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Synthesis and Characterization of Copolymer Derived from 8-Hydroxyquinoline 5-Sulphonic acid, Acrylamide and Formaldehyde.

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ABSTRACT

The copolymer was synthesized from 8-hydroxyquinoline 5-sulphonic acid, acrylamide and formaldehyde by the polycondensation method in 1:1:2 molar ratio using 2M HCl as catalyst and refluxing for 5h at 122^{0}C. Copolymer resin compositions have been determined on the basis of their elemental analysis. The number average molecular weights of these copolymers were determined by gel permission chromatography(GPC) method The copolymer resins has been further characterized by absorption spectra in non-aqueous medium, infrared (IR) spectra and nuclear magnetic resonance (^{1}H NMR) spectral studies. The physico-chemical and spectral methods were used to elucidate the structures of 8-HQ-5-SAAF copolymer. The morphology of the copolymer was studied by scanning electron microscopy and X-Ray Diffraction techniques showing crystalline nature of the copolymer.

Keywords: - Copolymer, polycondensation, synthesis, 8-hydroxyquinoline 5-sulphonic acid, Spectral.

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INTRODUCTION

Polymer science has experienced a rapid evolution, capturing the keen interest of researchers and scientists globally, thanks to the widespread applications of polymeric materials. Copolymers, in particular, have emerged as versatile compounds with a myriad of uses, serving as adhesives, high-temperature materials, flame-resistant fibers, coatings, semiconductors, catalysts, and ion exchange resins [1]. The thermal stability exhibited by copolymers and their polychelates is noteworthy, significantly contributing to the advancement of polymeric materials [2]. Gurnule and colleagues conducted an investigation into the thermal decomposition of a copolymer synthesized from 1, 5-diaminonaphthalene, 2-hydroxy-4-methoxybenzophenone and formaldehyde.

The copolymer HMBPDANF-II was synthesized through the incorporation of 2-hydroxy-4-methoxybenzophenone and 1,5-diaminonaphthalene with formaldehyde. Rahagdale and collaborators conducted a study on the application of this copolymer for the separation of toxic metal ions from wastewater [4]. S ynthesis, characterization and ion-exchange properties of 4-hydroxyacetophenone, biuret and formaldehyde terpolymer resins was studied by Gurnule and coworkers [5]. Mujaferkani and Ahamed collaborated on the coordination and investigation of the thermal degradation of terpolymeric polychelates obtained from p-phenylenediamine-thiosemicarbazide-formaldehyde [6].

The copolymer was prepared through bulk polymerization, involving monomers such as phenylhydrazine (0.1 mol), 2, 4-dihydroxybenzoic acid, and formaldehyde in a ratio of 3:1:5. The polymerization was conducted in the presence of an acid catalyst. The thermal stability of the resulting copolymer was then evaluated and reported [7].

Sidharaj undertook a comprehensive investigation into the synthesis, characterization, and ion-exchange properties of a terpolymer, incorporating 4,4'-oxydianiline, 2,6-diaminopyridine, and formaldehyde [8].Thermal degradation studies of copolymer was carryout by Rahangdale derived from 2-Hydroxy-4-Methoxybenzophenone, 1,5-Diaminonaphthalene, and formaldehyde [9]. The study of copolymer properties has recently gained attention, particularly its crucial role in determining thermal stability and processability. Various thermally stable polymers have been synthesized and their Thermogravimetric Analysis (TGA) properties extensively examined. These polymers, known for their thermal stability, find diverse applications, including in areas such as particle exchangers [10].

Thermal degradation studies of 2-amino 6-nitro benzothiazole-oxamide-formaldehyde copolymer was carryout the composite exhibits a stronger thermal stability than the copolymer, perhaps as a result of more carbonized residues, according to the TGA data of the copolymer and its composite [11-13]. Thermal degradation study of copolymer derived from 2,4- dihydroxypropiophenone, 4-pyridylamine with formaldehyde was carried out by Rahangdale et al. Gurnule and co-worker studied the non-isothermal degradation of copolymer resin derived from 1,5- diaminonaphthalene, 2,4-dihydroxypropiophenone and formaldehyde [14-15]. Synthesis and characterization studies of copolymer derived from 4-hydroxybenzoic acid – Adipamide –Formaldehyde by Thakre [16].

Numerous scientists attempted to work on the warm security at raised temperature by change of the monomer creation in polymer synthesis [17]. 2-hydroxy, 4- metoxybezophenone, 1, 5-diaminonapthalene, formaldehyde by Das [18]. In general, copolymers are useful in packaging, adhesives, and coatings in electrical sensors and semiconductors [19-20] because they occupy a middle ground between organic and inorganic compounds that are both thermally stable and useful as producing materials. Applications for activators, ion exchangers, catalysts, and thermally stable materials have all been discussed. Synthesis and characterization of the copolymer derived from 2-hydroxy-4-methoxyacetophenone, guanidine hydrochloride and formaldehyde was carryout by Bisen and colleagues [21].

The main application of polymers in the making of plastic stuffs like cups, buckets, toys, synthetic materials, automobile parts, gears, electrical insulating materials, floor mat, table cloths and instrument parts has completely revolutionized the regular like as well as the industrialized field. Usually polymer products will not be decomposed easily but recent researchers are finding out decomposing polymer products [22-23].

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The current correspondence manages to synthesis and Characterization of a newly synthesized copolymer derived 8-hydroxyquinoline-5-sulphonic acid-acrylamide-formaldehyde (8-HQ-5-SAAF), through a polycondensation method. The primary focus is on characterization involves elemental analysis and spectral studies, scanning electron microscopy and X-Ray Diffraction techniques is employed to analyse the surface features of copolymer.

EXPERIMENTAL

Materials

8-Hydroxyquinoline-5-sulphonic acid, acrylamide (Sigma Aldrich), and formaldehyde (SD Fine) were obtained from Central Scientific Company, Nagpur. Solvents, including hydrochloric acid, N,N-dimethylformamide, and dimethyl sulfoxide, were procured from Himedia. All chemicals used were of analytical grade and employed as received.

Synthesis Of Copolymer

The copolymer derive from 8-hydroxyquinoline-5-sulphonic acid-acrylamide-formaldehyde (8-HQ-5-SAAF) was synthesized through polycondensation. 8-hydroxyquinoline-5-sulphonic acid, formaldehyde, and acrylamide were combined in a 1:1:2 molar ratio in a 2M HCl medium. The synthesis occurred in an oil bath at 122 °C with over a 5h period to ensure thorough reaction. The resulting resinous substance, observed in a yellow shade, was washed with diethyl ether and hot distilled water to remove impurities. Purification involved dissolving the copolymer in 8% aqueous NaOH, followed by recovery through a 1:1 (v/v) conc. HCl/distilled water drop-wise addition. The copolymer resin was then finely ground through a 300-mesh size sieve and stored in a vacuum over silica gel. The proposed reaction scheme is given Fig. 1.

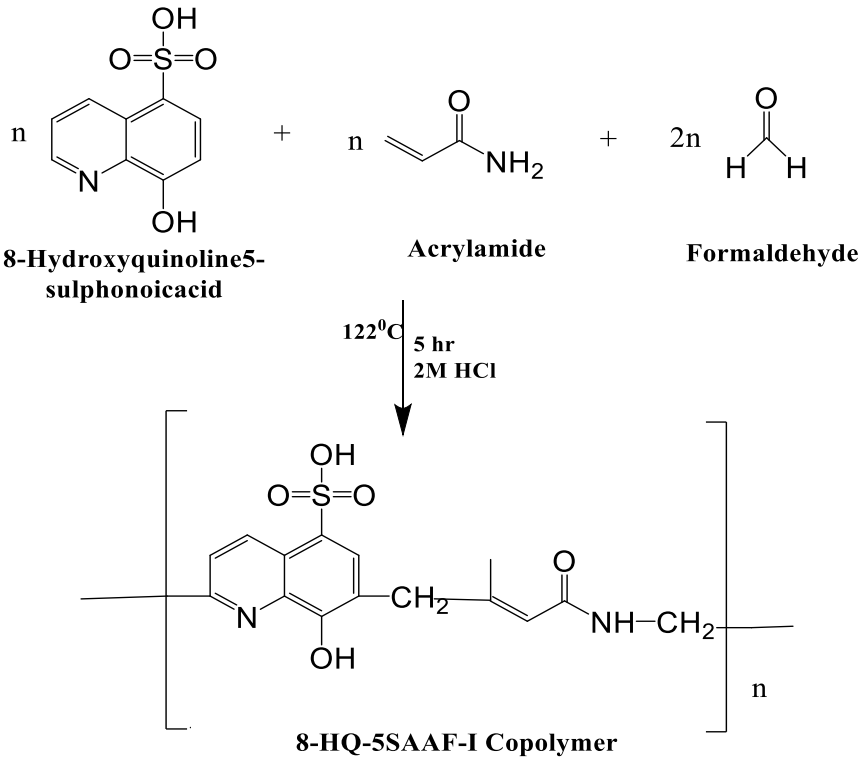

Figure 1: Synthesis of 8-HQ-5-SAAF Copolymer

Characterization

The copolymer resin underwent characterization through various experimental techniques. Elemental analysis was conducted using the Perkin Elmer 789N QP-2010 instrument. UV visible spectra of the recorded in DMSO in the wavelength range of 200–800 nm. The FTIR spectra were recorded in KBr

pellets within the range of 4000-5000 cm^{-1}. ^1H NMR spectra were acquired in DMSO-d_6 solvent with a 400 MHz Bruker spectrometer. Surface morphology was examined through a scanning electron microscope and X-ray Diffraction studies for crystalline nature of the copolymer.

RESULTS AND DISCUSSION

The copolymer 8-HQ-5-SAAF was viewed as yellow in colour. The solubility profile of the 8-HQ-5-SAAF copolymer was investigated across a spectrum of solvents in order to discern its dissolution characteristics. The copolymer exhibited pronounced solubility in tetrahydrofuran (THF), dimethylsulfoxide (DMSO), and dimethylformamide (DMF), while displaying partial solubility in concentrated nitric acid (Con. HNO_3). These findings contribute to a comprehensive understanding of the copolymer's interaction with diverse solvent environments, providing valuable insights for potential applications and further research endeavors.

Elemental analysis

Microanalysis was conducted to determine the elemental composition of the 8-HQ-5-SAAF copolymer, focusing on carbon (C), hydrogen (H), nitrogen (N), and sulfur (S). The obtained findings align well with the measured values. The empirical weights of a single repeating unit, derived from the empirical formula, are summarized in Table 1.

Table 1: Elemental Analysis of 8-HQ-5-SAAF copolymer

Copolymer	% of C Observed (Cal.)	% of H Observed (Cal.)	% of N Observed (Cal.)	% of S Observed (Cal.)	Empirical Formula of repeated unit	Empirical Formula Weight
8-HQ-5-SAAF	52.60 (53.83)	3.11 (4.18)	6.42 (8.37)	7.62 (9.57)	$C_{15}H_{14}N_2O_5S$	334.35

UV-Visible Spectra

The UV–visible spectra of 8-HQ-5-SAAF copolymer are show in Fig. 2. UV visible spectra of the recorded in DMSO in the wavelength range of 200–800 nm [24]. The spectra of these copolymers exhibit two maxima in the district 266.50 and 305.50 nm. These noticed places of the retention groups show the presence of hydroxyl gathering, which is in formation with the aromatic nucleus. The presence of previous band (more extreme) can be represented π → π * transition, while the later band (less extreme) might be expected to n → π * electronic transition. The presence of hydroxyl group is for hyper chromic shift for example ∑max higher qualities. This perception is inacceptable concurrence with the proposed generally likely designs of these copolymer transition in a benzene ring is acceptable transition, whereas the n → π * transition accounted for –NH group [25].

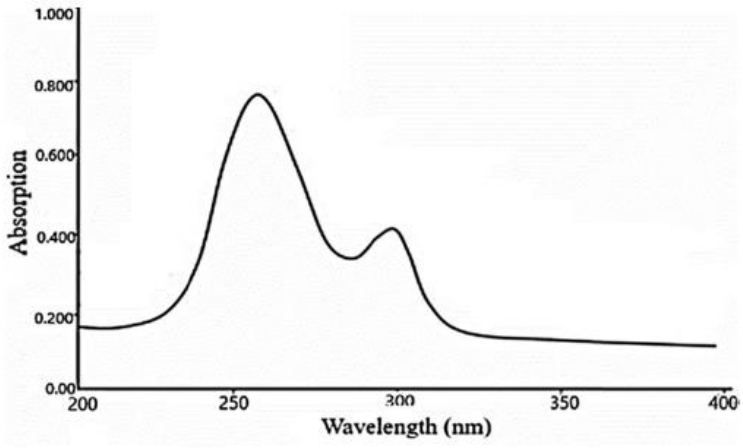

Figure 2: Ultraviolet-Visible spectrum of 8-HQ-5-SAAF copolymer

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FTIR Spectra

The FTIR spectra of8-HQ-5-SAAF copolymer is shown in Fig. 3 a broad band displayed at 3325 cm $^{-1}$may be attributed to the stretching vibration of phenolic –OH [26] group exhibiting intramolecular hydrogen bonding. The sharp and strong band appeared at 1625 cm $^{-1}$ may be on account of stretching vibration of carbonyl group (Ar-CO group). The presence of methyl and methylene vibration has been indicated by the medium band at 2978 $^{-1}$ and 2600 $^{-1}$[27]. The medium band obtained at 2939 cm $^{-1}$ may be due to –NH– group in pyridine moiety. A weak band appearing at 1482 cm $^{-1}$ describes the presence of >C=C< (aromatic) group. The sharp and strong band at 1373 cm $^{-1}$, suggested the presence of –CH_2– Methylene Bridge in copolymer chain [28].

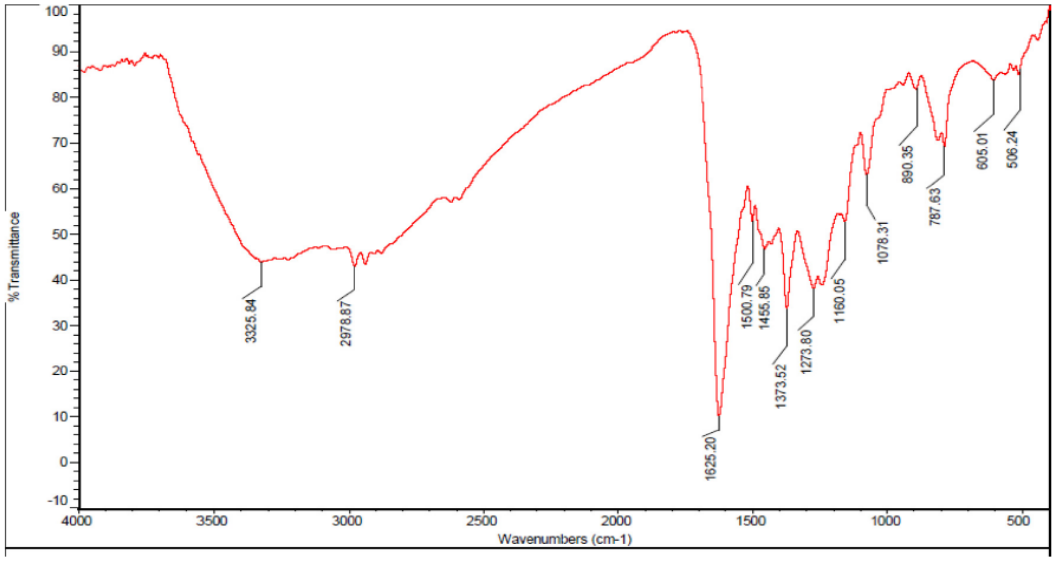

Figure 3: FTIR spectra of 8-HQ-5-SAAF copolymer

Nuclear Magnetic Resonance

The ^{1}H nuclear magnetic resonance (NMR) spectra of the 8-HQ-5AAF copolymer is presented in Fig. 4 The singlet signals in the range of 2.2 – 2.5 ppm (δ) are attributed to the methylene protons of the Ar-CH_2-Ar bridge. [29] The Ar – CO – CH_3 group exhibits a medium singlet peak assigned at 2.5 to 3 ppm (δ) for the methyl protons. The amino proton of the –C–NH–CS- linkage manifests as a triplet signal in the region of 3.0 to 4.1 ppm (δ).[30] An intense signal observed at 3.5 to 4.5 ppm (δ) is assigned to the methylene protons (CH_2) of the polymer chain. The aromatic protons display an unsaturated pattern with a weak signal in the range of 6.5 to 8.5 ppm (δ). Additionally, a proton weak signal is identified in the region of 7.5 to 8.2 ppm (δ), attributed to the phenolic –OH proton [31].

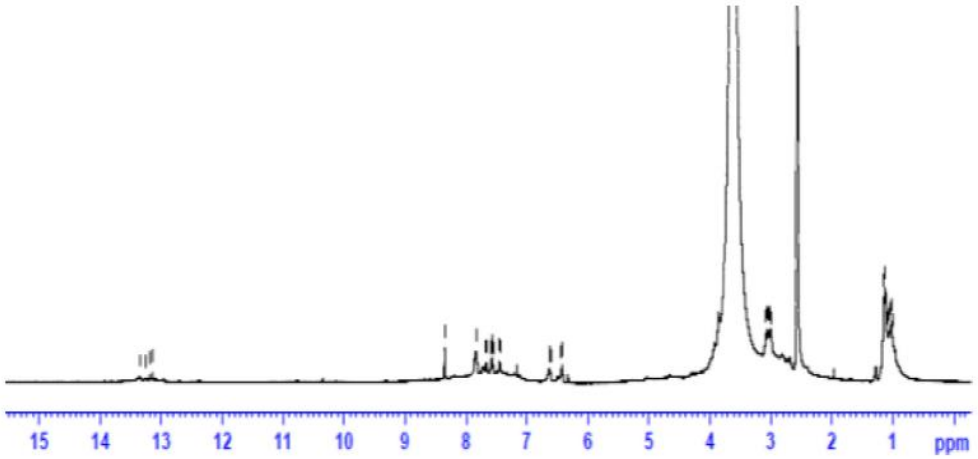

Figure 4: ^{1}H NMR Spectra of 8-HQ-5SAAF Copolymer

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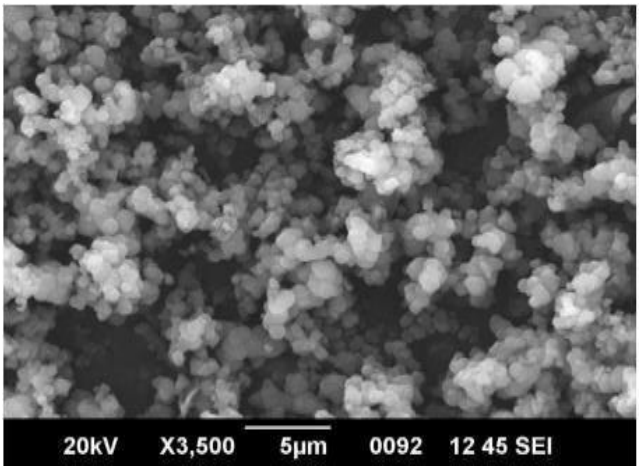
SEM Morphology

The SEM analysis of the 8-HQ-5SAAF copolymer's morphology Fig. 5 reveals spherules with a smooth polycrystalline surface, indicating crystallinit [32]. A fringed model suggests an amorphous-crystalline structure. The degree of crystallinity is linked to monomer acidity. Amorphous characteristics include a densely packed surface with deep pits, indicating reactive sites shows a yellow appearance of the synthetic copolymer with a fringed pattern, representing the transition between crystalline and amorphous phases. Surface analysis highlights small holes and cracks, possibly from air voids useful for ion exchange studies the copolymer's crystal formation from copolymer solutions aligns with larger-scale organization in polymers, like spherulites a few millimeters in diameter [33].

Figure 5: SEM images of 8-HQ-5SAAF Copolymer



X-Ray Diffraction

X-ray Diffraction (XRD) was used to analyze the crystal structure of the 8-HQ-5SAAF Copolymer Fig. 6. The degree of crystallinity [31-33] was determined, indicating a highly crystalline character. The X-ray Diffraction confirmed the crystalline structure, as evidenced by prominent peaks at coordinates 2 = 32, 47, 57 in the XRD data.

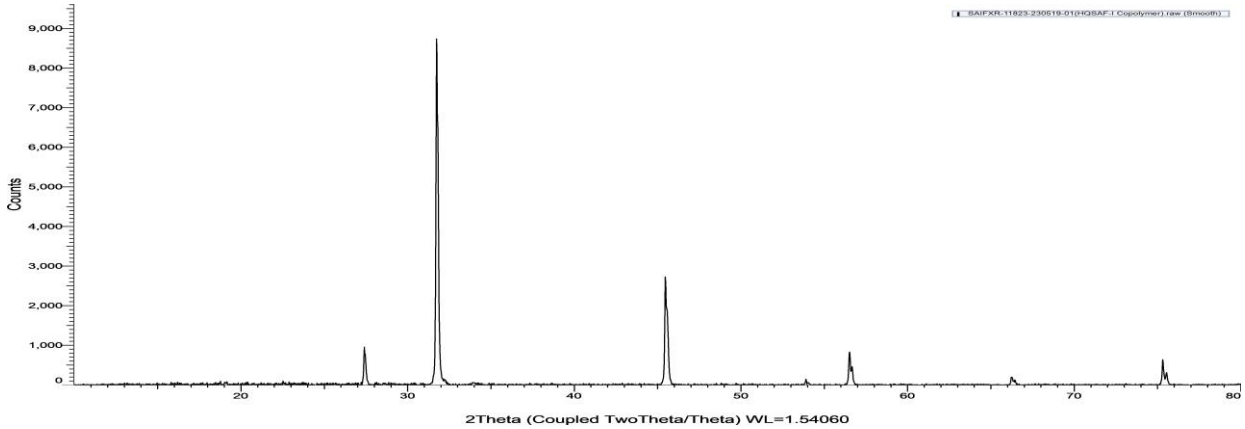


Figure 6: XRD Spectra of 8-HQ-5SAAF Copolymer

CONCLUSION

The copolymer derive from 8-hydroxyquinoline 5-sulphonic acid, acrylamide and formaldehyde was synthesized by a polycondensation method in a 1:1:2 molar ratio, using 2M HCl as a catalyst and refluxing at 122°C for 5 h. Characterization of copolymer included absorption spectra in a non-aqueous medium, infrared (IR) spectroscopy, and nuclear magnetic resonance (^{1}H NMR). Physico-chemical and spectral analyses elucidated the copolymer structure. Scanning electron microscopy revealed the

copolymer's crystalline nature, providing insights into its morphology. This comprehensive approach enhances our understanding of the synthesized copolymer's structure and properties in polymer chemistry.

REFERENCES

[1] Das NC, Rathod YU, Pandit VU, Gurnule WB. Mat. Tod. Proc 2020; 53: 80-85.
[2] Rathod YU, Pandit VU, Bhagat DS, Gurnule WB. Mat. Tod. Proc 2022; 53: 123-129.
[3] Gupta PM, Rathod YU, Pandit VU, Gupta R.J, Gurnule WB. Mat. Tod. Proc 2020; 53: 101-106.
[4] Rahangdale SS, Das NC, Vajpai KS, Gurnule WB. Int. J RBAT 2020; 8: 194-204.
[5] Gurnule WB, Rahandale PK, Paliwal LJ, Kharat RB, Reac. Funct. Polym 2003; 55:255–265.
[6] Mujafarkani N, Ahamed AJ. Mat. Tod. Proc 2021; 49: 1920-1928.
[7] Gurnule WB, Das NC, Vajpai KS, Rathod YU. Mat. Tod. Proc 2020; 29: 1071-1076.
[8] Sidharaj N, Rajaran G, Senthil. M, Mat. Tod. Proc 2020; 42: 1030-1036.
[9] Rahangdale SS, Das NC, Gurnule WB. I J R B A T, 2020:1:194-204.
[10] Chakole SP, Rathod YU, Pandit VU and Gurnule WB. Mat. Tod. Proc2022; 53:96-100.
[11] Gurnule WB, Gupta PG, Gupta RH, Rathod YU, Singh NB. Int. J. Earth. Env. Sci 2023; 1281.
[12] Mandavgade SK, Gurnule WB. Mat. Tod. Proc 2022; 60: 1814-1818.
[13] Yaxinli H, Cheng B, Yishang C. Polym Sci 2020: 323-332.
[14] Rahangdale SS, Das NC, Vajpai K, Gurnule WB. Int. J. Recent Sci. Res 2019; 10: 31772–31778.
[15] Gurnule WB, Das NC. Mat. Tod Proc 2019; 15: 611–619.
[16] Thakre MB, Gurnule WB, Mat. Tod Proc. 2019; 3: 516–525.
[17] Kohad CG, Gurnule WB. Mat. Today Proc 2019; 15: 438–446.
[18] Das NC, Gurnule WB. Int. J. Curr. Eng. Sci. Res 2019; 6: 1414–1425
[19] Gurnule WB, Rathod YU, Belsare AD, Das N C. Mat. Tod. Proc 2020; 29: 1044.
[20] Gurnule WB, Rathod YU. Curr. Appl. Polym. Sci 2020: 4: 102-109.
[21] Bisen VR, Gurnule WB, Res. J. Phys. Bio. Chem. Sci 2014; 5: 1283–1297.
[22] Morsch S, Liu Y, Lyon SB, Gibbon SR., Gabbriele B, Malanin M, Eichhorn K. Polym. Degrad. Stabil. 2020; 176.
[23] Chinaglia S, Tosin M. F. Polym. Degrad. Stabil 2020; 147: 237–244.
[24] Gurnule WB, Rathod YU. Current Appl. Polym. Sci 2021; 4: 47-54.
[25] Gurnule WB, Khobragade. J, I JCESR 2019; 6: 116-122.
[26] Kamdi DD, Gurnule WB. I JCESR 2019; 6: 1297-1302.
[27] Barkade SS, Bansod PG, Doss VR, Mardikar SP. Adv. Sci. Engg. Medic 2020; 12: 198-206.
[28] Mohurle RK, Rathod YU, Ghatole AM, Gurnule WB. Int. J. of Adv. Res. Sci. Comm. and Tech. 2021; 12.
[29] Gupta RH, Gupta PG, Gurnule WB. I JCESR 2019; 6: 101-107.
[30] Gupta PG, Gupta RH, Gurnule WB. Appl. Polym. Sci 2020; 8: 156-162.
[31] Chakole SP, Nandekar KA, Gurnule WB. J. Phys. Conf. Ser 2021; 1913: 1–8.
[32] Mandavgade SK. Imt. J. Innovat. Eng. Sci 2020; 3: 137-141.
[33] Rathod YU, Gurnule WB. Mat. Tod. Proc 2020; 6: 163-170.