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Comparative Study of Different Methods of Synthesis and Their Effect on the Thermomechanical Properties of a Halogenated Epoxy-Based Flame-Retardant Resin

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ABSTRACT: The work presented in this paper deals with the comparative synthesis of diglycidyl ether-based tetrabromobisphenol-A(TBBPA) using both conventional and nonconventional methods in order to explore materials for better industrial applications with respect to effective yield, cost, and time consideration. The conventional method involved the polycondensation of TBBPA and epichlorohydrin in the presence of an alkali catalyst. The nonconventional routes adopted for the synthesis of the material involved ultrasonication, microwave irradiation, and UV light exposure. The Fourier transform infrared spectroscopy spectra of all the synthesized materials of the resin were found to be identical, and the X-ray diffraction analysis showed the material as amorphous. The mechanical studies of the resins revealed that all these resins synthesized by different methods are strong and possess high viscosity. Based on the overall thermal, rheological, and excellent hydrophobic properties, it can serve as an excellent flame retardant.
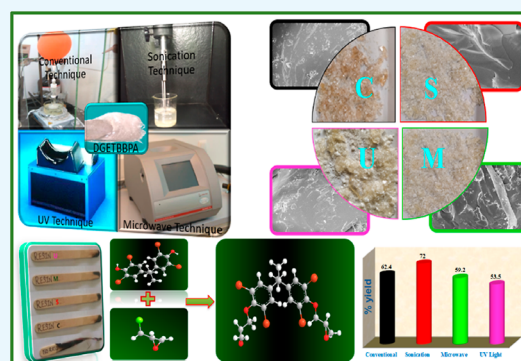
1. INTRODUCTION

One of the challenges which scientists and researchers in recent times are facing is to explore new materials having immense potential for applications in the field of modern science and industry. In this context, epoxy resins are the materials which have been modified time to time by keeping in view the development of electronic technology that rendered the use of conventional epoxy resins as heat-resistant and flame-retardant (FR) materials questionable. Another driver for this shift has been a declining reliance on steel and aluminum as composite materials, having been replaced in a wide array of industrial applications over the past few decades. Polymers and polymer-based materials have become a mainstay in our daily lives nowadays.

Epoxy resin is a crucial engineered resin/polymer that has received much attention in recent years due to its industrial applications and economic benefits on account of its versatility and immense characteristics such as good adhesive property[1] to different substrates, moisture,[2] solvent resistance,[3] chemical resistance,[4] and outstanding mechanical and electronic resistance properties.[5] It has a broad range of applications in the industries currently ranging from extensive use in coatings,[6,7] industrial floorings,[8,9] construction materials,[10] adhesives,[11−15] recreation, marine systems,[16−18] foams, composites[19−22] painting,[23−25] potting, laminates,[26,27] matrix materials for electronics, and transport and aerospace industries.[28−32] However, the commercially available epoxy resins do not possess some applications where the exposure of high temperatures is unavoidable. Thus, their strength and usage could be further augmented in order to enhance their commercial applicability and industrial acceptance.

One of the ways to expand the commercial spectrum of epoxy resins involves the synthetic tailoring/modification in order to make these as fire-retardant materials and curing agents.[33] By considering epoxy resin as an organic matrix, its thermal resistance and flame retardancy attributes can be improved further for better usage. Nowadays, flame retardancy, as an outstanding element of safety, is one among the key challenges for scientists to fabricate advanced materials for multidimensional applications such as FR paints,[34] firefighting clothes, home insulations, fiberglass, and microencapsulation for electronics.[35,36]

In this connection, some techniques and approaches have been put forward to enhance the fire retardancy of epoxy resins. The halogen-based FRs are being used for some time now for improving and uplifting the flame retardancy of epoxy resins[37] and can also be used as essentially applied flame-retardant materials in particular as resins in composite organic matrices or in other fields.[38,39]

FRs have been exploited in the polymer industry since 1960 specially to enhance the flame retardancy of polymers/resins without changing their mechanical properties or any of their composites.[40,41] Different types of halogen-based FRs are in practice since the past few decades to predominantly enhance the flame retardancy of epoxy resins.[37] Among these halogen FRs, fluorine- and iodine-based retardants are not in use, whereas brominated FRs are extensively reported, and among these, tetrabromobisphenol-A (TBBPA), tetrabromophthalic anhydride, decabromodiphenyl ether, hexabromocyclododecane, and polybromodiphenyl ether are more prominent.

The significance of brominated FRs to prevent fires ensures their wide application in the fields such as plastics, textiles, electronic circuitry, and other materials. A majority of the epoxy resin formulations are investigated to have flammability attributes ranging from slow burning to self-extinguishing properties. The flame retardancy of epoxy resin can be achieved by the addition of halogenated compounds or phosphorated compounds or a mixture of both classes of compounds. The halogen[42] or phosphorus[43,44] moiety in the modified resin will act as a curing agent. FR epoxy resins comprising halogens incorporated directly into the epoxy resin molecule are now available and growing consistently. The structure outlined in Figure 1 is a FR epoxy resin derived from tetrahalobisphenol-A.[45]
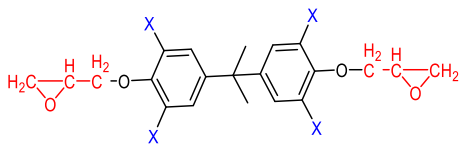

Figure 1. Tetrahalobisphenol-A, where X = Br.

The halogen-based FRs work by releasing halogen radicals, which react with the high-energy H$^\bullet$ and OH$^\bullet$ radicals that cause the chain reaction of burning organic gases in the gas phase. Brominated phenols, which react with the epoxy portion of the polymer system, are the most common halogen-containing FRs for epoxy resins, and so bromine is incorporated into the organic polymer matrix. The most utilized resins are diglycidyl ether of bisphenol A and TBBPA. TBBPA is a type of reactive monomer or FR additive that is widely used in epoxy resins, especially in electronic materials where flame retardancy is needed.

In a normal procedure, the chain extension process is started by the prereaction of TBBPA with epoxy resin, with a 20–30 mass % of TBBPA and V-0 rating in printed wiring boards. Among the brominated products, TBBPA is the highest-volume brominated product that is currently sold in the market.[46] There is a growing demand for brominated epoxy resins as FRs in buildings, electronic/computer equipment, and transport industries due to the increasing use of polymeric materials in these areas.

In an electronic industry, high thermal stability, high conductivity, low dielectric constant, and low coefficients of thermal expansion of the substrate and packaging materials are needed. The most abundantly used FRs in printed circuit boards are the brominated epoxy resins.[47,48] The chemical structure and polymeric nature offer many advantages to brominated epoxy resin such as excellent processability, good thermal stability and thermal aging, better UV stability, and anticorrosive nature. Brominated resins must contain 16–22% bromine to provide acceptable FR performance.

Even though condensed-phase reactions with a polymer matrix can be involved, halogen-based FRs, which are used in most cases in conjunction with metal compounds, display chemical activity in the gas phase. These compounds use chlorine and bromine to react with flammable gases and reduce the rate of combustion dramatically by radical transfer. Thus, during the first step of the reaction, the halogen compounds obstruct the chain reaction of combustion by the liberation of halogen hydracids, which transform the highly reactive radicals, OH$^\bullet$ and H$^\bullet$, with lesser reactive radicals. Therefore, the efficacy of halogen compounds usually depends on the ease of liberation of the halogen and on the nature of the group having the halogen.

To attain acceptable levels of flame retardancy, 40 wt % of chloride and 20 wt % of bromide are needed.[49] Hence, to decrease the halogen concentration and to improve FR properties, various metallic compounds, such as metal oxides, can be utilized as synergists and among these, antimony trioxide acts as an inhibitor in the gas phase. The other commonly used synergists are zinc, nitrogen, phosphorus, and tin compounds.[50]

To date, the most widely used fire-retardant additives are halogen-based compounds such as TBBPA for fire suppression in electronic and industrial applications owing to their cost-effectiveness, high FR properties, and ease of mixing with other compounds. Its environment-friendly properties make TBBPA a suitable material because it has been extensively reported that TBBPA has almost no effect on flora or fauna.[51,52]

The synthesis of TBBPA is reported in the literature by a conventional method using nitrogen,[53] but the process is complicated and time-consuming. With the advent of technology, novel and efficient methods such as sonication and microwave irradiation have gained popularity due to the advantages of being environment-friendly, less time-consuming, and cost-effective. In the present work, a comparative study on the synthesis of TBBPA diglycidyl ether was made by different nonconventional methods such as ultrasonication, microwave irradiation, and in the presence of UV light in addition to the conventional method in order to explore its effect on the thermomechanical properties such as thermal stability, rheology, tailored morphology, and high value of flame retardancy in addition to its effectiveness with respect to cost, yield of the material, and time of the reaction.

2. RESULTS AND DISCUSSION

Epoxy resins are synthesized by step-growth polymerization also known as polycondensation reaction. In the present case, when TBBPA and epichlorohydrin (ECH) are reacted in an alkaline medium, we get a polymer called as TBBPA epoxy resin. In this long polymeric chain, epoxy groups are attached to the terminal ends of the resin chain.

2.1. TBBPA Has an Active Hydrogen Which Is Extracted by the OH$^-$ of NaOH to Give the TBBPA Sodium Salt. The base (NaOH) extracts the active proton (H$^+$) of the hydroxy group of TBBPA, leading to the generation of a negative charge on oxygen, which then interacts with Na$^+$ ions and forms the sodium salt of TBBPA. The elimination of a water molecule also takes place in the process. As there are two OH groups and under the basic conditions, the molecule will ultimately form the disodium salt

Scheme 1. Reaction Mechanism Involved in the Synthesis of Diglycidyl Ether TBBPA (DGETBBP-A)
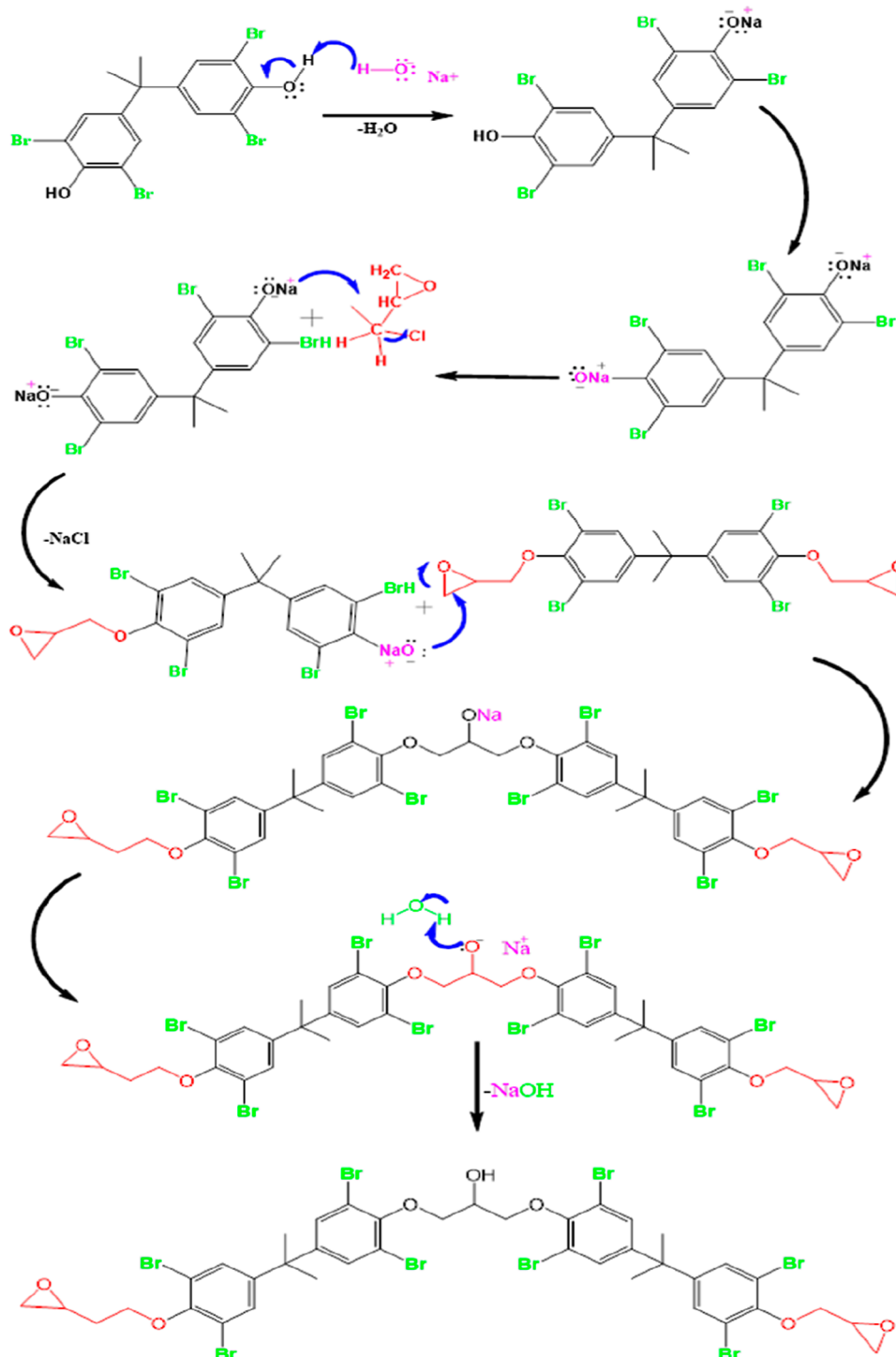
of TBBPA; therefore, the negatively charged oxygen anions act as reactive centers and behave as good nucleophiles.

2.2. TBBPA Sodium Salt Acts as a Nucleophile and a Substitution Reaction Takes Place to Remove Cl⁻ from ECH. As the O⁻ charge on TBBPA acts as a good nucleophile, it attacks the partial positively charged carbon attached to the chlorine and in the process leads to the elimination of the Cl⁻ ion. The Cl⁻ ion thus generated interacts with Na⁺ to form NaCl, and the process leads to the formation of a carbon–oxygen bond, thus generating the diepoxide polymer, comprising two epoxy groups at the terminal ends (Scheme 1).

2.3. FTIR Analysis. The Fourier transform infrared spectroscopy (FTIR) spectra of the resin prepared by four different routes are depicted in Figure 2. The typical peaks observed at 3461−3469 cm^{-1} are due to the association of hydroxyl groups, and the band at 3059−3068 cm^{-1} is assigned to the C−H tension of the methylene group of the epoxy ring owing to the strong O−H absorption; this band is not clearly apparent and, therefore, not important. However, the presence of the epoxy group becomes apparent in the low degree of polymerization of these epoxy monomers. The peaks observed at 2961−2863 cm^{-1} are attributed to the C−H asymmetric and
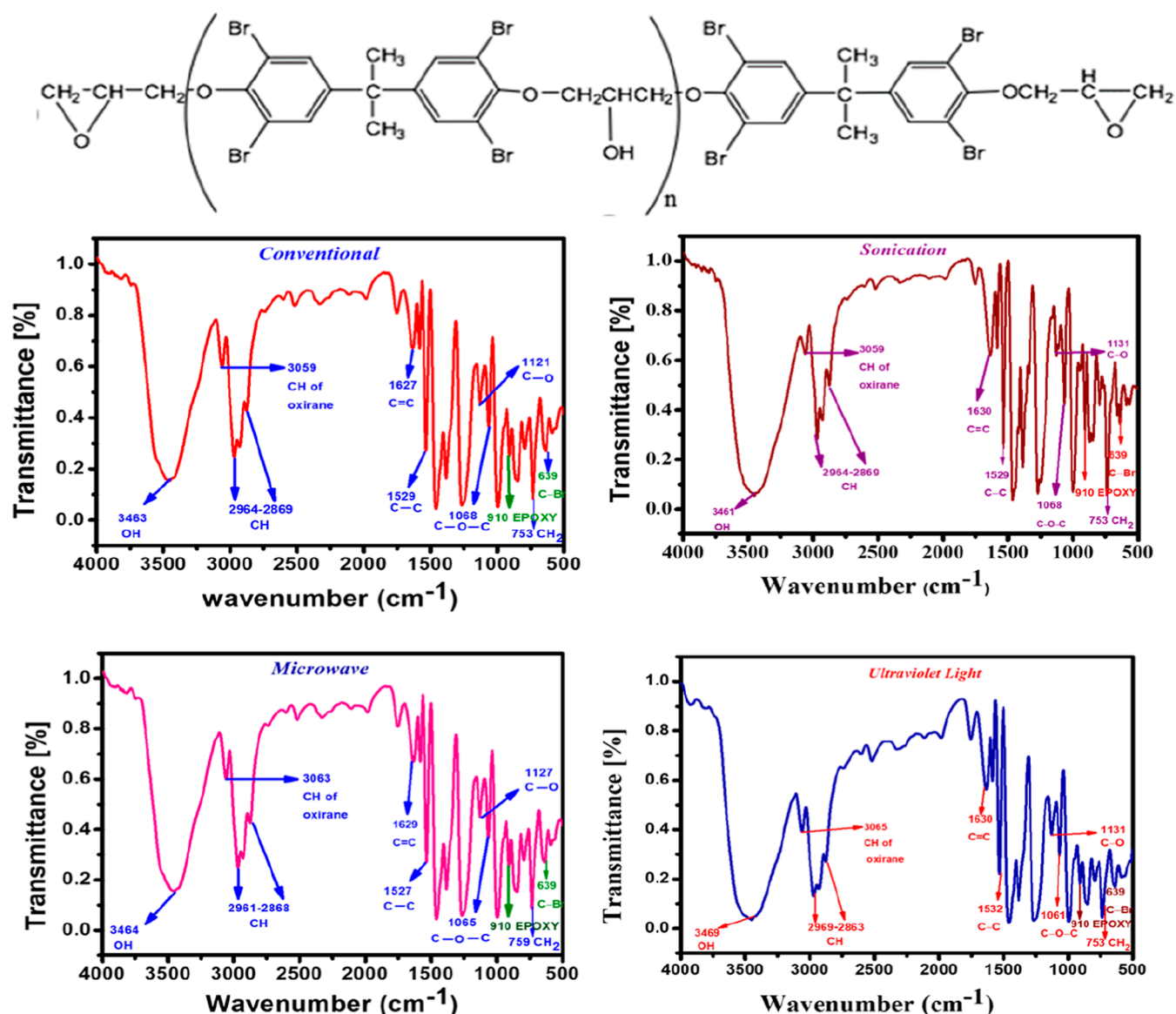
Figure 2. FTIR spectra of TBBPA epoxy resins synthesized by different methods.

symmetric stretching of the methyl groups. The characteristic peaks at 1627−1630 cm^{-1} correspond to the C=C aromatic stretching. The characteristic peaks from 1505−1595 cm^{-1} are attributed to the C−C stretching of the benzene ring. The bands at 1442 and 1387 cm^{-1} are assigned to the C−H in-plane bending vibration of methyl groups. The characteristic stretching of secondary alcohol C−O appears at 1121−1131 cm^{-1}, which indicates that the secondary alcohol was connected to the molecular structure of the synthesized bromo epoxy resin. The peaks at 1061−1068 cm^{-1} appear due to the C−O−C stretching of the ether groups of the resin. The characteristic peak at around 910 cm^{-1} appears due to the C−O stretching of epoxide, confirming that an epoxy group is present in the resinous skeleton, and the peaks at 830−835 cm^{-1} are attributed to the C−O−C stretching of an oxirane group. The band at 741−749 cm^{-1} shows the existence of an ortho-substituted aromatic ring in the molecular backbone of the synthesized bromoepoxy resin. The characteristic peak at 639 cm^{-1} belongs to the C−Br stretching, implying that bromine is present in the molecular organic framework of the resin.[54,55]

2.4. ^{1}H NMR Analysis. The structure of the synthesized halogenated resins was also elucidated by ^{1}H NMR spectroscopy. All the signals were appropriately assigned as depicted in Figure 3A,B. The ^{1}H NMR spectrum shows δH, ppm (TMS, DMSO-d_6, 500 MHZ): 2.6 **A** (2H, terminal CH$_2$ protons of the oxirane ring), 3.3 **B** (1H, CH proton of the oxirane ring), 3.9 **C** (2H, CH$_2$ protons of the oxirane ring attached to TBBPA), 7.2 **D** (2H, aromatic protons of TBBPA), 1.6 **E** (3H, CH$_3$ protons of TBBPA), 3.4 **F** (2H, CH$_2$ protons of TBBPA), 4.3 **G** (1H, CH proton attached to OH), and 5.7 **H** (1H, proton attached to OH).[56−58]

The nuclear magnetic resonance (NMR) analysis showed sharp and well-resolved peaks for the resin and especially the terminal hydrogens on the epoxide moiety. The proton NMR combined with rheological studies does lead to the conclusion that the resin is indeed linear.

2.5. UV−Visible Spectroscopy and XRD Analysis. The absorption spectra of all the synthesized materials are shown in Figure 4. The results demonstrate a π−π* transition originating from the aryl backbone in all the synthesized samples. However, all the samples obtained by different
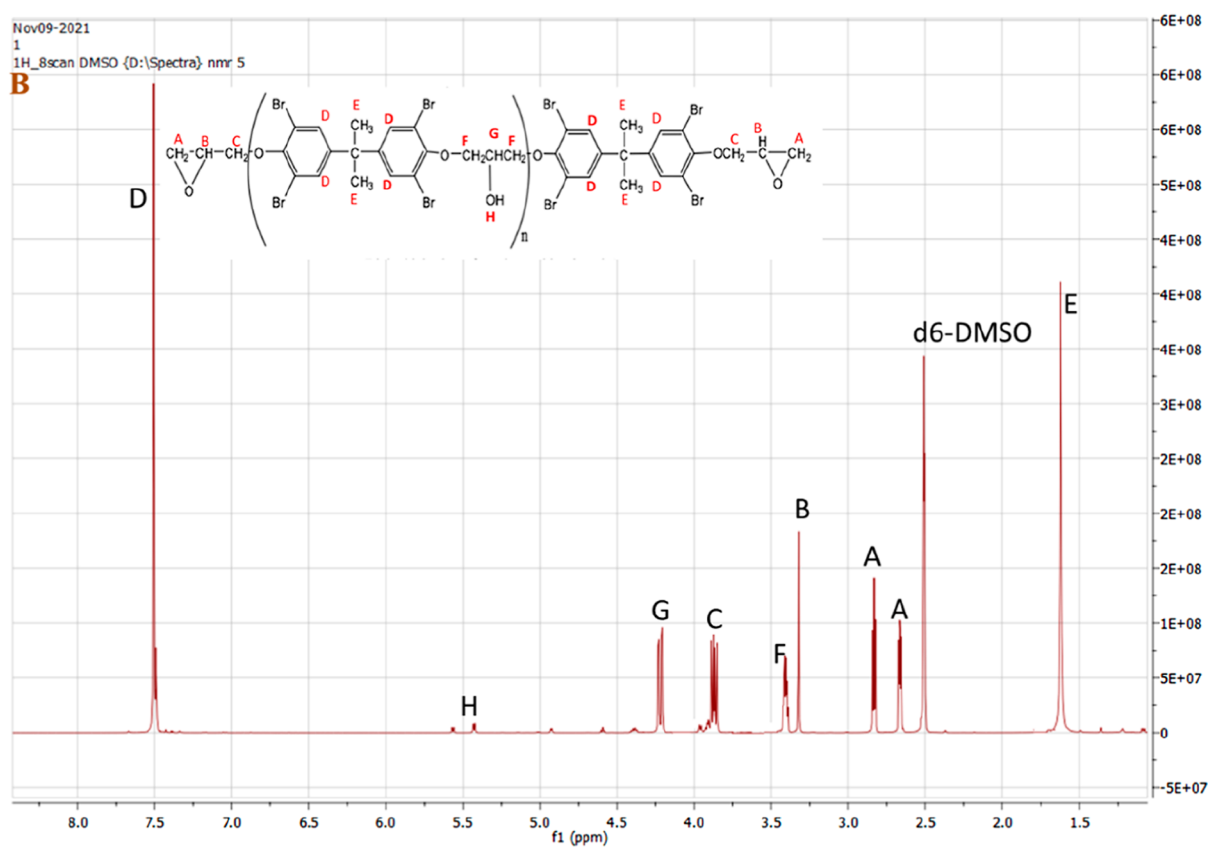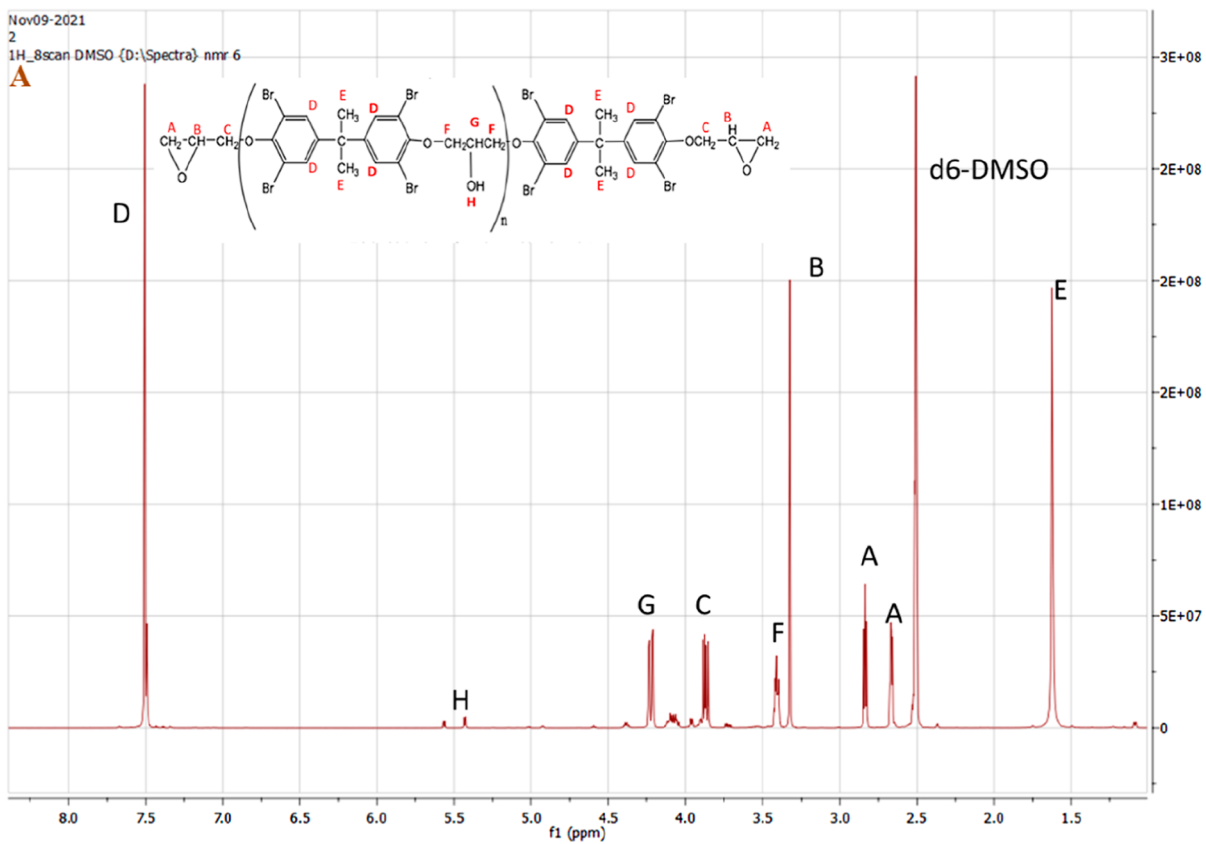
Figure 3. ^{1}H NMR spectra of TBBPA epoxy resins synthesized by the conventional method (A) and nonconventional method, sonication (B).
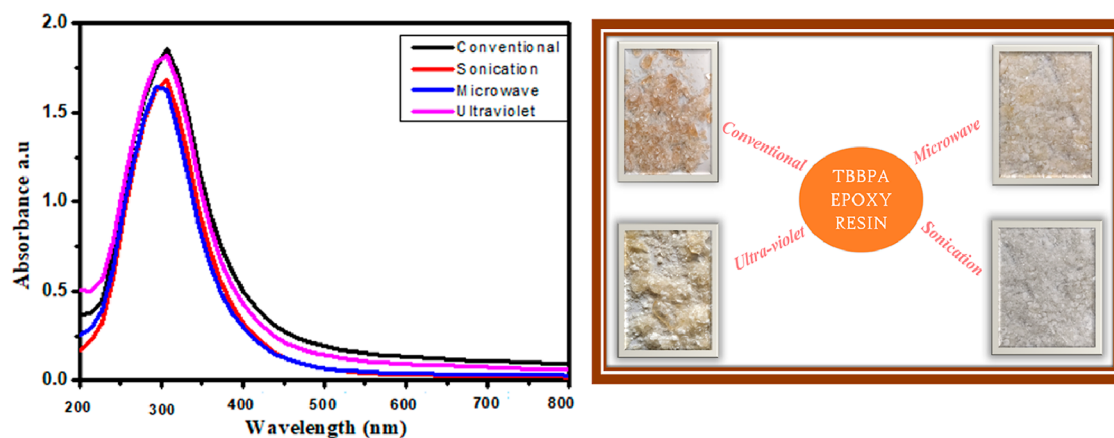
Figure 4. UV−visible absorption spectra and the transparency of the resins synthesized by different methods: C: conventional method, S: sonication, UV: ultraviolet irradiation, and M: microwave irradiation.

synthetic routes depict similar spectral features and the transparency of all the resins was not affected by the method of synthesis; thus, all possess the same transparency.[59] The powder X-ray diffraction (XRD) patterns of washed and vacuum-dried resins synthesized by different methods are depicted in Figure 5, and from the diffraction patterns of these samples, the amorphous nature of the material stands confirmed with a broad hump observed in all the samples at about 23°.[60]
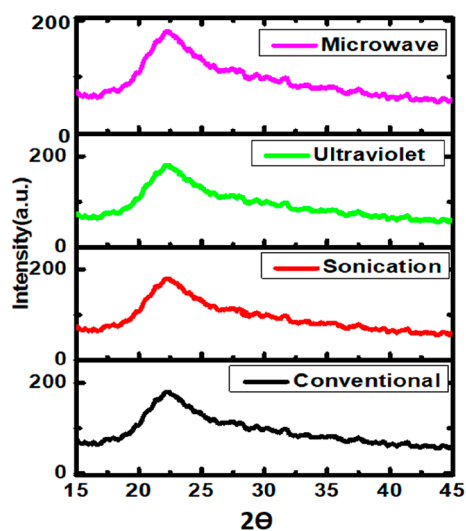

Figure 5. XRD patterns of the TBBPA epoxy resins synthesized by different methods.

2.6. Morphological Analysis. The field-emission scanning electron microscopic investigation of the halogenated epoxy resin (TBBPA) synthesized by four different methods was made by [field-emission scanning electron microscopy (FE-SEM), Hitachi-S-3600N] to monitor the surface morphology and roughness of the synthesized resins. It can be easily manifested that under ultrasonication, the TBBPA develops the resin with a smooth surface and well-defined edges (Figure 6B), which otherwise is absent in case of the conventional method (Figure 6A). More interestingly, under microwave irradiation, TBBPA develops into a morphology with visible cracks as is clearly seen from the FE-SEM micrographs depicted in Figure 6C. Based on these observations, it is found
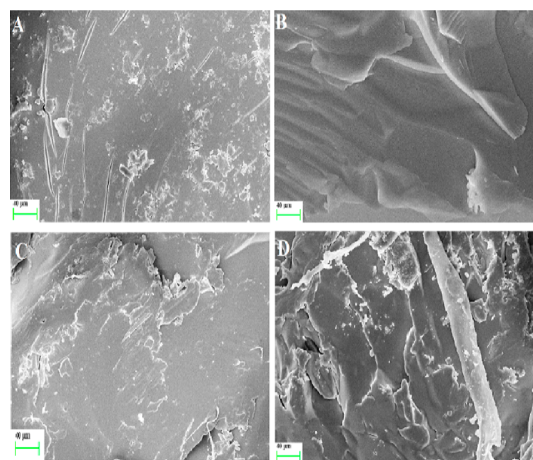

Figure 6. FE-SEM images of the resin synthesized by different methods: conventional method (A), sonication (B), microwave irradiation (C), and UV light exposure (D).

that the method of synthesis influences the surface morphology of the resin. Based on this, it is seen that the resin synthesized by the sonication method shows a better morphology as compared to the materials synthesized by other methods.[61] We also carried out energy-dispersive X-ray spectrometry (EDX) studies for all the samples of the TBBPA resin. The EDX spectra shown in Figure 7 infer that the resin can be successfully synthesized by any of the procedures; however,
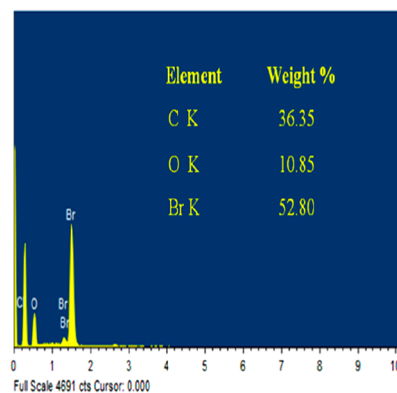

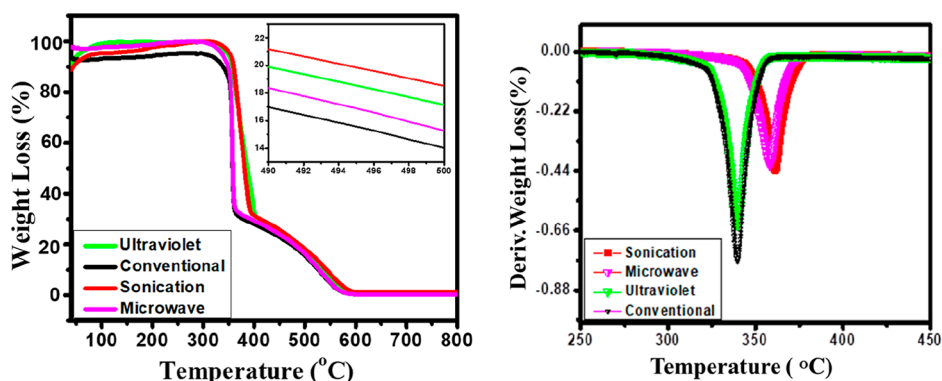**Figure 7.** EDX spectra of the TBBPA resin.

Figure 8. TG and differential thermal analysis thermograms of the TBBPA epoxy resins.
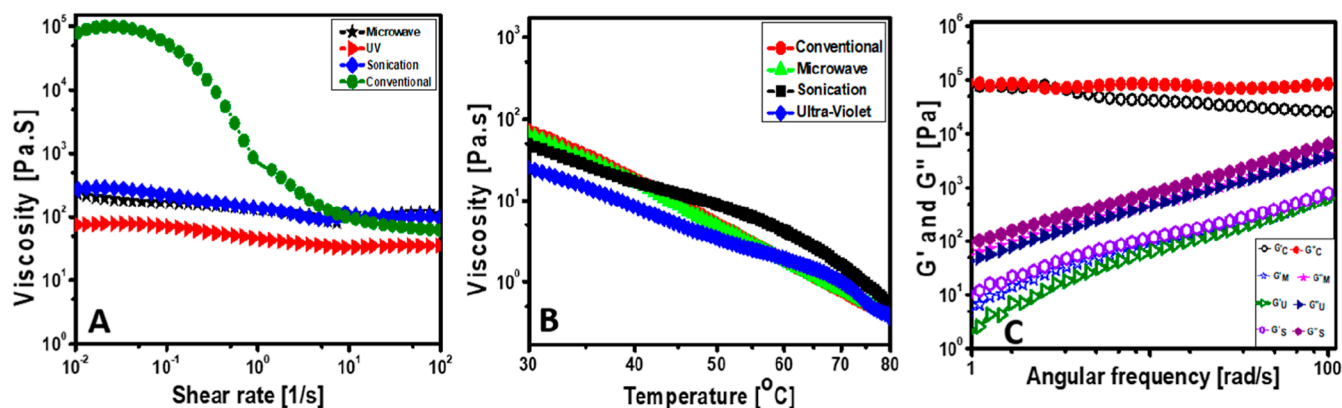

Figure 9. (A) Steady shear viscosity as a function of the shear rate, (B) steady shear viscosity as a function of temperature, and (C) dynamic shear moduli (G' and G'') as a function of the angular frequency measured at 25 °C for the TBBPA epoxy resin synthesized by different methods.

the sonication method offers better morphological control on the TBBPA epoxy polymer. Moreover, the EDX spectra do not show any peak due to impurities, which stands as a testimony to the purity of the synthesized TBBPA resin.

2.7. Thermal Analysis. The thermal properties of the synthesized resins were evaluated using a simultaneous thermal analyzer (STA) (Linseis, Germany). The technique has a lot of significance for the quick evaluation of different resins and polymers. The thermal degradation behavior of all the synthesized samples is depicted in Figure 8, and it was found that the synthesized samples show an almost identical degradation behavior, but the resin synthesized by the sonication method exhibits slightly higher thermal stability than that of the resins synthesized by the other methods. The change in thermal stability can be due to the strong bonding of the molecules within the resin and the difference in their molecular weights. The thermal degradation process of all epoxy resins has three major steps.[62] For example, the resin synthesized by the nonconventional method starts decomposing approximately at 340 °C with a maximum rate at 350−390 °C (first step), followed by a slow weight loss in the temperature region at 390−495 °C (second step), and then a quick weight loss occurs in the temperature region at 495−600 °C (third step). In the first step of degradation, the weight loss of the resin is approximately 65.9%, which is caused by the elimination process of hydrogen bromide, bromine, and thermal cracking of the oligomer molecules into low-molecular-weight fragments.[50] In the second stage of degradation, a weight loss of 12.8 % is observed and the results are manifested to the unreacted monomer and the

phenoxy group.[63,64] The final weight loss of 19.7% is mainly due to the oxidation of oligomer molecules and elimination of residual bromine.[50]

2.8. Rheology and Molecular Mass of the Synthesized Resin. The rheological behavior of resins is essential in understanding the processability and structure−property relationships, which has a significance to its industrial applications.[65−67] The rheology of the resin depends upon various factors such as molecular weight distribution, monomer distribution, molecular weight of the material, presence of hydrophilic and hydrophobic functional groups, and macrostructure of the chains.[68] The rheological properties of the resins synthesized by different methods were evaluated from the flow curves taken at 25 °C. The resin synthesized by the conventional method shows a higher viscosity value as compared to the resins synthesized by nonconventional methods, which can be attributed to its orderly chemical structure. The resin synthesized by the conventional method consists of macromolecules with linear structures, and their packing density can be higher. However, the viscosity value of the resin synthesized by the nonconventional method is lower, indicating the less ordered structure of the resin.[53]

Furthermore, the resin synthesized by the conventional method exhibits a non-Newtonian behavior and the resins synthesized by the nonconventional methods exhibit a Newtonian behavior. The change in the behavior of the resins may be due to their different molecular weights.[60] In the flow curve shown in Figure 9A, it is seen that the relationship between the viscosity and shear rate is approximately constant for the resin synthesized by the nonconventional methods;
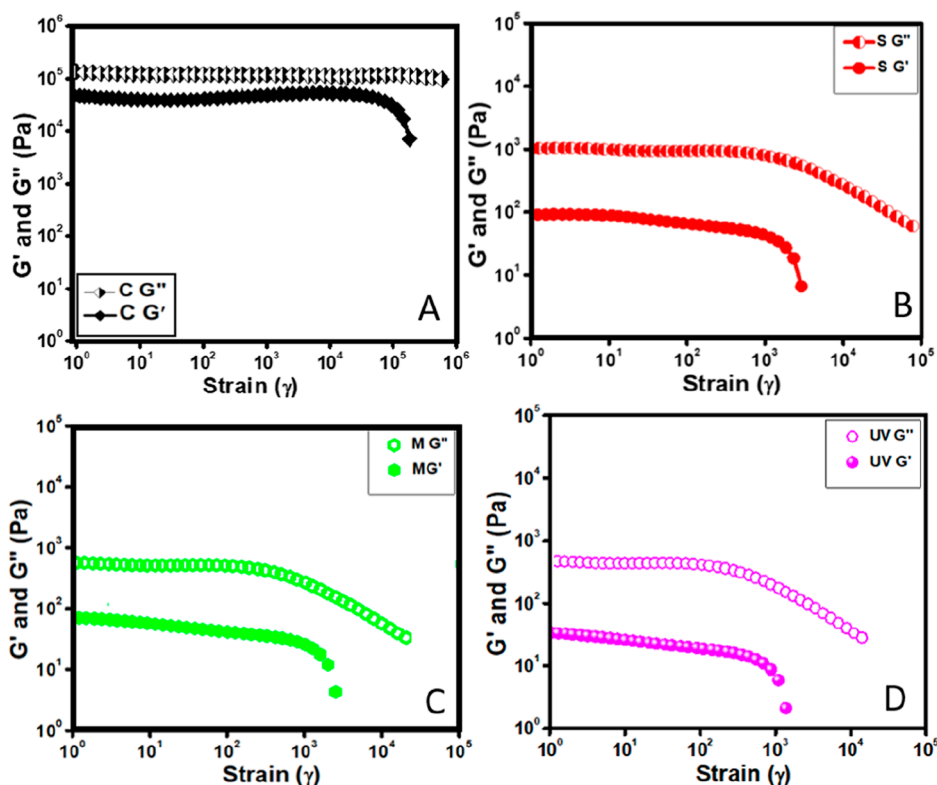
Figure 10. Amplitude sweep of the resins synthesized by different methods: conventional method (A), sonication (B), microwave irradiation (C), and ultraviolet irradiation (D).

however, shear thinning is observed at shear rates (from 10^{-2} to 10^{-1}), after which the resin attains a Newtonian behavior all over the measured frequency range. For flame retardancy, the Newtonian behavior is usually preferred. Also, it is seen in Figure 9B that the resin prepared by the sonication method (nonconventional method) possesses better resistance to decrease in viscosity at higher temperatures as compared to the resins synthesized by other methods.

The dynamic rheological behavior of the resins was also evaluated from Figure 9C, which shows the loss modulus G'' and storage modulus G' as a function of the angular frequency for resins at room temperature (25 °C), although G'' and G' are taken as descriptors of the magnitude and scaling behavior pertaining to the liquid-like and solid-like response, respectively. The resin synthesized by the sonication method exhibits higher G' values, especially at low frequencies. Furthermore, G' and G'' both increase at different rates by increasing the angular frequency.[60] The frequency dependence of storage and loss moduli of the resin synthesized by different methods is shown in Figure 9C, suggesting that the viscoelastic behavior of the resin is dominated by viscous liquid behavior[69] (as $G' < G''$ through the frequency range measured and no cross-over frequency was observed).

The mechanical strength of the synthesized resins was evaluated by the amplitude sweep test. The tests were carried out to measure the linear viscoelastic region (LVR). It is the range at which the test can be performed without destroying the structure of the samples. The results show that all of the synthesized resins indicated a much greater LVR response. This study is used to determine the mechanical strength and stability of the material. The test was carried out for the halogenated resins synthesized by conventional and non-conventional methods, and the results are shown in Figure 10.

It is clear from the figure that the resins synthesized by different methods show G'' greater than G', depicting the viscous-like behavior dominating over the solid-like behavior,[70,71] and also, the LVR regions of all the halogenated resins differ with the method of synthesis. The resin synthesized by the conventional method shows a constant G'' value (10^5) over the entire range of strain. However, in case of the resins synthesized by the nonconventional approach, it is observed that the G'' values remain constant up to the strain value of 10^3 and then decrease, and the same was observed for G' values. Thus, the mechanical strength of the resin synthesized by the conventional method is found to be more than that of the resins synthesized by the nonconventional approach.[72]

The molecular mass of the synthesized halogenated epoxy resins was determined by dynamic light scattering/particle size analysis (Anton Paar, Litesizer 500), in which the measurements were conducted at 25 °C. Three different concentrations of the synthesized resins were made using tetrahydrofuran (THF) as the solvent. It was observed that the synthesized resins possessed different numbers of repeating units owing to different routes of synthesis (Figure 11), and thus, the molecular weight of the samples synthesized by the conventional method, sonication, microwave irradiation, and under UV light differs.[73] Therefore, due to the difference in the molecular weights, the packing is affected owing to which the low-molecular-weight polymer will be less dense, and accordingly, the rheological and other properties of these materials will differ.

2.9. Water Absorption. Water absorption is a method for assessing how much water is absorbed under particular conditions. According to ASTM D570, the synthesized resin samples were dried in a vacuum oven for a specified period of time at a temperature and then kept in a desiccator to cool.
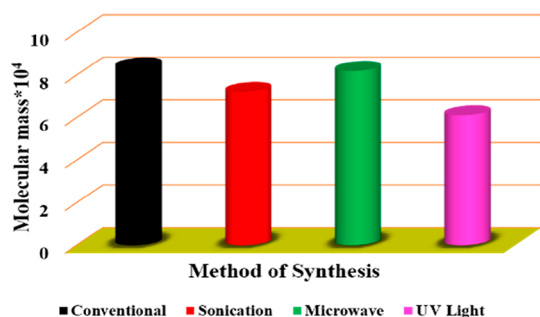
Figure 11. Molecular mass of the resins synthesized by different methods.

Figure 13. Flame test under the Bunsen burner (A) and self-extinguished specimens (B).

Immediately after cooling, the specimens were weighed. The material was then placed in water at 23 °C for 24 h to reach equilibrium. The specimens were removed, patted dry by a lint-free cloth, and then reweighed. The reweighing of these samples was carried out for 6 days after every 24 h to monitor the change in the weight. However, no gain in the weight of these samples was found until 6 days (Figure 12).

2.9.1. Flame Retardancy. The FR properties of the synthesized resins were evaluated in the lab. In this experiment, five wooden specimens were taken, out of which four were loaded with the resin and the fifth one was without the resin. On placing both the types of specimens near a Bunsen burner, it was observed that the resin-applied specimens burned momentarily and then immediately self-extinguished. However, the specimen without the resin burned to ashes, as shown in Figure 13B; therefore, the experiment confirmed the FR behavior of the synthesized halogenated resins. Thus, the synthesized DGETBBPA has a significant role as a fire suppressant in electronic and related industries.

3. CONCLUSIONS

The synthesis of a halogenated FR resin DGETBBPA was carried out by both conventional and nonconventional methods such as ultrasonication, microwave irradiation, and under UV light in order to study the comparative effect of different methods of synthesis on the physiochemical and thermomechanical behavior of the material. It was found that the nonconventional methods such as sonication and micro-wave irradiation are the novel routes of synthesizing the resin as these are environment-friendly methods and have an edge over the reported conventional method in terms of yield, time, and morphology. The resin synthesized by sonication showed a
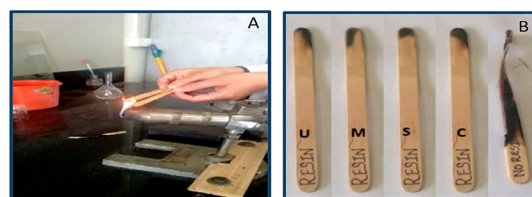
higher thermal stability, better yield (71%), and smooth surface. The synthesis was completed in 30 min as compared to the material synthesized by the conventional method which took several hours for the completion of the reaction, and it was found to be thermally less stable and had a rough and coarse surface. Moreover, the yield was also less than that of the resin synthesized by other methods. However, the resin synthesized by the conventional method showed a higher viscosity value and non-Newtonian behavior as compared to the Newtonian behavior exhibited by the resin obtained through the nonconventional methods. Based on the overall thermal, rheological, and excellent hydrophobic properties of the diglycidyl ether of TBBPA, it can serve as an excellent FR composite in the industry.

4. EXPERIMENTAL SECTION

4.1. Materials. TBBPA, 99.0% (Sigma Aldrich); ECH (Sigma-Aldrich); THF (Merck); sodium hydroxide (Merck); isopropanol (Merck); chloroform (Merck); 1,4-dioxane (Merck); 1,2-dichloromethane (Merck); methylethylketone (Merck); pyridine (Merck); N,N'-dimethylformamide (Merck); methanol (Merck); and dimethyl sulfoxide (Merck) were obtained.

4.2. Characterization. The FTIR spectra of the epoxy resins were recorded from 4000 to 400 cm^{-1} using a FTIR spectrometer (Bruker, ALPHA) using the KBr pellet method, in which 0.15% epoxy resin was mixed uniformly with almost 100−200 mg of KBr; the whole mixture was then transferred into a pellet-forming die for pellet formation. The ^{1}H NMR studies of the synthesized halogenated resins were recorded by a Fourier transform-NMR spectrophotometer (500 MHZ), AVANCE Neo (Bruker), and about 7 mg of the sample was used for the analysis. The solvent used was DMSO-d_6, and TMS was the internal standard. The XRD patterns of the synthesized resins were obtained using a D8 ADVANCE X-ray diffractometer (Bruker) with Ni filter and a Cu Kα tube. The
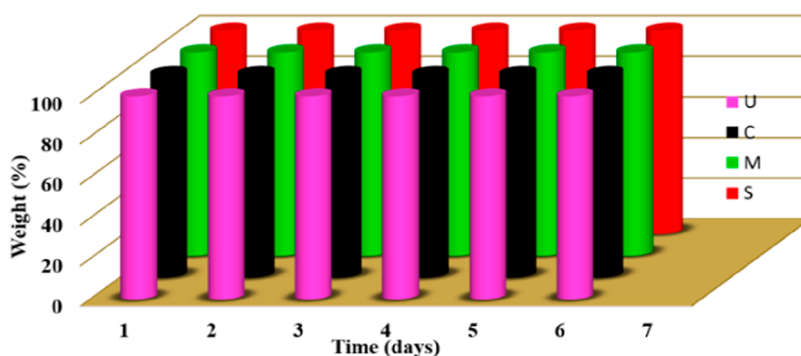

Figure 12. Water absorption graph of the TBBPA epoxy resin synthesized by different methods: C: conventional method; S: sonication; UV: ultraviolet irradiation; M: microwave irradiation.

sample's X-ray diffractogram was recorded in open quartz sample holders on an X-ray diffractometer running at known voltages and currents and employing $\lambda = 0.15406$ nm over a 2θ range from 10 to 100 in 0.01 increments at room temperature. The molecular mass of these resins was determined using a particle size analyzer (Anton Paar, Litesizer-500). The measurement was carried out at ambient temperature using three different concentrations of the resins. The transparency of the resins was measured using a UV−vis spectrophotometer (Shimadzu, UV-2600), in which barium sulfate was used as the reference, and the sample was pressed by using a glass taper at the middle of the disc and then subjected to UV−visible light for measuring the absorbance. Thermogravimetric (TG) thermograms of the synthesized materials were obtained on a STA (Linseis) in a nitrogen atmosphere at 10 °C min^{-1}. The weight change of the 10 mg sample specimen was monitored as a function of temperature, loaded on alumina crucible, and subjected to a controlled-temperature program in a controlled atmosphere. The surface morphology of the material was characterized by FE-SEM (Hitachi-S-3600N), and the elemental analysis of the resin was done by EDX operated at 200 kV using a JEM 2100F (UHR) instrument. The surface of the synthesized resins was coated with a gold layer prior to the examination. The rheological behavior of the resin was measured using a rheometer (Anton Paar, MCR102) at 25 ± 0.01 °C. All of the rheological measurements were performed by using parallel plates with 40 mm diameter, a gap distance of 1 mm, and at 25 °C (Figures 13 and 14).

Figure 14. Different forms of the resin.

4.3. Synthesis of the Halogenated FR Epoxy Resin.

The diglycidyl ether of TBBPA (DGETBBPA was synthesized by the polycondensation reaction of TBBPA with ECH in the presence of an alkali catalyst via different synthetic routes such as the conventional route, microwave irradiation, sonication, and in the presence of UV light.

4.3.1. Synthesis of DGETBBPA by the Conventional Method. The diglycidyl ether of TBBPA was synthesized according to the procedure of Rainer et al. 0.1 mol TBBPA and 0.8 mol ECH were mixed together, and the mixture was stirred at 60 °C for 5 h. The reaction was performed in a round-bottom flask acquainted with a reflux condenser, nitrogen inlet, and a thermometer. After an hour, the reaction was pursued by the continuous and steady addition of 0.2 mol of 20% NaOH with the help of a syringe for 1 h and the reaction mixture was further refluxed for another 3 h. A voluminous viscous mass appeared upon the completion of the reaction, which was washed thrice with methanol and further purified by recrystallization in the THF solvent. The yield of the desired product (DGETBBPA) was 62.4%.

4.3.2. Synthesis of DGETBBPA by the Sonication Method. The resin was synthesized by the nonconventional synthetic route using probe ultrasonication. In this method, 0.1 M TBBPA and 0.8 M ECH were dissolved in isopropanol and the reaction mixture was irradiated with ultrasonic waves using a probe sonicator (Q-Sonica). After 10 min, 0.2 mol of 20% NaOH was added dropwise to the reaction and it was allowed to proceed for another 25 min. After the completion of the reaction, the mother liquor containing the salt was decanted and the organic layer was washed by methanol several times and subsequently collected through filtration. The product obtained was viscous, and it was purified by recrystallization in THF and then dried in the oven at 80 °C for 24 h, as shown in Figure 14. The yield of the desired dried product (DGETBBPA) in the powder form was 70−73%.

4.3.3. Synthesis of DGETBBPA by Microwave Irradiation. In an archetypical procedure, TBBPA and ECH at a molar ratio of 1:8 were dissolved in isopropanol under constant stirring. After some time, 0.2 mol of 20% NaOH was added to the reaction mixture and then the said mixture was transferred to a 30 mL glass vessel specified for the microwave oven (Monowave 300, Anton Parr, USA), and the reaction mixture was irradiated by microwaves at an autogenerated pressure with a hold time of 15 min at 110 °C. The viscous product obtained was washed thrice with methanol and dried in an oven at 80 °C for 24 h. The yield of the product was 60%.

Scheme 2. Synthesis of the Diglycidyl Ether of TBBPA Epoxy Resin
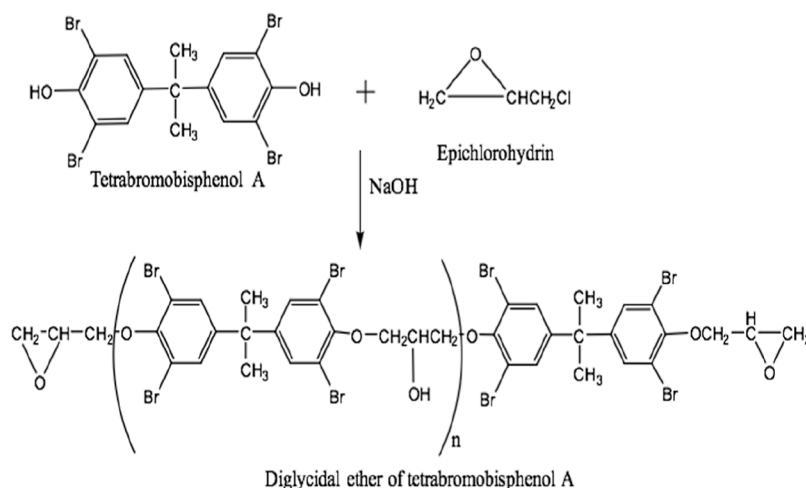
4.3.4. Synthesis of DGETBBPA by UV Radiation. In this experiment, TBBPA and ECH at a molar ratio of 1:8 were dissolved in 2-propanol under constant stirring. After some time, the reaction mixture was irradiated with UV light in a UV chamber. After 1 h, 0.2 mol of 20% NaOH was added to the reaction mixture and it was kept for another 5 h inside the UV chamber until a viscous product (resin) was obtained. The resin was purified by alcohol and eventually dried in an oven for 24 h at 80 °C, as shown in Figure 14. The yield of the resin was 54% (Scheme 2).

■ ASSOCIATED CONTENT

ⓈⒾ Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c05626.

> Stretching and vibration frequencies of different bonds and comparative account of syntheses through different routes (PDF)

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Notes
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