphological structure of PVA.

KEYWORDS: *Biodegradability; Resin Bonded Sand Casting; Polyvinyl Alcohol; FTIR; Weight Loss*

1.0 INTRODUCTION

Resin bonded sand casting is proven has a great improved property in terms of strengthening the mould as compared to a traditional sand casting which use clay as a binder. Recently, resin bonded sand casting industry uses furan and phenolic as a binder to strengthen the mould. Hussein et al. [1] found that these materials have improved the properties of the mould significantly in term of tensile, transverse and compression properties. However, the use of furan and phenolic materials have an issue of environmental pollution at the disposal phase [1-2], in which increase in awareness to substitute for greener and more environmental friendly materials. Few polymers such as polyvinyl alcohol (PVA), polylactic acid and microbial biopolymers are found to be biodegradable [3-6]. The polymer becomes an interest as a biodegradable material because of its excellent mechanical properties, low cost and good bonding agents [7-9]. Theses excellent properties are desirable to maintain the shape of the mould during pouring process.

Among most of the biodegradable polymer that rises the attention of researchers is polyvinyl alcohol (PVA). PVA is a kind of synthetic polymer that has a vast application in many industries as an option to substitute a non-biodegradable material [10-11]. PVA has very great physical properties such as viscosity, film forming, emulsifying, dispersing power, adhesive strength, flexibility and good bonding agent [12-13]. PVA is known as a versatile polymer and the only polymer that contains a backbone made up from primarily –OH bonds that is totally biodegradable [14]. The biodegradability of PVA is determined by its degree of hydrolysis, molecular weight [15], the degree of polymerization and hydrolysis, the distribution of hydroxyl groups, and the stereoregularity and crystallinity of PVA [16]. However, as claimed by Kawai [15], crystallinity does not give much effect to biodegradation of PVA because the presence of functional group i.e –OH is more significant. The hydrolysis of ester groups will trigger the biological degradation in the amorphous phase.

Biodegradation of materials is mainly caused by enzymatic and chemical degradation by living microorganisms [17]. The enzymatic biodegradation of a material depends on the microbes, the pH-value, temperature, moisture, low glass temperature (high mobility), and low crystallinity. Campos et al. [16] had stated that other factors that affect biodegradation process are the nature of the polymer, the interaction among the blend components, its crystallinity and environmental conditions i.e. light, temperature, O_2 concentration and humidity. Researchers commonly use the method of thermogravimetric analysis (TGA) [18], direct observation on the morphological structure of materials, spectrophotometric (concentration) analysis [19] and measuring the weight loss [5] as an indicator of the biodegradability of PVA. It is essential to understand the techniques to measure the degradation of PVA according to the desired condition.

This study employed a method of measuring the weight loss coupled with FTIR and Raman analysis to study the degradation process of PVA. The aim of this study is to examine the biodegradability of polymeric resin in sand mould. The objectives of this paper are to measure the weight loss of PVA in a soil as an indicator of biodegradation process, analyse the microstructure of the resin and to compare the molecular bonding of PVA.

2.0 EXPERIMENTAL METHODS

This research has been specified to study the weight loss of pure PVA in soil under natural environment. Their relationship is defined in such a way that the set of factors will give impact on weight loss, which in turn determines the final outcome in terms of biodegradation rate of PVA. The parameters used in this study are obtained from previous researches, which claimed that temperature and moisture condition are the factors that affect the soil microbial activity towards the degradation rate. The most suitable condition for soil microbial activity is the best when the temperature between is 25 to 30°C in low soil moisture [20].

PVA was procured from Merck Schuchardt, Germany. The PVA used was 100% hydrolyzed with a molecular weight of 60000. As this study focuses on the natural degradation of PVA, it is important to conduct the study close to the natural environment but with some modification to increase the biodegradation rate. There were five samples used in this study. These samples were left in a room temperature of 30°C with 10% of soil moisture content. The weight loss of PVA was measured every 9 days. Weighing routine started with drying the samples in the oven to make sure there was no water left in the soil before the samples were weighed. At the end of the experiment, one sample was taken to observe the colonization of the PVA using Scanning Electron Microscope (SEM).

The sand was from a beach sand type from Johor. To obtain the dry sand, 1 kg of sand was left on A4 paper and distributed evenly as thin as possible so that no moisture trapped between the sand particles. It was dried in a room temperature for one day. Then the sand was further dried in a vacuum oven at a temperature of 80˚C for 6 hours to completely dry the sand. The weight of the sand was taken before and after each procedure.

Biodegradability of PVA was studied in a natural environment where the samples were exposed in a laboratory with no control over temperature and humidity. Sand of 100g was mixed with 20g of PVA and 20% of deionized water for the initial moisture in an aluminum container with the ratio of 5:2:2 for sand, PVA and water. There were five replicates that contain the mixture of sand, PVA and water. There were two control samples that contained a mixture of sand and PVA and a mixture of sand and water. The samples were placed in an open area for 90 days. The weight is taken every 9 days interval using digital weighing scale.

Throughout the experimental period, no moisture was added as to mimic the worst situation, which is a drought season. The moisture was monitored by comparing the weight loss of the mixture of sand, PVA and water with the mixture of sand and water. The weight loss of PVA was calculated in percentage using.

$$\%\ \text{weight loss} = (w_i - w_t) / w_t * 100 \tag{1}$$

where w_i is the initial weight of PVA and water w_t is the weight of the PVA and water at the time of weighing.

FTIR was used to study the molecular vibration of polymer. The IR spectra were obtained using a Jasco 6100 FTIR spectrometer. The FTIR spectra were presented in absorbance range 400 to 4000 cm^{-1} acquired with a resolution of $4cm^{-1}$. FTIR analysis is employed to identify the absorption peaks, which correspond to the frequencies of vibrations between the bonds of the atoms that making up the material.

Raman spectroscopy was also employed in this study to support the findings in FTIR but with different medium. Raman spectroscopy used in this study was from UNIRAM-3500 model with a wavelength of 532 nm. Apart from that, Raman spectroscopy was also employed to capture the microstructure of the PVA.

3.0 RESULTS AND DISCUSSION

The weight of the samples, weight loss and its percentage are tabulated in Table 1. The data analysis is presented in the form of graphs to compare the weight loss throughout the experimental period. Figure 1 shows the percentage of weight loss of PVA. The first 9 days shows significant reduction in the weight loss that is 41%. The reduction in weight is due to the water molecules that escape into the air. The remaining days shows a nearly constant weight loss percentage. At this period, water molecules are completely escaped from the sand mixture. The weight loss from PVA particles is observed to be very insignificant. The phenomenon of minor weight reduction of PVA under natural condition has been due to the absence of specific microorganisms to perform degradation process since the PVA degrading microorganisms is hardly found in the environment [19, 21].

Table 1 : Test Model Specifications and Test Conditions of PVA Weight Loss.

Day	Weight of Mixture (g)	Weight Loss of PVA (g)	Weight Loss (%)
0	140.00	0	0
9	123.54	16.46	41.15
18	123.26	16.74	41.85
27	123.01	16.99	42.48
36	122.89	17.11	42.48
45	122.61	17.39	43.48
54	122.23	17.77	44.43
63	121.98	18.02	45.05
72	121.69	18.31	45.78
81	121.32	18.68	46.70
90	120.83	19.17	47.93

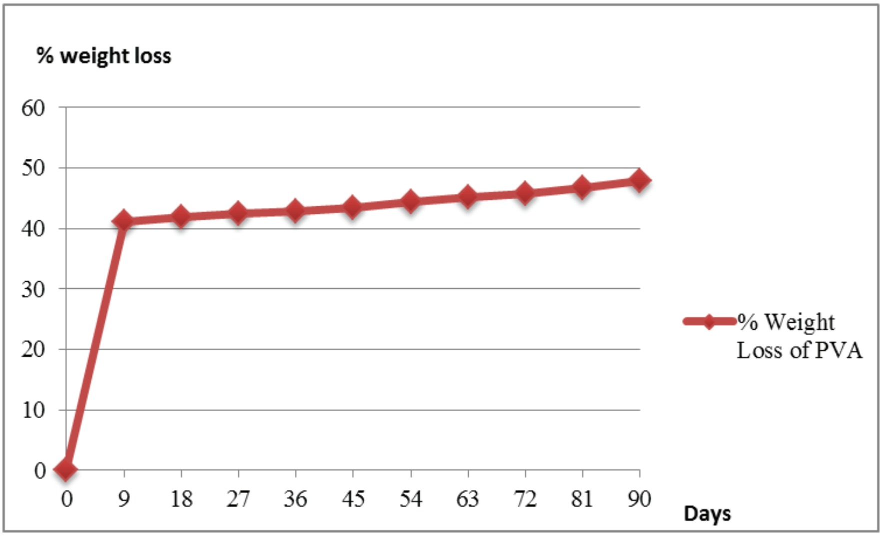

Figure 1 : Percentage weight loss of PVA

Apart from that, the degradation rate of PVA is observed to be very slow and not significant under natural environment due to the degree of hydrolysis of PVA used in this study. As claimed by Azahari et al. [14], the biodegradability of PVA is dependent on its degree of hydrolysis. Higher degree of hydrolysis makes the PVA more water resistant in the natural environment and more difficult to crystallize [11]. Rolf [22] stated that it is difficult for the microorganism to transport the material directly into cells for the biochemical takes place if the material is water resistant. Moreover, the high degree of hydrolysis always has high molecular weight that is also another factor that influences the biodegradability of PVA. Biodegradability decreases with increasing molecular weight as reported by [23]. Tudorachi et al. [17] highlighted that the PVA biodegradability can be increased by combining with other natural polymers such as starch, chitosan or cellulose specifically if the process is desirable in a natural environment. These natural polymers can initiate de-polymerization by soil microbes to begin the breakdown of the polymer chain [23].

Figure 2 shows the FTIR spectra of fully hydrolyzed PVA. Some of the major peaks are observed related to hydroxyl and acetate groups. Referring to the peaks obtained from PVA before degradation, there are hydroxyl, carbon-hydrogen bonding and carbonyl bonding exist. Large band is observed from 3200-3550 cm^{-1} due to hydroxyl (O-H) stretching mode. The hydroxyl stretching mode at this peak occurred because of the elimination of water in which occurred in the first step of the degradation process. It was evident that the stretching of hydroxyl is due to the loss of water in the first stage of the biodegradation process.

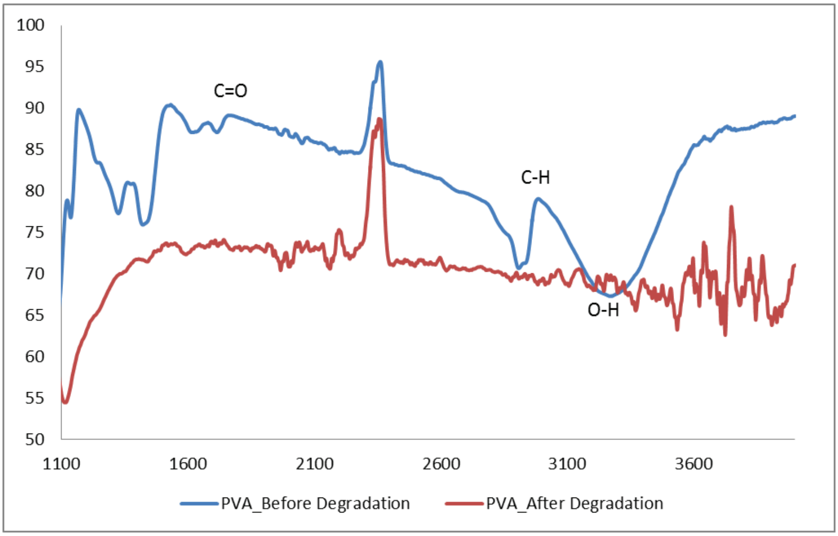

Figure 2 : FTIR spectra from PVA particles before and after degradation process

The band was observed between 2840 and 3000 cm^{-1} because of the stretching of carbon-hydrogen (C-H) bond as the carbon was used for source of energy of microbial growth and the formation of water and/or methane in biodegradation process [12]. Another peak observed between 1735 and 1750 cm^{-1} due to the stretching of carbonyl double bond stretching. Figure 2 also depicts significant reduction intensities of the absorption before and after PVA degradation process. It clearly shows that there is significant molecular distortion occurred during degradation process. Carbonyl and hydroxyl group are completely distorted as it used for the formation of carbon dioxide and water and/or methane in the degradation process.

The investigation of molecular vibration is supported using Raman spectroscopy of the samples before and after the biodegradation process as illustrated in Figure 3. It is observed that PVA peaks in Raman spectrum have two different shifts, which are at 1450 and 2919. The peak at 1450 Raman spectrum is corresponds to the presence of C-H bonding. Another peak is observed at 2919 Raman spectrum, which corresponds to the presence of C-H bonding. Observe the increase in intensity after the biodegradation process. It is a result from more of the functional group present in the sample. This graph shows insignificant changes in the molecular structure of PVA. This finding is supported by the statement made by Premraj and Doble [6] that claimed PVA can only degrade in the PVA-degrading environment, with the presence of specific microorganisms (from Pseudomonas strain) that is hardly found in the natural environment.

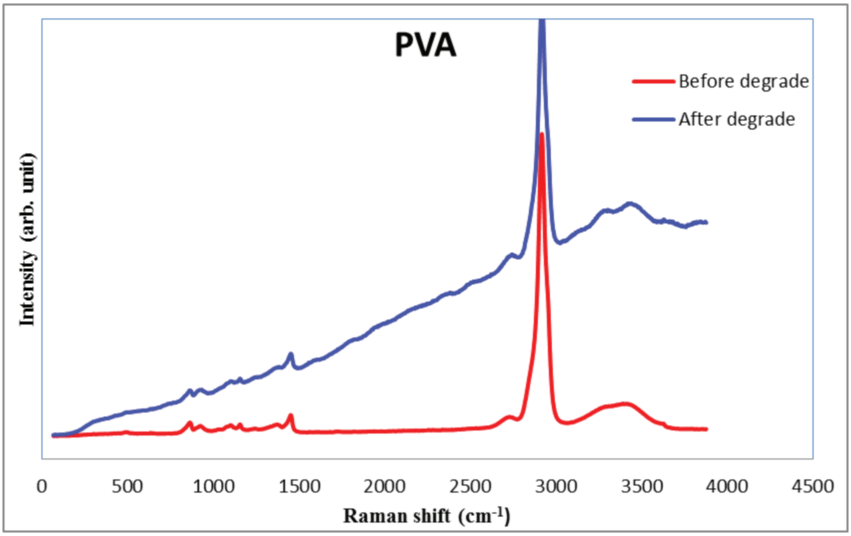

Figure 3 : Raman spectrum of PVA before and after biodegradation

Figure 4 shows the morphological structure of PVA particles before and after biodegradation process. It is observed that there is a significance difference in the structure. The grains before biodegradation process are intense and continuous (Figure 4a). However, the grains after the biodegradation process are observed to be shorter and discrete (Figure 4b). The visible change in the morphological structure clearly indicates that there is distortion in a molecular structure. The distortion might due to the change in the crystalline structure by microbial activity. The distortion is an evidence of biodegradation of PVA that occurred after 90 days mixed with soil under natural environment.

From the findings above, the soil burial technique is insignificant to evaluate the biodegradability of pure PVA. This is due to the minor change in weight loss obtained from this method. However, further investigation is carried out using FTIR and Raman analysis. Distortion is observed in both FTIR and Raman analysis result from a stretching and scissoring of hydroxyl and carbonyl bonding. The morphological study also shows a remarkable difference before and after biodegradation process. Therefore, it can be concluded that only some part of pure PVA is degraded by soil burial technique. The PVA will not degrade solely in a natural environment without the presence of PVA-degrading microorganisms or blending it with natural polymer as starch.

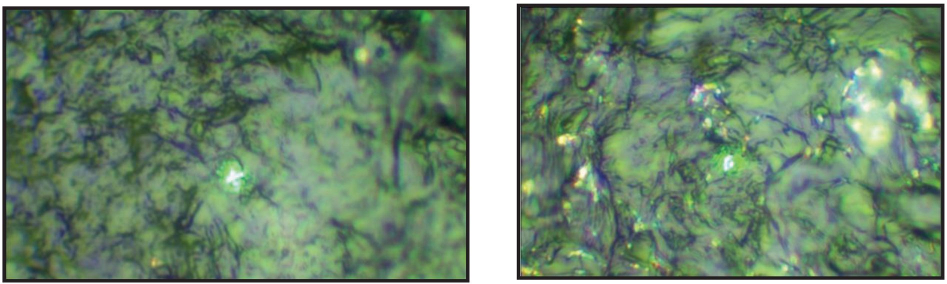
(a) (b)

Figure 4 : PVA molecular structure (a) before and (b) after degradation observed by using Raman spectroscopy

4.0 CONCLUSION

This study investigates the biodegradability of PVA using an evaluation of weight loss of PVA as an indicator of physical change due to biodegradation process. Apart from that, this study employed FTIR and Raman analysis that has a different spectrum to examine the change of the material chemically. The morphological study is performed using Raman imaging to observe the structural change of the PVA.

Results from weight loss evaluation shows that soil burial is not significant in determining the biodegradability of pure PVA. This is due to the PVA characteristic of PVA used in this study. Fully hydrolyzed PVA has a high degree of hydrolysis, in which the molecular weight is also high that lead to decreasing the biodegradability of the resin. High degree of hydrolysis PVA should not to be exposed to the environment alone without combining with other natural polymer such as starch. Blending the material could increase the biodegradation rate of PVA. Some modification of the parameters in this study also could improve the result by setting the parameter constant such as temperature by using humidity chamber.

However, the result from FTIR and Raman shows different findings where it is observed that there is a change in the IR spectra of PVA before and after degradation process. The peaks in FTIR and Raman spectra shows the existence of some of the chemical groups that correspond to the bonding that making up the PVA. The change in intensity of both spectra indicates the distortion of the molecular structure of PVA after biodegradation process. Image in Figure 4 also depicts that a change in morphological structure corresponds to the biodegradation process. From these results, it can be concluded that the rate of biodegradation of PVA is very slow under normal environment without the presence of natural polymer as a catalyst in the process.

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REFERENCES

[1] N.I.S. Hussein, M.N. Ayof and N.I. Mohd Sokri, "Mechanical properties and loss on ignition of phenolic and furan resin bonded sand casting", *Journal of Mining, Metallurgy and Mechanical Engineering,* vol. 1, no. 3, pp. 223-227, 2013.

[2] A. Ghandini, *Biopolymers – New Materials for Sustainable Films and Coatings.* Denmark: Wiley, 2011.

[3] E. Chiellini, A. Corti and R. Solaro, "Biodegradation of polyvinyl alcohol based blown films under different environmental conditions", *Polymer Degradation and Stability,* vol. 64, no. 2, pp. 305-312, 1999.

[4] M. Kolybaba, L.G. Tabil, S. Panigrahi, W.J. Crerar, T. Powell and B. Wang, "Biodegradable polymers: past, present, and future", in CSAE/ASAE Annual Intersectional Meeting, Fargo, North Dakota, 2003, pp. 1-15.

[5] S.K. Mohan and T. Srivastava, "Microbial deterioration and degradation of polymeric materials", *Journal of Biochemistry and Technology*, vol. 2, no. 4, pp. 210-215, 2010.

[6] R. Premraj and D. Mukesh, "Biodegradation of polymers", *Indian Journal of Biotechnology*, vol. 4, pp. 186-193, 2005.

[7] E. Rudnik, *Compostable Polymer Materials.* Amsterdam: Elsevier, 2008.

[8] B. Grabowska, M. Bulwan, S. Zapotoczny and G. Grabowski, "Biodegradation of new polymer foundry binders composition of poly(acrylic acid)/dextrin", *Polymers,* vol. 57, no. 7-8, pp. 529-534, 2012.

[9] M. Chandra and S.K. Roy, *Industrial Polymers. Specialty Polymers, And Their Applications*. Boca Raton: CRC Press, Taylor & Francis Group, 2009.

[10] G. Paradossi, F. Cavalieri, E. Chiessi, C. Spagnoli and M.K. Cowman, "Poly(vinyl alcohol) as versatile biomaterial for potential biomedical applications", *Journal of Material Science: Material in Medicine,* vol. 14, no. 8, pp. 687-691, 2003.

[11] C.M. Hassan and N.A. Preppas, "Structure and applications of poly(vinyl alcohol) hydrogels produced by conventional crosslinking or by freezing/thawing methods", *Advanced in Polymer Science*, vol. 153, pp. 37-65, 2000.

[12] K. Leja and G. Lewandowicz, "Polymer biodegradation and biodegradable polymers – a review", *Polymer Journal of Environmental Studies*, vol. 19, no. 2, pp. 255-266, 2010.

[13] D. Rong, K. Usui, T. Morohoshi, N. Kato and M. Zhou, "Symbiotic degradation of polyvinyl alcohol by novosphingobium sp. and xanthobacter flavus", *Journal of Environmental Biotechnology*, vol. 9, no. 2, pp. 131-134, 2009.

[14] N.A. Azahari, N. Othman and H. Ismail, "Biodegradation studies of polyvinyl alcohol/corn starch blend films in solid and solution media", *Jounal of Physics Science*, vol. 22, no. 2, pp. 15-31, 2011.

[15] F. Kawai, "The biochemistry and molecular biology of xenobiotic polymer degradation by microorganisms", *Biosciece, Biotechnology and Biochemistry*, vol. 74, pp. 1743-1759, 2010.

[16] A. Campos, J.C. Marconato and S.M. Martins-Franchetti, "Biodegradation of blend films pva/pvc, pva/pcl in soil and soil with landfill leachate", *International Journal Brazilian Archives of Biology and Technology*, vol. 54, no. 6, pp. 1367-1378, 2011.

[17] N. Tudorachi, C. Cascaval, M. Rusu and M. Pruteanu, "Testing of polyvinyl alcohol and starch mixtures as biodegradable polymeric materials", *Polymer Testing*, vol. 19, no. 7, pp. 785–799, 2000.

[18] O. Nadras, N.A. Azahari and H. Ismail, "Thermal properties of polyvinyl alcohol (pvoh)/corn starch blend film", *Malaysia Polymer Journal*, vol. 6, no. 6, pp. 147-154, 2011.

[19] D. Cetin and S. Citak, "Degradation of polyvinyl alcohol by a mixed microbial culture isolated from paper mill treatment", *Gazi University Journal of Science*, vol. 27, no. 2, pp. 839-845, 2014.

[20] S. Choi, T.W. Fermanian and L.A. Spomer, "Effect of temperature, moisture, and soil texture on dcpa degradation", *Agronomy Jornal*, vol. 80, pp. 108-113, 1998.

[21] M. Shimao, "Biodegradation of Plastics", *Current Opinion in Biotechnology*, vol. 12, no. 3, pp. 242-247, 2001.

[22] J.M. Rolf, *Biopolymers - Biodegradability of Polymers: Regulations and Methods for Testing*. Munster: Wiley, 2004.

[23] B. Bharathiraja, J. Jayamuthunagai, M. Jayakumar, P.V. Arulkirubakaran, M. Chandran and P. Praveen Kumar, "Biodegradation of polyvinyl alcohol using pseudomonas alcaligenes", *Asian Journal of Chemistry*, vol. 25, no. 15, pp.1-5, 2013.