RJC

RASĀYAN *J. Chem.*
Vol. 17 | No. 2 |611-620| April - June | 2024
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

$CaCO_3$-TiO_2 IMPREGNATED AlOE VERA-ALLYL METHACRYLATE ANTIMICROBIAL NANOEMULSION FOR COATING

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ABSTRACT

The present work aims to utilize AMA/MMA/BA/Aloe Vera (AMBA) nanoemulsion for the preparation of sustainable antimicrobial coating materials. The AMBA was synthesized using a semi-continuous seeded emulsion polymerization methodology. The developed coating material has been synthesized by SEM, DSC, TGA/DTA, XRD, and FT-IR spectroscopy. Some properties such as viscosity, hot box stability gloss retention, solid content, freeze-thaw stability, scrub resistance, electrolytic stability, weather resistance, solvent resistance, and opacity of the coating material were also investigated. It has been found that the coating developed with a 70:30 monomer ratio shows the best results the with highest antimicrobial activity.

Keywords: Aloe Vera, Sustainable Coating Materials, $CaCO_3$-TiO_2 Composites, Antimicrobial, Nanoemulsion.

RASĀYAN *J. Chem.*, Vol. 17, No.2, 2024

INTRODUCTION

Over the last few years, antimicrobial activity remained the most fascinating characteristic among the coating materials. Aloe Vera has been evaluated to exhibit anti-tumor, anti-fungal, anti-cancer, anti-inflammatory, anti-diabetic, anti-aged, anti-oxidative, and antimicrobial properties.[1-8] However, few efforts have been made to synthesize a cross-linked polymeric network of Aloe Vera. So, it encouraged us to conduct a thorough study on the synthesis of the copolymers derived from Aloe Vera and also explore their vital role in the field of nanoemulsion and coating. So far, no work has been carried out on the synthesis of materials with antimicrobial coating of AMBA nanoemulsion. Acrylate-based polymers and copolymers have been widely used as polymeric binders for coating material.[9–13] Acrylic binders were prepared using different industrial ingredients in the coating materials. Several research groups have been trying to improve the different properties of an emulsion including mechanical, optical, and weather ability via the addition of nano-fillers.[14] A semi-continuous seeded emulsion polymerization process was used to synthesize the allylic or acrylic nanoemulsion and considered as a binder in the combined form *i.e.,* poly(BA/AMA/BDA)) and poly(AMA/BA)[15-16] and also AIE polymeric nanoparticles with a susceptible AIEgen prepared in miniemulsion.[9] Because of the improved mechanical, physical, and thermal qualities, $CaCO_3$ has been broadly employed as a less expensive filler in polymers.[17-19] $CaCO_3$ is abundantly available in earth's crust and carries a relatively more positive charge than negatively charged TiO_2, which results in the electrostatic interaction among them at the neutral pH of paint.[20,21] The main use of TiO_2 in waterborne coating is attributed to its high refractive index, good dispersion, and less precipitation.[9,22-23] The stability of both $CaCO_3$ and TiO_2 in water-borne paints is very poor. So, the composite pigment with high stability is quite desired. Consequently, numerous methods for making $CaCO_3$-TiO_2 composites have been discovered.[24-26] MMA as the "hard" component and BA as the "soft" component are considered to achieve

the desired glass transition temperature (Tg) in emulsion paints.[27] Several researchers have reported the preparation of paints/coating with different monomers such as MMA with $CaCO_3$, styrene/methyl acrylate using SiO_2, MMA/BA/Styrene with $CaCO_3$, MMA/BA with TiO_2, and MMA/BA with $CaCO_3$ or TiO_2.[14,28-31] Over the last few decades, environmental-friendly coating/paints have been versatile materials with a significant impact in the field of paint, wastewater, and adhesive.[32-34] Recently, waterborne coatings have become a rapidly emergent field of research because of eco-friendly alarms over traditional solvent-based paints enriched with volatile organic components.[27] Waterborne paint is mostly used to decorate and protect many surfaces including houses, cars, underground storage vessels, and roads.[9] Additionally, some waterborne coatings are named after the binding constituents e.g. coatings of acetylated Mandua starch, epoxy paints, chlorinated rubbers, and alkylated paints, etc. Both components of waterborne paints, including organic and water, could work as nutrients, which have been quickly attacked by different microbes.[35-38] Further, some methods outlined the analysis of industrial dye utilizing bentonite clay coated with acrylic polymer emulsion and the application of cationic fluorinated polyacrylate copolymer as an effective waterborne textile finishing agent.[37] In this work, we proposed a novel combination of eco-friendly AMBA emulsion and $CaCO_3$-TiO_2 composite pigment to develop sustainable coating materials. Also, various characteristics such as viscosity, hot box stability, gloss/gloss retention, solid content, freeze-thaw stability, scrub resistance, electrolytic stability, weathering resistance, solvent resistance, antimicrobial performance, and opacity of the prepared sustainable antimicrobial coating material were measured. The prepared coating materials were also characterized by XRD, FTIR, SEM, TGA/DTA, and DSC techniques.

EXPERIMENTAL

Materials

Aloe Vera gel extracted from the leaves grown in the Uttarakhand state of India was stored at 4°C temperature in the refrigerator. AR grade Sodium lauryl sulfate, span 80, and sodium hydrogen carbonate were procured from *E. Merck*. Three typical monomers allyl methacrylate (99% pure), methyl methacrylate (99% pure), and butyl acrylate (99% pure) were used in copolymerization. All monomers and water-soluble initiator potassium persulphate (98% pure) were purchased from *E. Merck* and *Sigma-Aldrich.* To obtain the coating material formulation, AR grade titanium dioxide, calcium carbonate (99% pure), sodium hydroxide, cellulose, benzyl alcohol (99% pure), deformer (99% pure), and dibutyl phthalate were purchased from CDH and Sigma-Aldrich.

Synthesis of AMA/MMA/BA/Aloe Vera(AMBA) Emulsion

A semi-continuous seeded emulsion polymerization method was considered to synthesize the AMBA emulsion for coating material and used the proportion of the different components given in Table-1.

Table-1: Quantity of Ingredients Used in Semi-Continuous Seeded Emulsion Polymerization

	Ingredients	Quantity (gm)
Pre-emulsion	Conc. Aloe Vera	70
	Allyl methacrylate	10
	Methyl methacrylate	10
	Butyl acrylate	70
	Acrylic acid	5.0
	Sodium lauryl sulphate	5%
	Span 80	3%
	Water	Variable
Reactor	Sodium lauryl sulphate	2.5%
	Sodium hydrogen carbonate	1%
	Water	Variable
Initiator (addition-1)	Potassium per sulphate	0.5
	Water	5.0
Initiator (addition-2)	Potassium per sulphate	0.5
	Water	5.0
Neutralisation	Ammonia	Variable

The synthesis of the allyl/acrylate-based nanoemulsion was already reported in previous literature.[16,39-40] AMBA emulsion was employed as a binder in the sustainable antimicrobial nanoemulsion coating material.

Fabrication of $CaCO_3$-TiO_2 Composite

The $CaCO_3$ -TiO_2 composite was synthesized by the reflux method.[24,25] For this, about an equal ratio of TiO_2 and $CaCO_3$ was dissolved in DI water. NaOH solution (dispersant) was added to the mixture to maintain the pH at ~11.0 then reflux at 110°C and stirred over a rota mental. The material was centrifuged for five minutes at 8000 rotations per minute and the solid materials were collected and washed with DI water as well as ethanol. The final $CaCO_3$-TiO_2 composite dried at 80°C in the oven. Additionally, $CaCO_3$-TiO_2 composite was used for the preparation of the sustainable antimicrobial coating material.

Synthesis of Sustainable Coating Material

Different ratios such as 70:30, 60:40, 50:50, 40:60, and 30:70 of emulsion coating materials were formulated using various amounts of monomers. The coating material was prepared by mixing 250.0g $CaCO_3$-TiO_2 composite, 3.0g sodium lauryl sulfate, and 175.0g DI water which was later stirred over a high-speed motor for 01h. 20.0g AMBA nanoemulsion binder, 2.0g C_7H_8O, 2.0g NaOH, 0.5g $C_{16}H_{22}O_4$ 0.2g deformer, and 2.0g cellulose were then added to the preparation of the paste and mixed with the help of ball mill for 3 hr. The pH (~8) of the formulated nanoemulsions was fixed using (30% v/v) ammonia solution.

Characterization of Sustainable Coating Material

The functionality of the developed coating material was investigated by FT-IR (Shimadzu, 8400S). The Tg of the synthesized coating material was investigated by DSC **(**DSC, 60 Shimadzu). The coating material was heated by 10°C/min under an N_2 gas environment within the range of 30- 500°C. Further, TGA/DTA analysis was done for the measurement of the thermal stability of the prepared coating material. For this purpose, an instrument (Shimadzu TGA–50) was used and operated within the temperature range of ambient temperature to 800°C under a nitrogen-controlled atmosphere with a constant heating rate of about 5ºC/min. The structural phase of the $CaCO_3$-TiO_2 composite and the existence of other components in coating materials were examined by XRD analysis (Scanning rate of 2θ=2º/min, at 2θ scale within a range of 5°−80°. The surface morphology of the coating materials was examined by scanning electron microscopy. The particle dimensions of the synthesized coating material were analyzed by Image *J*-software from SEM pictures.

Physicochemical Characteristics

The physicochemical characteristics such as weather resistance, pH, viscosity (Brookfield viscometer (DV-E)) at 50rpm, hotbox stability (at 70°C), change in viscosity on storage, film opacity, gloss/gloss retention of the coating film with a 60° head gloss meter (KI-353) were also investigated.[23] Further, scrub resistance (ASTM 2486-06), and electrolytic stability of coating materials were also determined.[14,41] For several days, a certain quantity of the synthesized coating materials along with a certain quantity of NaCl solution was kept at 27°C for the determination of electrolytic stability. The freeze-thaw stability of the coating material was determined after storing it at -4°C for 24 hours. To explore the resistance towards diverse solvents the solvent resistance was determined and represented by (+) no change, (±) the solvent swelled the coating material, and (-) the coating material was dissolved.

Solid Content

The gravimetric method was used to determine the solid content in the sustainable coating material. A constant weight was obtained after drying eight grams of the coating material taken on a petri dish at 105±5˚C for 3 hours. The following equation was applied to calculate the solid content (%):

$$\text{Solid content}(\%) = \frac{M_3 - M_1}{M_2 - M_1} \times 100 \qquad (1)$$

Where, M_1 = Weight of the empty Petri plate, M_2 = Weight of the Petri plate with the coating material before drying, and M_3 = Weight of the coating material after drying.

Antimicrobial Activities

Antimicrobial activity was determined by using the nutrient agar plates. The freshly prepared cultures of two *gram* (*+ve*) & (*-ve)* pathogens (*MTCC442, MTCC1144, MTCC2474, and MTCC40*) were swabbed on the surface of agar plates using sterile cotton swabs, and the plates were schematically labeled. The wells in the agar plates were made with the help of a sterile cork borer. Approximately, 50 µL of the coating material taken in water or DMSO solvent was carefully placed in every properly labeled well which was eventually incubated after 2 hr at 37°C for 48 hr. All tests were performed at least three times in order to ensure consistency in the results. Zones of inhibition were examined and measured in millimeters.

RESULTS AND DISCUSSION

FT-IR Spectroscopy

The chemical structure and various functional groups of the sustainable coating materials were investigated using FT-IR spectroscopy as shown in Fig.-1(a). The FT-IR spectrum of the coating material of $CaCO_3$displays well-resolved characteristic absorption peaks at 1788 cm^{-1} and 2854 cm^{-1}which indicates the presence of the ester carbonyl group and C-H stretching of methyl ether O-CH_3, respectively.[14] The absorption peak at 1029 cm^{-1} indicated the Ti-O-Ca bond in $CaCO_3$–TiO_2 composite.[42,24] The characteristic absorption peak that appeared at 1003 cm^{-1} demonstrates the stretching vibration of vinyl and allyl group, respectively from MMA, BA, and AMA of the coating material.[43] The stretching vibration at 1735 cm^{-1} indicates the presence of the CO group in the acrylate monomers of the MMA-BA-acrylic acid.[44] The peak in the coating material appeared at 3480 cm^{-1} indicating the existence of the phenolic -OH group in Aloe Vera.[45] Likewise, the characteristic peaks observed at 1224 cm^{-1} and 2930 cm^{-1} indicate the bond stretching frequencies of the C–C–O stretch and the C–H stretch of the MMA-BA-acrylic acid.[38,46,47]

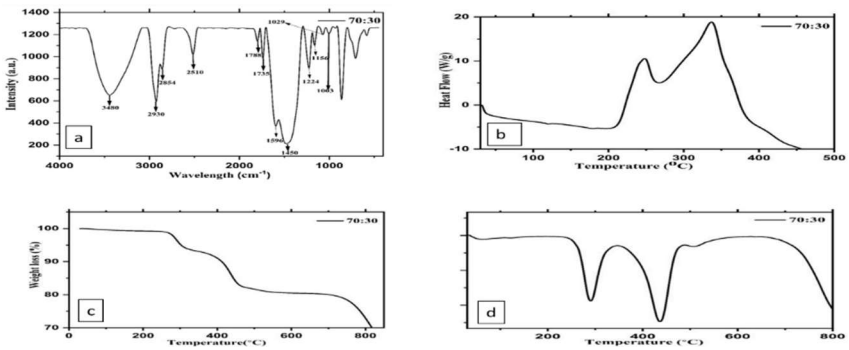

Fig.-1: FTIR Spectrum of the Sustainable Coating Material (a), DSC Thermogram of the Sustainable Coating Material (b), TGA and DTA Thermogram of the Sustainable Coating Materials (c, d)

DSC Analysis

The DSC thermogram of the coating material is displayed in Fig.-1(b). The small endothermic peak that appeared at 118ºC was used to determine the T_g of MMA in the coating material which was then verified from the literature.[48-49] Similarly, the T_g of the broad exothermic peak (247-337ºC) centered at 267ºC which clearly indicates the sustainable coating material.

Thermal Stability Analysis

DTA & TGA techniques were employed to examine the stability of the produced sustainable coating material against the heat. It has been found that water was not present in the films since no mass loss corresponding to it was observed at temperatures below 250°C.[38] Initially, the weight loss seemed to be observed in the first stage from 250ºC to ~320ºC (Fig.-1(c, d)). At 1000°C, the paint film loses all of its weight, but it leaves a thermally stable char. The degradation of the AMBA nanoemulsion is primarily responsible for the weight loss in the 1st step.[50] The 2nd weight-loss stage was identified from 280ºC to 540ºC which could be ascribed to the maximum chemical decomposition of the coating material.[51] Similarly, 44% weight loss of $CaCO_3$ in the third stage appeared at 710°C from 540 to ~800ºC indicating CO_2 elimination as a result of the breakdown of the coating material.[52-53] The DTA thermogram peak maximum appeared at 290ºC in the temperature range of 230-350ºC due to degradation of the coating material. Further, the degradation peak maximum observed at 435ºC was due to the breakdown of Aloe Vera.[53]

XRD Analysis

The crystallinity and the structure of the synthesized sustainable coating material were examined by XRD. The XRD pattern of the prepared coating material is represented in Fig.-2. Calcium was expected to be found in the form of calcite ($CaCO_3$) (JCPDS#47-1743). The characteristic diffraction peaks of $CaCO_3$ was observed at 2θ=36.2º, 39.7º, 43.5º, 57.7º, and 60.9º. Similarly, the characteristic diffraction peaks at 2θ=27.3º, 41.5º, 56.5ºand 65.8º demonstrated the presence of titanium dioxide (JCPDS card #75-1753), which is less intense and described the poor crystallinity of the coating material.[54-56] The poly (BA-MMA) linkage was supported by the large diffraction peak displayed 2θ=29.8º which clearly describes the weak crystallinity and so the amorphous nature of the AMBA nanoemulsion in the coating material.[57-58] The large diffraction peaks for Aloe Vera could easily be seen at 33.2º, 47.8º, and 65.1º.[59]

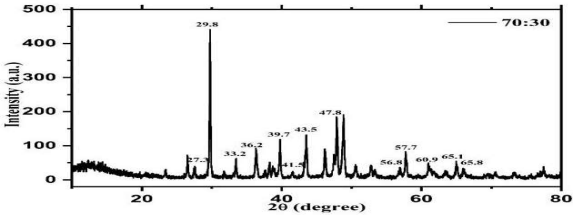

Fig.-2: XRD Pattern of the Sustainable Coating Material

Surface Morphology

Figure-3 (a, b) represents the SEM images of the coating material at different magnifications. SEM images of the coating material demonstrate the smooth, glossy, and opaque surfaces. The particle size in the sustainable coating material was in the range of 39-450 nm. The smooth surface of the coating material will provide a better appearance when applied on the surface of any object.[54,60,63]

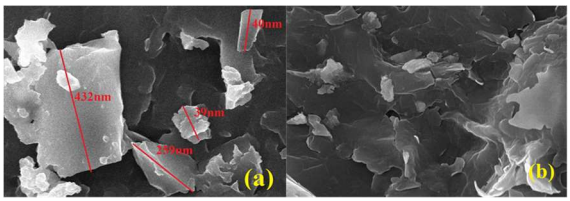

Fig.-3: SEM Images of the Sustainable Coating Material

Physical Properties of the Sustainable Coating Material

The results pertaining to the various physical properties of the sustainable coating materials are compiled in Table-2 it explains that both the scrub resistance and solid content enhance upon an increase in the number of monomer units and a decrease in viscosity.

Furthermore, the opacity and electrolytic stability of the 70:30 ratios are found to be better than others due to the higher hiding power and poor coagulation tendency of the sustainable coating material, respectively. The freeze-thaw stability and weathering resistance, the glass/glass retention of the 70:30 ratios was observed to be higher than that of other ratios. The solvent resistance of 70:30, 60:40, 50:50, 40:60, and 30:70 ratios of the film to the different organic solvents were examined and the results are compiled in Table-3. Apparently, the AMBA containing sustainable coating film of 70:30 ratio showed good resistance towards hexane and ethyl acetate.

Table-2: Physical Properties of the Sustainable Coating Materials

Properties	Aqueous mixed monomers ratio in the coating materials				
	70:30	60:40	50:50	40:60	30:70
pH	7.24	7.37	7.21	7.48	7. 53
Viscosity (C_p)	19	28	23	39	46
Hotbox stability	37	31	18	17	12
Opacity	lines not visible	lines not visible	lines not visible	lines partially visible	lines partially visible
Gloss at 60°C head initial/after 10 days	38/31	34/26	35/27	21/15	19/14

Gloss retention	81.57	76.47	77.14	73.68	71.42
Scrub resistance (cycle)	578	497	549	320	270
Electrolytic stability	no coagulation	no coagulation	no coagulation	no coagulation	less coagulation
Freeze-thaw stability	stable	stable	Stable	stable	less Stable
Weather resistance	stable (30 days)	stable (30 days)	stable (30 days)	stable (26 days)	stable (25 days)
Solid content (%NVM)	62.45	58.48	60.57	52.83	51.96
Density	1.177	1.179	1.173	1.152	1.180

Table-3: Solvent Resistance of Sustainable Coating Film

Solvent effect on coating ratio	70:30	60:40	50:50	40:60	30:70
Acetone	±	-	-	-	-
Methanol	-	-	-	-	-
Hexane	+	+	+	-	-
Ethyl acetate	+	-	-	-	-

The antimicrobial activity of the prepared AMBA nanoemulsion using sustainable coating materials was evaluated with the agar well diffusion assay method against different kinds of pathogens[64-66], *MTCC40, MTCC2474, MTCC1144,* and *MTCC442*. Table-4 shows the average inhibition zone which indicates the promising antimicrobial activity of the coating material against all tested bacteria. The average inhibition zones corresponding to the sustainable coating materials were recorded as 24.00, 22.33, 21.22, and 20.33 mm against *gram* (+*ve*) & (-*ve*) pathogens, respectively. The 70:30 ratios of the coating material show outstanding bactericidal activity against the tested bacteria in comparison to the other ratios which exhibited less activity.

Table-4: Antimicrobial Activity of Sustainable Coating Material Against *gram* (+*ve*) and *gram* (-*ve*) bBacteria

Phase ratio	Bacterial strains Zone of inhibition (mm)			
	MTCC1144	*MTCC442*	*MTCC2474*	*MTCC40*
70:30	22.33	24.00	21.22	20.33
60:40	19.00	19.66	18.66	18.66
50:50	20.66	21.00	19.66	19.66
40:60	19.00	18.66	18.00	19.33
30:70	18.33	18.33	18.33	19.00

CONCLUSION

The sustainable antimicrobial coating material of AMBA nanoemulsion with $CaCO_3$–TiO_2 composite pigment was successfully synthesized and characterized employing various analytical techniques *viz*., DSC, DTA/TGA, XRD, FTIR, and SEM. Many properties such as scrub resistance, hot box stability, gloss/gloss retention, solid content, freeze-thaw stability, viscosity, electrolytic stability, weathering resistance, solvent resistance, and opacity of the synthesized sustainable antimicrobial coating material were sequentially evaluated. XRD patterns and FT-IR spectra establish the structural properties of the sustainable antimicrobial coating materials. Similarly, DTA, TGA, SEM, and DSC analysis confirmed the thermal properties and the surface morphology of the sustainable antimicrobial coating material, respectively. The compiled results indicated the tremendous enhancement in the different physical properties of the sustainable antimicrobial coating material specifically for the 70:30 ratio of the organic to water phase relative to the other ratios. The sustainable coating material with different ratios showed excellent antimicrobial action against two *gram* (+*ve*) bacteria: *MTCC1144 & MTCC442* and two *gram* (-*ve*) bacteria*: MTCC2474 & MTCC40*.

Abbreviations

AMA: Allyl methacrylate
MMA: Methyl methacrylate
BA: Butyl acrylate

BDA: Butane diol diacrylate
KPS: Potassium per sulphate
DI: Deionized water
Tg: Glass transition temperature
AMBA (AMA/MMA/BA/Aloe Vera): Aloe vera-allyl methacrylate antimicrobial nanoemulsion

ACKNOWLEDGEMENTS

The authors sincerely acknowledge the Central Instrumentation Facilities (CIF) of Jamia Milia University (JMU), New Delhi, and the University Sophisticated Instruments Facility (USIP) of Aligarh Muslim University (AMU), Aligarh for providing their SEM and TGA/DTA facilities. We also acknowledge the Lovely Professional University (LPU), Punjab for availing of its XRD facility.

CONFLICT AND INTEREST

None of the authors have declared any conflicts of interest.

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All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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REFERENCES

1. S. Subasree and K. Murthykumar, *Research Journal of Pharmacy and Technology*, **9(5)**, 609(2016), https://doi.org/10.5958/0974-360X.2016.00116.5
2. F.I. Gorsi, T. Kausar and M.A. Murtaza, *Pure and Applied Biology*, **8(2)**, 1265(2019), http://dx.doi.org/10.19045/bspab.2019.80068
3. C. Liu, Y. Cui, F. Pi, Y. Cheng, Y. Guo and H. Qian, *Molecules*, **24(8)**, 1554(2019), https://doi.org/10.3390/molecules24081554
4. C. Tulshi, G. Sumeet, N. Anroop, C. Samrat and S. Vipin, *Drug Delivery Science and Technology*, **64**, 102601(2021), https://doi.org/10.1016/j.jddst.2021.102601
5. D.A. Giannakoudakis, A. Hosseini-Bandegharaei, P. Tsafrakidou, K.S. Triantafyllidis, M. Kornaros and I. Anastopoulos, *Journal of Environmental Manag*ement, **227**, 354(2018), https://doi.org/10.1016/j.jenvman.2018.08.064
6. V. Sujeesh, G. Ponraj and H. Ren, *Micromachines*, **13(2)**, 146(2022), https://doi.org/10.3390/mi13020146
7. V.A. Azevedo, P.A. Barroso, E.M. Vasconcelos, F.C. Costa, E.I. Assis, B.R. Silva, L.R. Paulino, A.W. Silva, M.M. Donato, C.A. Peixoto and J.R. Silva, *Animal Reproduction Science*, **247**, 107078(2022), https://doi.org/10.1016/j.anireprosci.2022.107078
8. S. Anjum, A. Gupt, D. Sharma, D. Gautam, S. Bhan, A. Sharma, A. Kapil and B. Gupta, *Materials Science and Engineering C*, **64**, 157(2016), https://doi.org/10.1177/0883911516668665
9. X. Liang, Y. Hu, J. Lou, Z. Cao, L. Liu, Y. Wang, Z. Zhao, D. Qi and Q. Cui, *Dyes and Pigments*, **160**, 572(2019), https://doi.org/10.1016/j.dyepig.2018.08.051

10. J. Beetsma, *Pigment and Resin Technology* **l27**, 12(2019), https://doi.org/10.1108/03699429810194401
11. J.M. Asua, Polymeric Dispersions: Principles and Applications, *Springer Science & Business Media, Germany,* p.421, 335(2012), https://doi.org/10.1007/978-94-011-5512-0
12. J. Khanjani, A. Hanifpour, S. Pazokifard and M.J. Zohuriaan-Mehr, *Progress in Organic Coat*ings, **141**, 105267(2020), https://doi.org/10.1016/j.porgcoat.2019.105267
13. H. Abd El-Wahab, M. Attia, W.A. Hassan, A.M. Nasser and A. Kazlauciunas, *Nano Science and Nano Technology: An Indian Journal*, **12**, 1(2018), https://doi.org/10.35840/2631-5084/5522
14. V.J. Patil, U.D. Patil, R.D. Kulkarni and N. Ghosh, *Polymer Composites*, **39**, 1350(2018), https://doi.org/10.1002/pc.24075
15. Y. Zhang, S. Pan, S. Ai, H. Liu, H. Wang and P. He, *Iranium Polymer Journal*, **23**, 103(2014), https://doi.org/10.1007/s13726-013-0205-8
16. J. Zhou, X. Chen and J. Ma, *Dyes and Pigments*, **139**, 102(2017). https://doi.org/10.1016/j.dyepig.2016.11.035
17. W.S. Wu, M.E. Queiroz and N.D.S. Mohallem, *Journal of Coatings Technology and Research*, **13**, 277(2016), https://doi.org/10.1007/s11998-015-9740-x
18. W. Gao, X. Ma, Y. Liu, Z. Wang and Y. Zhu, *Powder Technology*, **244**, 45(2013), https://doi.org/10.1016/j.powtec.2013.04.008
19. S.J. Charde, S.S. Sonawane, S.H. Sonawane and S. Navin, *Chemical Engineering Communications*, **205(4)**, 492(2018), https://doi.org/10.1080/00986445.2017.1404459
20. F. Karakaş, B.V. Hassas and M.S. Celik, *Progress in Organic Coatings*, **83**, 64(2015), https://doi.org/10.1016/j.porgcoat.2015.02.003
21. S. Nam, Y. Park, M.B. Hillyer, R.J. Hron, N. Ernst, S. Chang, B.D. Condon, D.J. Hinchliffe, E. Ford and B.C. Gibb, *RSC Advances*, **10(58)**, 35214(2020), https://doi.org/10.1039/D0RA06265K
22. H. Fayaz, S. Rasachak, M.S. Ahmad, L. Kumar, B. Zhang, M.A. Mujtaba, M.E.M. Soudagar, R.,Kumar, and M.R. Omidvar, *Sustainable Energy Technologies and Assessments*, **52(A),** 102092(2022), https://doi.org/10.1016/j.seta.2022.102092
23. A. M. Gandhi, S. Shanmugan, R. Kumar, A.H. Elsheikh, M. Sharifpur, A.K. Bewoor, O. Bamisile, A.T. Hoang and B. Ongar, *Sustainable Energy Technologies and Assessments*, **52(A),** 101974(2022), https://doi.org/10.1016/j.seta.2022.101974
24. S. Sun, H. Ding and X. Hou, *Materials*, **11(7),** 1131(2018), https://doi.org/10.3390/ma11071131
25. R. Sang and F. Yang, *Coatings*, **13(12)**, 2071(2023), https://doi.org/10.3390/coatings13122071
26. L. Yang, H. Yang, W. Hao, Y. Li, Q. Li and T. Sun, *International Journal of Food Science and Technology*, **56(6),** 2675(2022), https://doi.org/10.1111/ijfs.14897
27. M. Eren and H.K. Can, *Progress in Organic Coatings*, **135,** 424(2019), https://doi.org/10.1016/j.porgcoat.2019.06.031
28. S. Grijalvo and C. Rodriguez-Abreu, *Beilstein Journal of Nanotechnology*, **14(1)**, 339(2023), https://doi.org/190.3762/bjnano.14.2
29. Z. Zhang, D. Zhang, G. Fu, C. Wang, F. Chu and R. Chen, *Polymers*, **12(1)**, 80(2020), https://doi.org/10.3390/polym12010080
30. M. Soleimani, E. Bagheri, P. Mosaddegh, T. Rabiee, A. Fakhar and M. Sadeghi, *Progress in Organic Coatings*, **156**, 106250(2021) https://doi.org/10.1016/j.porgcoat.2021.106250
31. A. Nurlybayeva, M. Sakhy, E.S. Negim, E. Rustem and A. Shinibekova, *International Journal of Chemical Sciences*, **13(2),** 922(2015).
32. S. Bilgin, S. Bahraeian, M.L. Liew, R. Tomovska and J.M. Asua, *Progress and Organic Coatings*, **162**, 106591(2022), https://doi.org/10.1016/j.porgcoat.2021.106591
33. J. Singh, R.D. Kaushik, P. Devi and P. Das, *Rasayan Journal Chemistry*, **13**, 761(2020), https://doi.org/10.31788/RJC.2020.1315563
34. A. González and C.I. Alvarez Igarzabal, *Journal of Polymers and the Environment*, **25**, 214(2017), https://doi.org/10.1007/s10924-016-0797-0
35. P. Dileep, S. Jacob, S.K. Narayanankutty, *Progress and Organic Coatings*, **142,** 105574(2020), https://doi.org/10.1016/j.porgcoat.2020.105574

36. S. Osemeahon, A., I.I. Nkafamiya, O.N. Maitera and A. Akintreinwa, *Journal of Polymer and Composites*, **3(2),** 11(2015).
37. J. Zhou, X. Chen and J. Ma, *Dyes and Pigments*, **139,** 102(2017), https://doi.org/10.1016/j.dyepig.2016.11.035
38. M.K. Malik, T. Kumar, V. Kumar, R.K. Singh, K. Saini and J. Singh, *Sustainable Energy and Technology Assessment,* **53(1),** 102398(2022), https://doi.org/10.1016/j.seta.2022.102398
39. J. Singh, R.D. Kaushik and M. Chawla, Emulsion of Some Monomers for Application in Paint Technology, Lambert Academic Publishing, London, p.1-76(2018)
40. S. Mishra, J. Singh and V. Choudhary, *Journal of Applied Polymer Science*, **115(1)**, 549(2010), https://doi.org/10.1002/app.30963
41. H.A. El-Wahab, M. Attia, W.A. Hassan and A.M. Nasser, *International Journal of Nanoparticles and Nanotechnology*, **5(1),** 10-35840(2019), https://doi.org/10.35840/2631-5084/5522
42. G. Subbiah, M. Premanathan, S.J. Kim, K. Krishnamoorthy and K. Jeyasubramanian, *Materials Express*, **4(5)**, 393(2014), https://doi.org/10.1166/mex.2014.1185
43. L.D. Rodrigues and C.R. Hurtado, *Progress in Organic Coatings*, **145,** 105693(2020), https://doi.org/10.1016/j.porgcoat.2020.105693
44. P. Pi, W. Wang, X. Wen, S. Xu and J. Cheng, *Progress in Organic Coatings*, **81**, 66(2015), https://doi.org/10.1016/j.porgcoat.2014.12.006
45. M.K. Malik, P. Bhatt, J. Singh, R.D. Kaushik, G. Sharma and V. Kumar, *ACS Omega,* **7(40),** 35506(2022), https://doi.org/10.1021/acsomega.2c01309
46. R. Shanti, A.N. Hadi, Y.S. Salim, S.Y. Chee, S. Ramesh and K. Ramesh, *RSC Advances*, **7(1)**, 112(2017), https://doi.org/10.1039/C6RA25313J
47. M.K. Malik, V. Kumar, J. Singh, P. Kumar, *Journal of Drug Delivery Science and Technology*, **81,** 104251(2023), https://doi.org/10.1016/j.jddst.2023.104251
48. W. Wang, M. Liu, J. Gu, Q. Zhang and J.W. Mays, *Journal of Polymer Research*, **21**, 1(2014), https://doi.org/10.1007/s10965-014-0502-8
49. D. Silvestri, M. Gagliardi, C. Cristallini, N. Barbani and P. Giusti, *Polymer bulletin*, **63,** 423(2009), https://doi.org/10.1007/s00289-009-0095-2
50. O. Topcuoglu, S.A. Altinkaya and D. Balkose, *Progress in Organic Coatings,* **56(4)**, 269(2006), https://doi.org/10.1016/j.porgcoat.2006.02.003
51. H.H. Wang, X.R. Li, G.Q. Fei and J. Mou, *eXPRESS Polymer Letters*, **4(11)**, 670(2010), https://doi.org/10.3144/expresspolymlett.2010.82
52. H. Zhang, S. Sun, W. Liu, H. Ding and J. Zhang, *Materials*, **13(7)**, 1508(2020), https://doi.org/10.3390/ma13071508
53. O.A. Jimoh, P.U. Okoye, K.S. Ariffin, H.B. Hussin and N. Baharun, *Journal of Cleaner Production*, **150**, 104(2017), https://doi.org/10.1016/j.jclepro.2017.02.200
54. R.L. Kovacs, L. Daroczi, P. Barkoczy, E. Baradacs, E. Bakonyi, S. Kovacs and Z. Erdelyi, *Journal of Coatings Technology and Research*, **18**, 523(2021), https://doi.org/10.1007/s11998-020-00421-5
55. D. Render, T. Samuel, H. King, M. Vig, S. Jeelani, R.J. Babu and V. Rangari, *Journal of Nanomaterials*, **2016**, Article ID 3170248(2016), https://doi.org/10.1155/2016/3170248
56. S. El-Sherbiny, F. Morsy, M. Samir and O.A. Fouad, *Applied Nanoscience*, **4,** 305(2014), https://doi.org/10.1007/s13204-013-0196-y
57. R. Kumar, S.A. Ali, P. Singh, U. De, H.S. Virk and R. Prasad, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms,* **269(14)**, 1755(2014), https://doi.org/10.1016/j.nimb.2010.12.025
58. G. Guo, J. Yu, Z. Luo, L. Zhou, H. Liang, F. Luo and Z. Qian, *Journal of Nanoscience and Nanotechnology,* **11**, 4923(2011), https://doi.org/10.1166/jnn.2011.4119
59. S.M. Rana, R. Al Amin, A. Uz-Zaman, S.H. Talukder, N.H. Mia, S. Tayyaba, and M. Hoq, *Materials Science-Poland*, **33(3)**, 635(2015), https://doi.org/10.1515/msp-2015-0069
60. R. Shanti, F. Bella, Y.S. Salim, S.Y. Chee, S. Ramesh and K. Ramesh, *Materials & Design*, **108**, 560(2016), https://doi.org/10.1016/j.matdes.2016.07.021

61. P. Devi, J. Singh, H. Rehmaan and R.D. Kaushik, *Journal of Polymer Research*, **29(12),** 511(2022), https://doi.org/10.1007/s10965-022-03339-1
62. M.K. Malik, V. Kumar, P.P. Sharma, J. Singh, S. Fuloria, V. Subrimanyan, N.K. Fuloria and P. Kumar, *ACS Omega*, **7(31),** 27334(2023), https://doi.org/10.1021/acsomega.2c02327
63. J. Singh, M. Chawla and R.D. Kaushik, *Journal of Indian Chemical Society*, **99(4)**, 100408(2022), https://doi.org/10.1016/j.jics.2022.100408
64. M. Ataeefard, *Colloid and Polymer Science, **296***, 819(2018), https://doi.org/10.1007/s00396-018-4282-2
65. M.I.H. Mondal and J. Saha, *Journal of Polymer and the Environment*, **27,** 405(2019), https://doi.org/10.1007/s10924-018-1354-9
66. M. Sultan, R. Masood, I. Bibi, I. Sajid, A. Islam, S. Atta, M. Uroos, Y. Safa, H.N. Bhatti, *Progress in Organic Coatings*, **133,** 174(2019), https://doi.org/10.1016/j.porgcoat.2019.04.051

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