Bismaleimide - Aluminium sulphate blends as 3D printing ink

A.S. Bhattacharyya [1, 2 §]. Tridha Ghosh[1], Priyanshu Kumar[1]

Department of Metallurgical and Materials Engineering, Central University of Jharkhand, Ranchi 835205, India[1]

Centre of Excellence in Green and Efficient Energy Technology, Central University of Jharkhand, Ranchi 835205, India[2]

[§]Corresponding author:
2006asb@gmail.com, arnab.bhattacharya@cuj.ac.in

ABSTRACT

Aluminium Sulphate (AS) used a precursor for Al based compounds has the capabilities of flocculation and coagulation imparting strength to the material it gets added to. Bismaleimide (BMI) on the other hand is a high temperature resin used for aerospace applications. An AS-BMI resin has therefore been studied in this communication having potential application as a 3D printing ink

Keywords: Aluminium Sulphate (AS). Bismaleimide (BMI),). Cross-linking, XRD.3D-printing ink

1. INTRODUCTION

A series of high-performance thermosetting polymers known as bismaleimide (BMI) resins has several desirable qualities that make them ideal for use in a variety of industrial applications, especially those involving aerospace components. They have excellent mechanical qualities, low shrinkage, chemical resistance, fire resistance, and great resistance to a wide range of solvents, acids, and water. Additionally, BMI coating has been used to prevent corrosion. The characteristics of the polymer as an inorganic-organic composite can be affected by the addition of inorganic elements, such as metal oxides. Applications for organic-inorganic composites are numerous in the fields of chemistry, medicine, electronics, and optics **[1-5]**.

Utilising BMI resins' special combination of high temperature

https://doi.org/10.26434/chemrxiv-2024-1ls4s **ORCID:** https://orcid.org/0000-0003-4426-9194 Content not peer-reviewed by ChemRxiv.

performance and good processability has generated a lot of interest since they first became known as competitive high-performance solutions. BMI has been blended with titania, Ferric chloride as well as Graphene sheet. Metallization and APPJ treatment of Bismaleimide have shown better performance as corrosion protection and EMI shielding **[6]**. BMI monomers are molecules with two maleimide functional groups terminating them; they frequently contain several aromatic moieties to improve their curing properties **(Fig. 1a)** shows the typical structure of these compounds) **[7].** The crystalline and structural configuration of the composite system generated at various temperatures was revealed through XRD and FTIR measurements **[8-12]**.

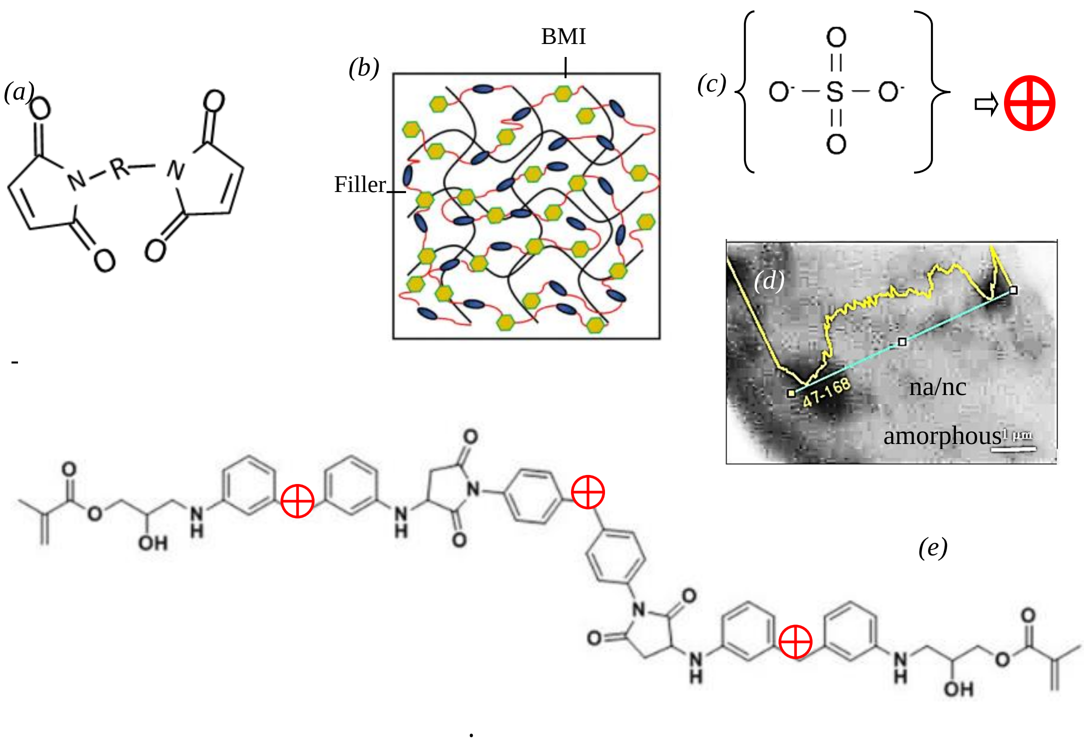

Fig 1: Basic structure of BMI **[9]** (self-drawn) (b)cross-linking of BMI (CC BY 4.0.) **[18]** (c) polyatomic sulphtate anion (CC BY 4.0) **[12]** and microstructure of BMMI (CC BY 4.0) **[19]** and (d) sulphate ion in BMI chain

Additive manufacturing, also known as fast prototyping or 3D printing, is widely used in the creation of optical components, lab-on-a-chip devices, titanium scaffolds for orthopaedic implants, sophisticated biomedical devices, and aerial vehicle wing constructions. A low-cost and straightforward method for producing unique, customised components for biomedical as well as other uses is to use techniques like digital light processing (DLP) and polymer jetting. Compounds like poly(lactic acid) (PLA), acrylonitrile butadiene styrene (ABS-T), polycarbonate (PC), polydimethylsiloxane (PDMS), polyethylene terephthalate glycol (PET-G), polyurethane filaments (TPU) and also polyamide (PA) [13]. BMI which is also from the family of polyamides having commendable chemical and mechanical properties is a potential ink for polyjets.

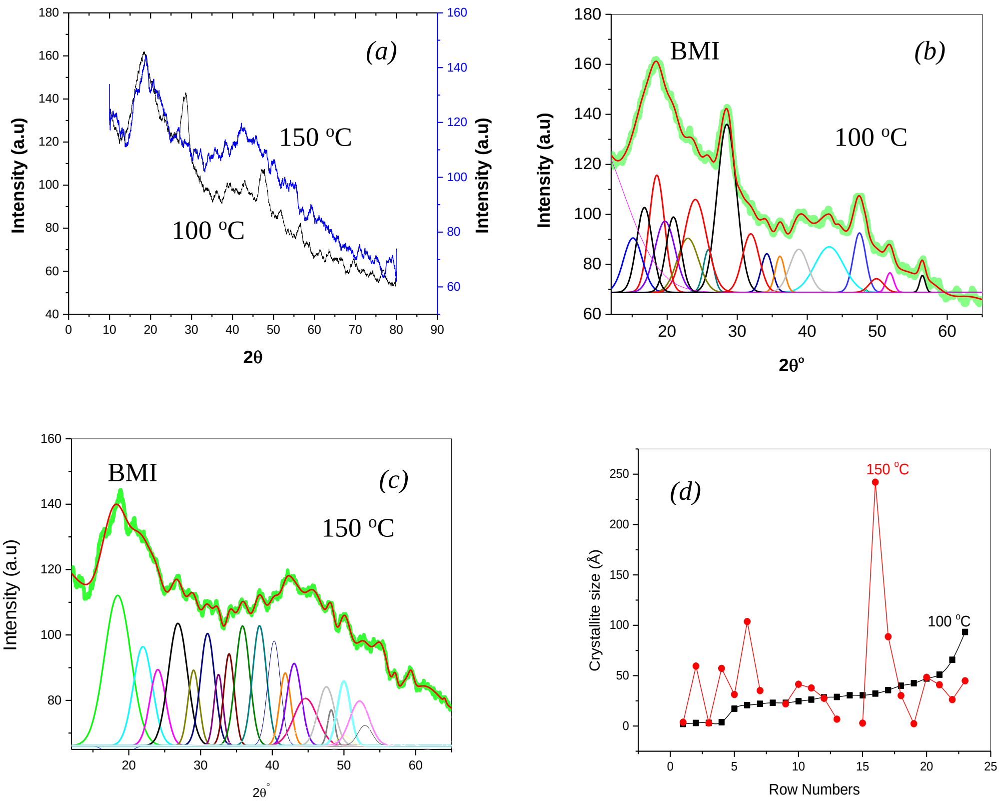

Fig 2 (a): XRD of BMI-$Al_2(SO_4)_3$ Composite at different temperatures [12] Deconvolution of AS-BMI for (b)100°C (c)150°C and (d) comparison of crystallites size

Aluminium sulphate $Al_2(SO_4)_3$ which is precursor to many Aluminium based compounds, acts as a flocculant to purify water. It also acts as a coagulant causing fibres to clump together. enhancing its strength. The blending of BMI with aluminium sulphate $Al_2(SO_4)_3$ has been shown in this communication. The objective was to study the flocculating or coagulating properties of aluminium sulphate in BMI. for possible photosensitive ink material with relatively low viscosity at the same time having good cross-linking due to inclusion of inorganic fillers (Fig 1b).

2. MATERIALS & METHODS

Homide 250 (Diamino diphenyl methane bismaleimide-diamino diphenyl methane copolymer) was used as the BMI details of which are given in ref [2, 6]. The process consisted of BMI being dissolved in distilled water and stirred and $Al_2 (SO_4)_3$ added gradually along with PVA and stirred. The thick solution formed was then applied on glass slides and heated at 100 and 150 °C to form a solid coating. XRD (Proto, Canada) with Cu-Kα (1.54 Å) was used and the crystallites size(D) were determined by Scherer equation (D =k λ/β cos ϴ where β is the FWHM and k(0.9) is the shape factor.

3. RESULTS & DISCUSSIONS

XRD of the two samples heated at different temperatures is shown in Fig 2a. The initial hump around 19°C is due to BMI. With rise in temperature there is diminishing of sharp peaks which is indicative of the fact that crystallinity is decreased. This may be due to production of excess amorphous carbon due to heating as well as flocculating property of aluminium sulphate which was also evident from the fact that the colour changes from greenish black to black with rise in temperature as reported previously [12]. The line profiles shown the larger crystallites formed because of coalescence of the crystallites are almost three times larger. The deconvolution (Gaussian) of the peaks were done (Fig 2 b, c) and the specifications of the deconvoluted peaks are given in **Table 1 and 2**.

Table 1. Deconvoluted parameters of BMI-AS formed at **100°C**

Peak position (2ϴ)°	cosϴ	FWHM (degree)	FWHM (radians)	Intensity (au)	Crystallite size (Å)	Remarks
18.5214	0.98696	2.56859	0.04483	46.914	30.51163	n-a
19.6825	0.98528	3.40994	0.05952	28.494	23.02031	n-a
28.52287	0.96918	2.76474	0.04826	69.9685	28.86304	n-a
47.47691	0.91538	2.1126	0.03688	23.76959	39.98908	n-a
43.14127	0.92995	4.83505	0.0844	18.251	17.20013	a

51.80871	0.8995	1.30746	0.02282	7.84751	65.76835	nc
56.45163	0.88107	0.94013	0.01641	0.94013	93.37159	nc
22.95985	0.97999	3.57998	0.06249	21.64945	22.04457	n-a
41.42586	0.93535	22.139	0.38644	0.11091	3.73489	a
25.89259	0.97458	1.68419	0.0294	17.1396	47.11606	n-a
34.22956	0.95571	1.90522	0.03326	15.49979	42.47031	n-a
36.10075	0.95077	1.59588	0.02786	14.49157	50.96561	nc
15.11943	0.99131	3.17397	0.0554	21.77582	24.58185	n-a
31.93727	0.9614	2.82442	0.0493	23.44715	28.4828	n-a
38.80997	0.94318	3.1303	0.05464	17.25724	26.19561	n-a
41.56958	0.93491	26.66419	0.46542	9.07812	3.10255	a
49.89316	0.90668	2.39097	0.04173	5.4829	35.68053	n-a
53.96769	0.89111	41.98361	0.73283	2.66093	2.06728	a
54.09622	0.8906	28.75861	0.50198	7.68513	3.01971	a
24.02013	0.97811	3.81254	0.06655	37.1868	20.73949	n-a
20.89566	0.98342	2.44094	0.04261	30.15417	32.21686	n-a
16.75503	0.98933	2.61405	0.04563	33.95717	30.51163	n-a
8.41674	0.9973	12.3639	0.21581	67.22039	23.02031	n-a

Table 2. Deconvoluted parameters of BMI-AS formed at **150ºC**

Peak position (2ϴ)^{O}	cosϴ	FWHM (degree)	FWHM (radians)	Intensity (au)	Crystallite size (Å)	Remarks
5.03321	0.99904	27.8021	0.48529	62.62863	2.8588	a
18.44616	0.98707	3.64229	0.06358	209.94585	22.08605	n-a
20.18729	0.98452	11.87721	0.20732	66.1371	6.79049	a
21.95693	0.9817	2.67591	0.04671	2.67591	30.22672	n-a
24.04214	0.97807	2.59023	0.04521	23.31198	31.34237	n-a
26.84724	0.97268	3.10874	0.05426	37.4345	26.25946	n-a
29.02729	0.96809	1.82609	0.03187	23.11706	44.91619	n-a
30.97207	0.9637	2.34315	0.0409	34.32484	35.16412	n-a
32.5001	0.96006	1.44611	0.02524	21.78774	57.1932	nc
33.97223	0.95638	1.71575	0.02995	28.09814	48.39012	nc
35.85464	0.95145	36.60314	0.63891	66.1371	2.28	a
49.96588	0.90645	2.13664	0.0373	3.11468	40.99852	n-a
49.98705	0.90637	2.11391	0.0369	19.71329	41.44293	n-a
52.17283	0.89815	3.20839	0.056	13.66248	27.55546	n-a
52.92297	0.89525	2.34779	0.04098	6.2045	37.77799	n-a
52.92297	0.89525	29.52308	0.51533	3.23714	3.00425	a
55.14536	0.88644	1.01022	0.01763	2.37889	88.66993	n-a
57.12398	0.87832	23.76872	0.41488	11.87721	3.80351	a
58.46512	0.87266	1.52859	0.02668	4.42466	59.52569	nc
59.37121	0.86877	0.88165	0.01539	4.66356	103.66654	nc
64.04304	0.84787	0.38689	0.00675	1.20391	242.06102	nc

The compound showed amorphous (a), near amorphous (n-a), homogenous nature but with crystallite size slightly on the higher size (nanocrystalline, nc) and increased randomness associated with increase in temperature **(Fig 2d).**The microstructure showing the "a", "n-a", "nc" states are given in **Fig 1d.** Contemporary methods for bismaleimide resin processing have been reported recently **[14]** BMI has also been beneficial in terms of imparting recently tensile strength and hardness for rheometer **[15]**.AS are effective additions to electrolytes in batteries as they reduce sulfation when charging and draining at high speeds, also being non-hazardous and inexpensive **[16]**. Like BMI, Furan–Maleimide Resins are beneficial eco-friendly thermosets and thermoplastics due to studies on their 3D printing, adhesive, and self-healing properties **[17]**. A new 3D printing photosensitive bismaleimide resin, bismaleimide -diamino diphenyl methane glycidyl methacrylate (BDM-DDM-GMA) and acrylic liquid-crystal resin (ALCR) known as BDM/ALCR resin (**Fig 1b**) was created by mixing bismaleimide-based and acrylic liquid-crystal photosensitive resins with a commercial ink Excellent mechanical qualities and heat resistance make them very suitable for use in electrical, automotive, and aerospace components **[18].**Being a high-performance thermosetting resin bismaleimide (BMI) is widely used in the aerospace, automotive, and mechanical electronics industries among other disciplines. It has exceptional dielectric characteristics, a high glass transition temperature, and great thermal stability.**[19]**

The BDM-DDM-GMA results in an increase in the number of benzene rings, which in turn increases the degree of crosslinking of the light-curable resin. Adding the polyatomic sulphate (SO_4^{-2}) (**Fig 1c**) at this stage using the mechanism for attaching > C=O during electrochemical polymerization in the $(SO_4)^{-2}$ aqueous electrolyte. will enhance the cross-linking enhancing the suitability to be used as ink for polyiets (**Fig 1e**) **[20]**. Inkjet printing assisted membrane has also been fabricated using sulphates **[21].** A faster curing rate (which has been quantified by a parameter α) is another determining factor for an efficient polyjet ink **[22]**. A smaller maleimide double bond width is indicative of a faster curing rate **[23]**.

4. CONCLUSIONS

Aluminium Sulphate (AS) has caused crystallinity in Bismaleimide (BMI) due to enhanced cross-linking due flocculation and coagulation due to the $(SO4)^{-2;}$ causing increased mechanical stability and efficient use as a 3D print ink. Deconvolution of the XRD peaks depicted the minute crystallinity in the blend. Pristine BMi showed maleimide bands of low width indicative of faster curing which may improve on sulphate addition and is left as future scope of research.AS-BMI. has thus been shown as an efficient ink for polyjet 3D printing;

ACKNOWLEDGEMENTS

The author hereby thanks Prof. S. Bhowmik for valuable suggestions

DECLARATIONS

Compliance with Ethical Standards

The manuscript has not been submitted in parallel either in full or partially to any other journal.

Conflict of interest

There is no conflict of interest among the authors

Research Data Policy and Data Availability Statements

Data shall be provided on request

FUNDING

No funding was received for conducting the research

REFERENCE

1. Kuriger RJ, Alam MK, Anderson DP, et al. Processing and characterization of aligned vapor grown carbon fiber reinforced polypropylene, *Compos A* 2002;33: 53. https://acnpsearch.unibo.it/journal/924374

2. Faraz MI, et al. Thermal, Morphological and Mechanical Characterization of Novel Carbon Nanofiber Filled Bismaleimide Composites, *J Appl Polym Sci* 2010; 117: 2159–2167.

3. HOS Technik. Production of high-temperature resins - polybenzimidazole, bismaleimide, catalysts. Available at: http://www.hos-tec.com

4. Cheng FT, Man HC, Chan WM, et al. Corrosion protection of Nd–Fe–B magnets by bismaleimide coating. *J Appl Phys* 1999; 85: 5690.

5. Bhattacharyya AS, Paul D, Dutta PP, Bhattacharjee G. Surface and Mechanical Studies of Bismaleimide Coatings *Adv. Eng. Tec. Appl.* 5, No. 1, 11-17 (2016) and arXiv 1509.01016 [cond-mat. mtrl-sci].

6. Bhattacharyya AS, Kumar S, Sharma A, Kumar D, Patel SB, Paul D, Dutta PP, Bhattacharjee G, Metallization and APPJ treatment of Bismaleimide, arXiv preprint arXiv:1508.04933, 2015 [cond-mat.mtrl-sci]

7. Bhattacharyya AS, Kumar S, Sharma A, Kumar D, Patel SB, Paul D, Dutta PP, Bhattacharjee G, Metallization and APPJ treatment of Bismaleimide, *High Performance Polymer,* 2017, 29 (7), 816-826 https://doi.org/10.1177/0954008316659123

8. Lu G, Huang Y Novel Bismaleimide Resin/Silsesquioxane and Titania Nanocomposites by the Sol-Gel Process: the Preparation, Morphology, Thermal and Thermo-mechanical Properties, arXiv:1304.0288 [cond-mat.mtrl-sci]

9. Wilson D, Stenzenberger HD, Hergenrother PM, Polyimides, Springer Science+ Business Media New York, 1990.

10. Liu M, Wang Y, Zhao Y, Diazonium functionalization of graphene nanosheets and impact response of aniline modified graphene/bismaleimide nanocomposites, *Mater. Des*, 2014, 53, 466 – 474.

11. Chao Liu, Hongxia Yan, Zhengyan Chen, Lingxia Yuan and Tianye Liu, Enhanced tribological properties of bismaleimides filled with aligned graphene nanosheets coated with Fe_3O_4 nanorods, *J. Mater. Chem A*, 2015,3, 10559–10565

12. Dash R, Kumari N, Kommu P, Bhattacharyya AS, Structural characterization of fillers of Inorganic materials in Bismaleimide resins, *J. Polymer Eng.* (2022) https://doi.org/10.1515/polyeng-2022-0171

13. I. Gouzman, N. Atar, E. Grossman, R. Verker, A. Bolker, M. Pokrass, S. Sultan, O. Sinwani, A. Wagner, T. Lück, Ch. Seifarth, 3D Printing of Bismaleimides: From New Ink Formulation to Printed Thermosetting Polymer Objects. *Adv. Mater. Technol.* 2019, 4, 1900368. https://doi.org/10.1002/admt.201900368

14. Evsyukov, Sergey & Pohlmann, Tim & Wiel, Matthijs. (2021). Modern approaches to the processing of bismaleimide resins; Review Current Trends in Polymer Science Vol. 20, 2020

15. Pöschl M, Gopi Sathi S, Stoček R, Kratina O. Rheometer Evidences for the Co-Curing Effect of a Bismaleimide in Conjunction with the Accelerated Sulfur on Natural Rubber/Chloroprene Rubber Blends. *Polymers*. 2021; 13(9):1510. https://doi.org/10.3390/polym13091510

16. Zhengyang Chen, Jiangmin Li, Jiajia Yu, Lei Wu, Shengquan Zhou, Yanzhao Rao, Jing Cao The critical role of aluminum sulfate as electrolyte additive on the electrochemical performance of lead-acid battery, Electrochimica Acta, Volume 407,2022,139877, 0013-4686, https://doi.org/10.1016/j.electacta.2022.139877.

17. McReynolds BT, Mojtabai KD, Penners N, Kim G, Lindholm S, Lee Y, McCoy JD, Chowdhury S. Understanding the Effect of Side Reactions on the Recyclability of Furan–Maleimide Resins Based on Thermoreversible Diels–Alder Network. *Polymers*. 2023; 15(5):1106. https://doi.org/10.3390/polym15051106

18. Shaoyun Chen, Lanqin Yu, Shiyu Zhang, Xiaolu Sun, Bo Qu, Rui Wang, Yanyu Zheng, Xiaoying Liu, Wenjie Li, Jianhong Gao, Dongxian Zhuo,Synergistic strengthening and toughening of 3D printing photosensitive resin by bismaleimide and acrylic liquid-crystal resin, Journal of Science: Advanced Materials and Devices, 8(3), 2023, 100565, https://doi.org/10.1016/j.jsamd.2023.100565.

19. Hua W, Lin Q, Qu B, Zheng Y, Liu X, Li W, Zhao X, Chen S, Zhuo D. Exceptional Mechanical Properties and Heat Resistance of Photocurable Bismaleimide Ink for 3D Printing. *Materials*. 2021; 14(7):1708. https://doi.org/10.3390/ma14071708

20. K. Hyodo, A.G. Macdiarmid, Effect of sulphate ion on the electrochemical polymerization of pyrrole and N-methylpyrrole, Synthetic Metals, 11, 3, 1985,167-176, https://doi.org/10.1016/0379-6779(85)90062-1

21. Wang, C., Park, M. J., Choo, Y. W., Huang, Y., Phuntsho, S., & Shon, H. K. (2023). Inkjet printing technique for membrane fabrication and modification: A review. *Desalination*, 116841.

22. Wagner, Annika, Gouzman, Irina, Atar, Nurit, Grossman, Eitan, Pokrass, Mari ana, Fuchsbauer, Anita, Schranzhofer, Leo and Paulik, Christian. (2019), Cure kinetics of bismaleimides as basis for polyimide-like inks for PolyJet™-3D-printing. *J. Appl. Polym. Sci.*, 136, 47244. doi: 10.1002/app47244

23. Bhattacharyya, A.; Ghosh, T. Faster Curing in BMI for 3D Printing Ink. Preprints 2024, 2024010112. https://doi.org/10.20944/preprints202401.0112.v1