Two-dimensional profiles of microvoids on hardness of bulk HTPB-based polyurethane

A Restasari¹*, LH Abdillah¹, R S Budi¹ and K Hartaya¹
¹National Institute of Aeronautics and Space (LAPAN)
(Jl. Pemuda Persil, Jakarta, Indonesia)
* Corresponding author, email: afnichemist@gmail.com

Abstract. Voids analysis is useful to develop further composition and mixing technique so that the hardness of materials can be improved. In HTPB-based polyurethane, this topic is more crucial, giving impact on the propellant and the performance of rocket. Thus, the aim of this paper is to uncover the profile of voids, such as shape, size, distribution and its consequences on the hardness of bulk polyurethane. The perimeter, area, circularity and the nearest distance between voids of fifty five voids were identified by using microscope and image measurement software. Statistic methods were used to get a detailed analysis. It is concluded that polyurethane with the lower hardness, PU B, has lower standard deviation in all profiles, shorter mean distance between voids, significant difference in distribution pattern of void area data and linear correlation between area and distance. All of them suggest that void cluster can reduce the hardness of polyurethane.

1. Introduction
Currently, polyurethane is developed as polymeric binder that provide matrices for inorganic oxidator as well as metal fuel particles in composite solid propellant, a sort of rocket fuel. The long carbon backbone of Hydrogen terminated polybutadiene (HTPB) as hydroxyl groups provider in polymerization described in figure 1, attribute to the excellent performances of polyurethane which include adequate compatibility with fillers, supporting the high loading of solid contents, enhancing specific impulse of rocket, worthwhile shock absorption, improving the ease of mixing and casting of propellant [1].

Although HTPB based polyurethane exhibit much advantages, the development in order to reach divine quality is still crucial. It is evolved by synthesizing the bulk form, taking accounts of some factors of the characteristics of its constituents such as distribution of functionality, hydroxyl number, molecular weight, diisocyanate compound, secondary hydroxyl group and cis/trans/vynil isomer ratio, properties of hard segments formed by urethanes links, soft segments which are long hydrocarbon chain of HTPB, as well as the technique terms used in the mixing of its prepolymer for instance Reynold and Froud number, also the type and clearance of the impeller [2][3][4][5][6][7][8][9][10][11][12].

One of frequent problems, such as reported in the recent case by Geni Rosita [13] in 11 of 30 samples, that occurs in bulk polyurethanes, having potentiation to form porous and crack as well in propellant, is voids of which involving two factors which are chemo-rheological temperature and site reaction with water.
molecule as described in figure 2. For the first origin, voids are possible to be found in bulk polyurethane constructed by different weight ratio of HTPB-TDI as identified by Geni Rosita [13] in composition of 4:1, 6:1, 7:1 and 12:1, whereas for the second reason, it can be appeared in similar contents but different manufacturing process and exhibit obvious different properties [4][10][14][15][16]. For the last determinant mentioned, it is primary to be studied further regarding the high air moisture in Indonesia as a tropic country, its role to fail the measurement of origin properties of bulk polyurethane and reduce the effectiveness of polymerization reaction [2][4][8][17].

![Figure 2. The site reaction that causes voids.](image)

The construction of voids includes the dispersion of water molecules, chemical reaction and the scission of polymer chain. The water molecules arise from air moisture through below mechanisms:

1. suctioned by vortex resulted around the impeller in the mixing process of prepolymer involving certain amount of Froud and Reynold number,
2. trapped while the prepolymer is poured into the cast [4][8].

Those water molecules induces the competitor reaction in that of reducing the expected polyurethane chain as explained in figure 3. In that chemical reaction, gas of carbondioxide are generated and empowered by elevated temperature in curing oven, introduce force over the chain strength (about 3 nN), lead to the scission of chain, leave a space, called voids [18].

![Figure 3. Reaction competition as the impact of void formation.](image)

As water molecules are introduced in different way and the strength of chemical bonds (hydrogen and covalent bonds) in bulk polyurethane are various along with the length and the shape of hard segments (spheres 5-20 nm, or long needles 5 nm thick and 50-300 nm long) that are stronger than soft segments, the profile and effects of void profiles on physical properties of polyurethane that provide the ease of measurement, such as hardness and density, are typical one to another [3][19][20].

The nature of voids have been reported along with its impacts in various materials. In composite materials, such as in Carbon Fiber Epoxy, voids with diameter of more than 0.2 mm is reported generating crack [21]. While in Carbon Fiber Reinforced Plastic, voids alter in decreasing of compressive and fatigue strength as well as fracture toughness by the contents of 4%, more than 2% and 5% respectively, tensile strength is affected by the amount, size and distribution of voids, whereas randomly shaped void have more severe in mechanical performance than homogenous shaped one [19].
As a variety of composite material, it is habitual that voids are also found in solid propellant. The tail-like void is able to hatch crack [17]. Homogenous voids with diameter less than 0.5 cm were also found in propellant [19][22]. While in elastomer bulk polyurethane, as its binder, observation of voids was analyzed visually, and the size is grouped into coarse classification, such as foam-like, small, big and identified as porous [4][13]. While the microscopic measurement is scarcely carried out, contrasting to its other category, foam and thermoplastic polyurethane which the shape, size, and distribution of its voids were interpreted clearly [20]. In elastomer itself, the topics are emphasized into the evolution of voids during deformation [20][23][24][25], not grasping the ramification on origin physical properties, such as hardness. Thus, the aim of this paper is to uncover the profile of voids, such as shape, size, distribution and its consequences on hardness of bulk polyurethane.

2. Experimental Section
2.1. Materials
The objects of this research were to reach fifty five voids on bulk polyurethanes composed by HTPB:TDI, weight ratio of 15:1, which were called PU A and PU B. PU A had higher shore A hardness (17) measured by durometer than PU B (16).

2.2. Instrumentation
HiROX Microscope adjusted at level of 128, edge of 8, FOV 8665.03 and lense of MXG-2500REZiLow-Range:x35 as well as Bersoft Image Measurement Software were used to observe and characterize voids. While, Precisa densitometer was used to measure the density.

2.3. Procedure
The surface of polyurethanes were cut into a slice of 22.5 – 23.5 mm² for being observed on the Microscope. The images obtained were characterized by applying Image Measurement Software. The profiles included perimeter, area, the nearest distance between two voids and circularity. The circularity was calculated based on equation (1).

\[
\text{Circularity} = \frac{(4\pi A)}{\text{perimeter}^2} 
\]

The difference of each void’s character in those polyurethanes were proven by chi-square as non-parametric statistic method for independent samples. The ranges were determined as shown in table 1. Meanwhile, to detect the correlation between area versus distance and circularity, Spearmann Rank method were used. The significance of all statistic relations was determined by p-level [26].

| Parameter                      | Small (μm) | Medium (μm)       | Large (μm)       |
|--------------------------------|------------|------------------|------------------|
| Perimeter                      | < 963.27   | 963.27 - 1,183.9 | > 1,183.9        |
| Area                           | < 82,553.36 | 82,552.36 - 130,776.02 | > 130,776.02    |
| Circularty                     | < 0.84     | -                | > 0.84           |
| Nearest Distance between Voids | < 237.02   | 237.02 - 474.04  | > 474.04         |
3. Results and Discussion

The examined voids are those on the surface of polyurethanes due to its most appearances and its impact in the hardness measurement. As known, the generated hardness value comes from the indenter of durometer that punch the material until 250 μm below the surface [27]. PU A and PU B show homogenous voids visually on its surface and thus, to obtain adequate resolution of image, as described in figure 4 and 5, and to support the analysis that the results are shown in table 2, the slice were 22.5 – 23.5 mm².

![Figure 4. Captured image of PU A.](image1)

![Figure 5. Captured image of PU B.](image2)
Table 2. Raw profiles of voids.

| Parameter                  | Parameter       | Perimeter (μm) | Area (μm²) | Circularity | Nearest Distance between Voids (μm) |
|---------------------------|-----------------|----------------|------------|-------------|-------------------------------------|
|                           | PU A            | PU B            | PU A       | PU B        | PU A                               | PU B                  |
| Minimum                   | 742.64          | 921.84          | 34,330.7   | 68,692.12   | 0.31                                | 0.79                  | 17.82                  | 12.63                  |
| Maximum                   | 1,845.79        | 1,408.2         | 275,444    | 158,912.16  | 1                                    | 1                     | 723.68                 | 581.27                 |
| Mean                      | 1,198.09        | 1,193.08        | 119,758.26 | 113,167.81  | 0.9529                              | 0.9734                | 239.91                 | 177.66                 |
| Median                    | 1,182.83        | 1,199.76        | 112,572.77 | 115,034.66  | 1                                    | 1                     | 239.78                 | 119.16                 |
| Standard Deviation        | 259             | 105.12          | 32,117.42  | 19,283.29   | 0.635                               | 0.422                 | 198.49                 | 167.44                 |

Table 2 shows the values of minimum, maximum, mean, median and standard deviation of the profiles of voids on PU A and B including perimeter, area, circularity and the nearest distance. Overall, the mean value between PU A and B is almost similar except in the distance where PU B is 52.25 μm lower than PU A, while in all profiles, standard deviation of PU B is always lower than PU A, indicates the more homogenous distribution. The lower standard deviation of voids circularity in PU B worse its properties and has potential to damage its mechanical properties [19]. The minimum value of PU B in all profiles are higher than PU A, except in the distance where PU A is 5.19 μm higher than PU B, while, in area and circularity PU B’s values are about twice of PU A’s. Contrary, the higher maximum values are owned by PU A which are almost twice of PU B in area. From the area void data, all of them, diameter less than 0.5 cm, have been found also in propellant [22]. The highest level of circularity is 1 and found on both polyurethanes, means the perfect circle shaped voids are contained and the potential of tail formation is not contained [17][26]. Further analysis of the distribution patterns are brought by non-parametric statistics method that presented in table 3.

Table 3. The results of distribution data analysis of voids.

| Parameter                  | Category | Frequency | Calculated Chi square | Probability Level as Significant Data | P-level | Conclusion of Difference |
|---------------------------|----------|-----------|-----------------------|--------------------------------------|----------|--------------------------|
|                           | A        | B         |                       |                                       |          |                          |
| Perimeter                 | Small    | 15        | 9                     | 6.167857                              | 0.05     | 0.0457                   | Statistically Significant |
|                           | Medium   | 9         | 15                    |                                       |          |                          |
|                           | Large    | 6         | 1                     |                                       |          |                          |
| Area                      | Small    | 6         | 1                     | 12.59598                              | 0.04     | 0.0018                   | Very Significant         |
|                           | Medium   | 11        | 21                    |                                       |          |                          |
|                           | Large    | 13        | 3                     |                                       |          |                          |
| Circularity               | Small    | 3         | 1                     | 0.727941                              | 0.4      | 0.3929                   | Statistically Not Significant |
|                           | Large    | 27        | 24                    |                                       |          |                          |
| Nearest Distance between Voids | Small | 15        | 17                    | 1.886042                              | 0.39     | 0.3887                   | Statistically Not Significant |
|                           | Medium   | 12        | 6                     |                                       |          |                          |
|                           | Large    | 3         | 2                     |                                       |          |                          |

Overall, the results shown in table 3, based on the classification in table 1, describe how far the distribution data of PU A is different from PU B in each profile statistically. Based on the significant chi square value, the possibility level of perimeter and area are similar as well as in circularity and the distance. The values of the last mentioned two parameters (0.4 and 0.39) are much higher than the first two mentioned (0.05 and 0.04), indicates the easier repeatability. It was revealed that based on p-level, the differences of data distribution between PU A and B are significant in area (0.0018) and perimeter (0.0457) because the data concentration in PU B is in medium size and it is concluded higher in the area. The unsignificant different parameters, i.e. circularity and distance, which indicate similar pattern of distribution, can be originated from the same composition and constituents between PU A and PU B that contain the same design of soft and hard segments, build same bond strength and easiness level to be broken by water vapour, bring typical distribution of voids distance and circularity [28][18]. As the distribution pattern of void area...
and the mean of void distance, in table 2, between PU A and B is different, further analysis about the correlation between area and the distance in each polyurethane is needed to be compared, as run by Spearmann Rank methods that the results are shown in figure 6, 7 and table 4.

![Figure 6. Spearmann correlation between area and distance in PU A.](image)

![Figure 7. Spearmann correlation between area and distance in PU B.](image)

**Table 4. The results of Spearmann rank analysis.**

| Parameter | PU A          | PU B          |
|-----------|---------------|---------------|
| ρ         | 0.920033      | 0.885837      |
| t         | 12.42435      | 9.15595       |
| p-level   | < 0.0001      | < 0.0001      |
| Conclusion| Extremely Significant | Extremely Significant |

In table 4, ρ, Spearmann correlation coefficient in both polyurethanes are positive, indicates the linear relationship between area and distance. Based on the student t-distribution, t, p-levels have been determined and they show that in both polyurethanes, those correlations are extremely significant. Those indicate that the small voids tend to have short distance among others, forming a cluster of voids and the bigger void may come from the combination of small voids in that cluster, taking a space, making the distance between the other big void farther. Appreciating its lower mean of distance and homogeneity, it also indicates that PU B has void cluster that shorten the group of hard segment of polyurethane and worse its hardness.

4. Conclusion
The perimeter, area, circularity and the nearest distance of fifty five voids from polyurethanes with different hardness have been analyzed to identify the cause of the difference. It is concluded that polyurethane with the lower hardness, PU B, has lower standard deviation in all profiles, shorter mean distance between voids, significant difference in distribution pattern of void area data and linear correlation between area and distance. All of them suggest that void cluster can reduce the hardness of polyurethane.
Acknowledgements
The author would like to thank the National Institute of Aeronautics and Space of Indonesia, for the financial and laboratory support as well as all who helped this research.

References

[1] Dey, A., Athar, J., Sikder, A. K., & Chattopadhyay, S. (2015). Effect of Microstructure on HTPB Based Polyurethane (HTPB-PU), 5(April), 145–151. http://doi.org/10.17265/2161-6221/2015.3-4.005
[2] Odian, G. (2004). Principles of Polymerization (4th ed., Vol. 58). New Jersey: A John Wiley and Sons, Inc. http://doi.org/10.1002/1088-1742-6596/1130/1/012032
[3] Prisacariu, C. (2011). Polyurethane Elastomers from Morphology to Mechanical Aspects. New York: Springer-Verlag/Wien. http://doi.org/10.1007/978-3-7091-0514-6
[4] Restasari, A., & Abdillah, L. H. (2017). Pengaruh Clearance Impeller dan Viskositas HTPB Terhadap Polimerisasi Binder Propelan. In Prosiding SIPTEKGAN XXI (pp. 331–338). Tangerang: Pusat Teknologi Penerbangan, LAPAN.
[5] Restasari, A., Ardianingsih, R., Abdillah, L. H., & Hartaya, K. (2015). Effects of Toluene Diisocyanate ‘s Chemical Structure on Polyurethane ‘s Viscosity and Mechanical Properties for Propellant t. In Proceeding ISAST III (pp. 59 – 67). Denpasar: Aeronautic Technology Center, National Institute of Aeronautics and Space.
[6] Restasari, A., Ardianingsih, R., & Abdillah, L. H. (2015). Pengaruh Massa Hidroxy-Terminated Polybutadiene (HTPB) terhadap Besarnya Pengaruh Vinil dalam Meningkatkan Laju Propelan Padat Komposit (The effects of hydroxy-terminated polybutadiene (HTPB)’s mass on the on the magnitude of vynil:s effects in, 61–70.
[7] Restasari, A. (2016a). Penelitian Laju Kenaikan Viskositas Dengan Impeller Baling - Baling dan Jangkar Dalam Pengembangan Komposisi Binder Propelan. In H. Septanto, Suhata, A. Bintoro, Mujtahid, E. Mugia, H. Supriyatno, … A. Marta (Eds.), Seminar Nasional IPTEK Penerbangan dan Antariksa XX-2016 (pp. 137–145). Rumpin: Pusat Teknologi Penerbangan, LAPAN.
[8] Restasari, A. (2016b). Pengaruh Parameter Pengadukan Terhadap Kandungan Gugus Fungsi Dalam Prepolimer HTPB: TDI 15:1 Gagal Matang. Majalah Sains Dan Teknologi Dirgantara, 11(2), 71–80.
[9] Wibowo, H. B. (2015b). Pengaruh Gugus Hidroksil Sekunder terhadap Sifat Mekanik Poliuretan Berbasis HTPB (Hydroxy-terminated polybutadiene). Jurnal Teknologi Dirgantara, 13(2), 103–112.
[10] Wibowo, H. B. (2015c). Peningkatan Sifat Mekanik Propelan Mandiri, Berbasis Pengaruh Bilangan OH terhadap Kinerja Propelan. In Teknologi Pesawat Terbang (pp. 273–290). Jakarta: Indonesia Book Project.
[11] Wibowo, H. B. (2010). Pengaruh Berat Molekul Terhadap Reaksi Pembentukan Poliuretan. In Prosiding SIPTEKGAN XIV. Jakarta.
[12] Wibowo, H. B. (2015a). Pengaruh Distribusi Fungsonalitas Polimer Terhadap Sifat Mekanik Poliuretan Berbasis HTPB. In Pengaruh Distribusi Fungsionalitas Polimer Terhadap Sifat Mekanik Poliuretan Berbasis HTPB (pp. 283–290). Indonesia Book Project.
[13] Rosita, G. (2016a). Perubahan Karakteristik Pembentukan Poliuretan Berbasis HTPB dan TDI Berdasarkan Komposisi Reaksi. Jurnal Teknologi Dirgantara, 14(2), 159–170.
[14] Dubois, C., Désilets, S., Ait-Kadi, A., & Tanguy, P. (1995). Bulk polymerization of hydroxyl terminated polybutadiene (HTPB) with tolylene diisocyanate (TDI): A kinetics study using13C-NMR spectroscopy. Journal of Applied Polymer Science, 58(4), 827–834. http://doi.org/10.1002/app.1995.070580416
[15] Rosita, G. (2016b). Retikulasi Hidroxy Terminated Polybutadiene (HTPB) Mandiri Dengan Toluene Diisocyanate (TDI) Membentuk Poliuretan Sebagai Fuel Binder Propelan. Jurnal Teknologi Dirgantara, 14(1), 51–60.
[16] Wineman, A. (2015). Time Dependent Void Growth in Elastomers Undergoing Chemo-mechanical Evolution. Journal of Elasticity, 121(2), 255–274. http://doi.org/10.1007/s10659-015-9527-4
[17] Remakanthan, S., Kk, M., Gunasekaran, R., Thomas, C., & Thomas, C. R. (2015). Analysis of Defects In Solid Rocket Motors Using X-Ray Radiography. The E-Journal of Nondestructive Testing, 20(6).

[18] Kausch, H. H., & Plummer, C. J. G. (1994). The role of individual chains in polymer deformation. Polymer, 35(18), 3848–3857. http://doi.org/10.1016/0032-3861(94)90267-4

[19] Liu, X., & Chen, F. (2016). A Review of Void Formation and Its Effects on The Mechanical Performance of Carbon Fiber Reinforced Plastic. Engineering Transactions, 64(1), 33–51.

[20] Noever, D. a., Cronise, R. J., Mathews, J., Mcmannus, S. P., Patel, D., & Wessling, F. C. (1996). Gravitational effects on closed-cellular-foam microstructure. Journal of Spacecraft and Rockets, 33(2), 267–271. http://doi.org/10.2514/3.26751

[21] Selmi, A. (2014). Void Effect on Carbon Fiber Epoxy Composites. In 2nd International Conference on Emerging Trends in Engineering and Technology (ICETET’2014) (pp. 179–183). http://doi.org/10.15242/IIE.E0514613

[22] Wibowo, H. B. (2013). Formulasi Propelan Padat Menggunakan HTPB Lokal untuk Mendapatkan Komposisi Propelan yang Memenuhi Persyaratan Proses Produksi. In JASAKIAI. Yogyakarta.

[23] Aït Hocine, N., Hamdi, A., Naït Abdelaziz, M., Heuillet, P., & Zaïri, F. (2011). Experimental and Finite Element Investigation of Void Nucleation in Rubber-like Materials. International Journal of Solids and Structures, 48, 1248–1254. http://doi.org/10.1016/j.ijsolstr.2011.01.009

[24] Heyden, S., Li, B., Conti, S., & Ortiz, M. (2016). Towards a one-parameter fracture model in soft matter mechanics, (August), 4–5.

[25] Prasad, A., Fotou, G., & Li, S. (2014). The Effect of Polymer Hardness, Pore Size and Porosity on the Performance of Thermoplastic Polyurethane (TPU) Based Chemical Mechanical Polishing (CMP) Pads. Illinois: Cabot Microelectronics Corporation.

[26] Sugiyono. (2011). Statistika untuk Penelitian. Bandung: Penerbit Alfabeta.

[27] Herrmann, K. (2011). Hardness Testing Principles and Applications. Ohio: ASM International.

[28] Hepburn, C. (1992). Polyurethane Elastomers. New York: Elsevier Science Publishers Ltd.