

Synthesis and Characterizations of Polybenzoxazines from Coal-Based Products Via Microwave and Conventional Heat Treatments

Tulay Y. İnan,¹ Birsen Y. Karaca,² H. Dogan¹

¹Chemistry Institute, TUBITAK, Marmara Research Center, 41470 Gebze, Kocaeli, Turkey

²Altçavuşoğlu Mah, Özel Cad, Hakkibey Apt, 13/5 Kartal/Istanbul, Turkey

Correspondence to: T. Y. İnan (E-mail: Tulay.Inan@tubitak.gov.tr)

ABSTRACT: About 43% clay containing humic acid (HA) was used as a phenol source for the production of polybenzoxazine composites. The use of humic acid as a phenol source from coal is the first attempt for the production of these materials. For poly(benzoxazine) precursor synthesis, solvent-less conventional and more economical and time-saving microwave heat treatments were applied. Molecular structures of the poly(benzoxazine) precursors were investigated by spectral analysis. Differential scanning calorimetry and thermal gravimetric analysis were used for the thermal characterizations. Nearly 300 and 250°C decomposition temperatures and 40 and 30% char yields were obtained at 900°C for HA-based polybenzoxazines and bisphenol-based polybenzoxazines, respectively. The morphology of the polybenzoxazines was examined by scanning electron microscopy (SEM) and X-ray analyses. The obtained results show the possibility of manufacturing the new polybenzoxazine composite materials by the method of solvent-less microwave process.

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INTRODUCTION

Novalac and resol type phenolic materials exhibit good heat-resistant, flame retardant, and dielectric properties. Thus they have been widely used in construction, household, and electrical facilities. Also these resins have inexpensive raw materials. However, there are some shortcomings like brittleness of materials, release of water and ammonia during curing process due to the condensation reactions, use of strong acids as catalyst, and poor shelf life. Also these products have significant environmental effects as well as to human health.¹ Benzoxazines (3,4-dihydro-3-substituted-1,3-benzoxazines), a new class of phenolic resins, provide a wide range of mechanical and physical properties that can be tailored to various needs. Benzoxazine-based phenolic resins are expected to yield significant advantages over many other plastic materials.

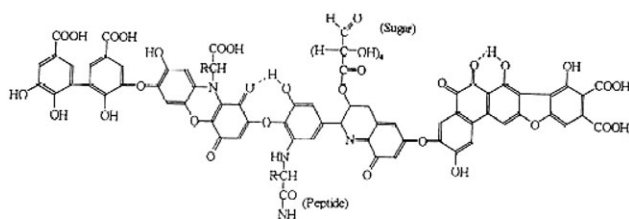
Benzoxazines can be easily synthesized from inexpensive and commercially available raw materials. The polymerization of benzoxazine monomers occurs by a simple cationic ring-opening addition reaction and does not yield any reaction by-products. Benzoxazines cure without the aid of the strong acid catalyst required by other phenolic materials.¹ Thermally accelerated polymerization is typically achieved at temperatures in the range between 160 and 220°C. At these temperatures,

gelation of multifunctional benzoxazine resins takes place in a time interval ranging from a few minutes (using initiators) to 10 min and more if no initiators are employed.^{2–7}

Humic substances are high-molecular-weight (HMW) cyclic compounds containing C, O, H, and N. In nature, humic substances are formed during complex processes from necrotic organic mass and constitute a complex of substances belonging to the polyphenol group. Humic substances can be operationally classified based on their solubility⁷; these are:

1. Humic acids (HA) are extracted from coal or soil with alkaline solutions and turn into insoluble precipitate after acidification.
2. Fulvic acids (FA) are yellowish in color and soluble both in acid and alkaline solutions.
3. Humins (H) are insoluble in acid and alkaline solutions.

Both FA and H are difficult to isolate or purify, therefore most of the studies have focused on the HA fraction. HA have complex macromolecular structures (Scheme 1); consisting of C, O, H, and sometimes small amounts of nitrogen and occasionally phosphorous and sulfur. The major functional groups in HA are carboxyl group (—COOH), phenolic, carbonyl (—C=O), and hydroxyl groups (—OH) connected with the aliphatic or aromatic carbons in the macromolecules (Scheme 1).^{7–10}



Scheme 1. Structural model of HA (Stevenson Model).⁷

The aim of this work was the development of the HA-based polybenzoxazine materials. Coal derived HA, containing ~43% inorganic materials, was directly used as a phenol source in the synthesis of poly benzoxazines and eventually, a new composite material was obtained. An economical and time-saving solvent-less process for the synthesis of the precursors was applied by conventional heat treatment, proposed by Ishida et al.⁵ and microwave heat treatment. There is a wide and continuously increasing literature available in the area of using microwave techniques in organic synthesis.¹¹ It was observed that microwave treatment provided homogeneous heating. Then, the obtained precursors were step-cured in an oven at 160 and 180°C for an hour and 200°C for 2 h. Thermal behaviors of polymers were investigated. The obtained results show the possibility of manufacturing the new composite materials by the method of solvent-less microwave process.

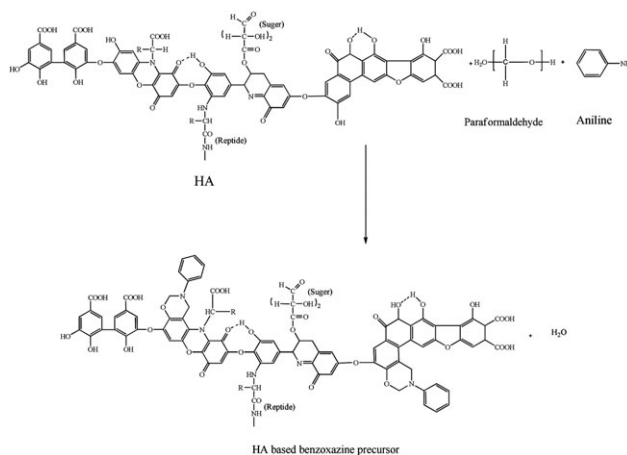
EXPERIMENTAL

Materials

The reagents including Bisphenol A (BisA, Dow Chemical Company, 99%), Paraformaldehyde, Aniline, Humic Acid (Turkish Coal Enterprises) were used as received.

Table I. Properties of Humic Acid

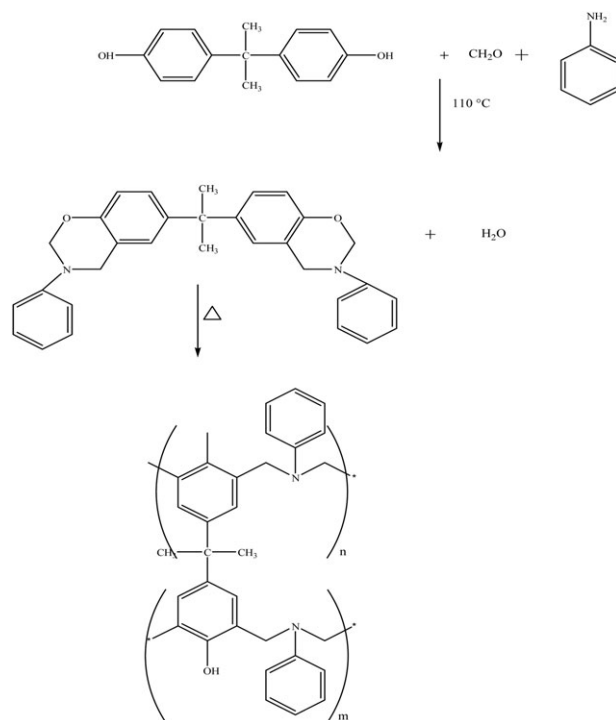
	TKI HA
Content (wt %)	
Moisture	11.8
Ash (at 950°C)	38.2
Organic matter	57.0
Inorganic matter	43.0
Humic acid	31.3
Elemental analysis (wt %)	
C	55.4
H	6.4
N	1.4
S	0.8
O	36
Functional groups (meq g ⁻¹)	
COOH	2.16
Phe-OH	6.84
Total acidity	9.0
E4/E6	3.26
Molecular weight	1075



Scheme 2. HA-Poly(benzoxazine) precursor synthesis (Poly(HA-a)).

Humic Acid Characterization

HA produced from coal by alkali extraction was obtained from Turkish Coal Enterprises (TKI). HA content was determined according to ISO 5073 (Table I). The amount of carboxylic groups and the total acidity in HA were determined using the calcium acetate and the barium hydroxide methods, respectively. Phenolic acidity was obtained by the difference between total acidity and carboxylic groups.⁷ Elemental composition (C, H, N, and S) was determined using a Thermo Finnigan Flash 1112 Series EA elemental analysis instrument. For the aromaticity of HA, E4/E6 ratio by using UV/VIS spectroscopy (the ratio of absorbances at 465 and 665 nm) for humic acid solutions was determined as 3.26. This value shows that HA used in this study has high content of aromatic groups.¹²



Scheme 3. BisA Polybenzoxazine synthetic reaction (Poly(BA-a)).

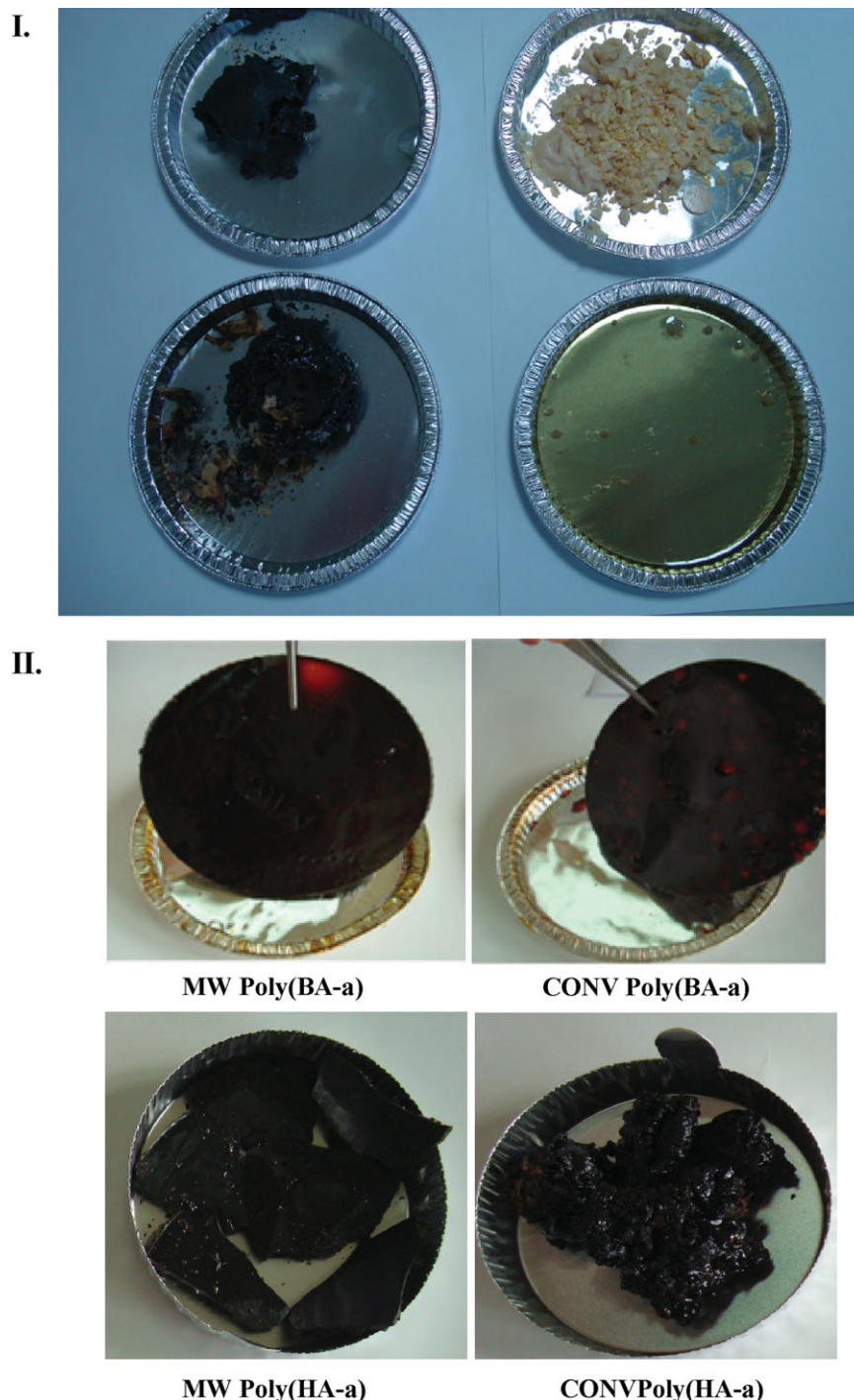


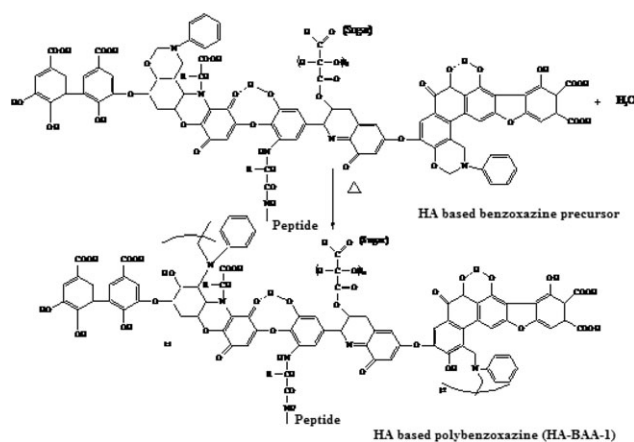
Figure 1. (I) BAAs after MW treatment with a) BisA (BA-a) and with b) HA (HA-a) (II) BAAs appearance after conventional and microwave heat treatments [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Humic acid was used without purification, and mineral analysis by X-ray diffraction (XRD) showed that the minerals kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), illite ($(\text{K}, \text{H}_3\text{O})(\text{Al}, \text{Mg}, \text{Fe})_2(\text{Si}, \text{Al})_4\text{O}_{10}[(\text{OH})_2, (\text{H}_2\text{O})]$), magnetite (Fe_3O_4), sylvite (KCl), and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) were present in the humic acid samples. The ash content of humic acid was reduced by HF/HCl treatment. The obtained pure humic acid was dissolved in 0.05M NaHCO_3 solution for

UV/VIS spectrophotometric measurements. The absorption values in the region of 270–280 nm were used for the calculation of molecular weight as described by Chin et al.¹³

Synthesis of Poly(benzoxazine) Precursors

Poly(benzoxazine) precursors (BAA) with HA were synthesized via solvent-less conventional heat process, proposed by Ishida



Scheme 4. HA-Polybenzoxazine synthetic reaction (Poly(HA-a)).

et al.¹ and solvent-less microwave heat process. The bisphenol A (BisA) based benzoxazine was also synthesized for comparison at the same conditions.

Solvent-less Conventional Heat Process

HA, aniline, and paraformaldehyde, at a 1 : 2 : 4 molar ratio, were mixed together and heated at 110°C for 60 min. until the mixture became transparent pale yellow color. The synthesis of HA based precursor is shown in Scheme 2. Same procedure is followed by using BisA as phenol source (Scheme 3). The monomer was used without further purification.

Solvent-less Microwave Heat Process

Microwave assisted reactions were conducted by using ETHOS D Microwave Labstation by Milestone equipment. Bisphenol A or HA, aniline, and paraformaldehyde, at a 1 : 2 : 4 molar ratio, were mixed in teflon container of the microwave system

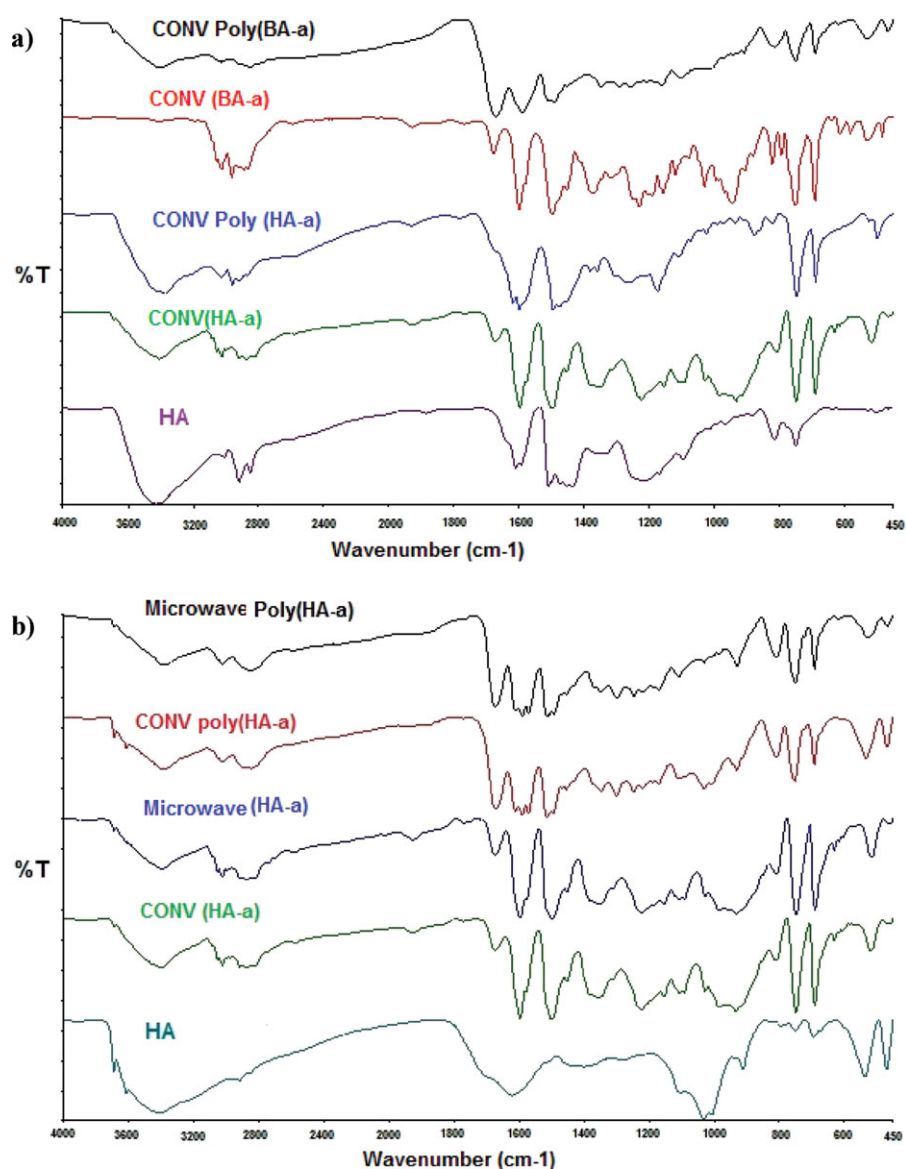


Figure 2. FTIR spectra of polybenzoxazines produced from BisA (BA-a) and HA (HA-a) by conventional and MW heat treatments. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

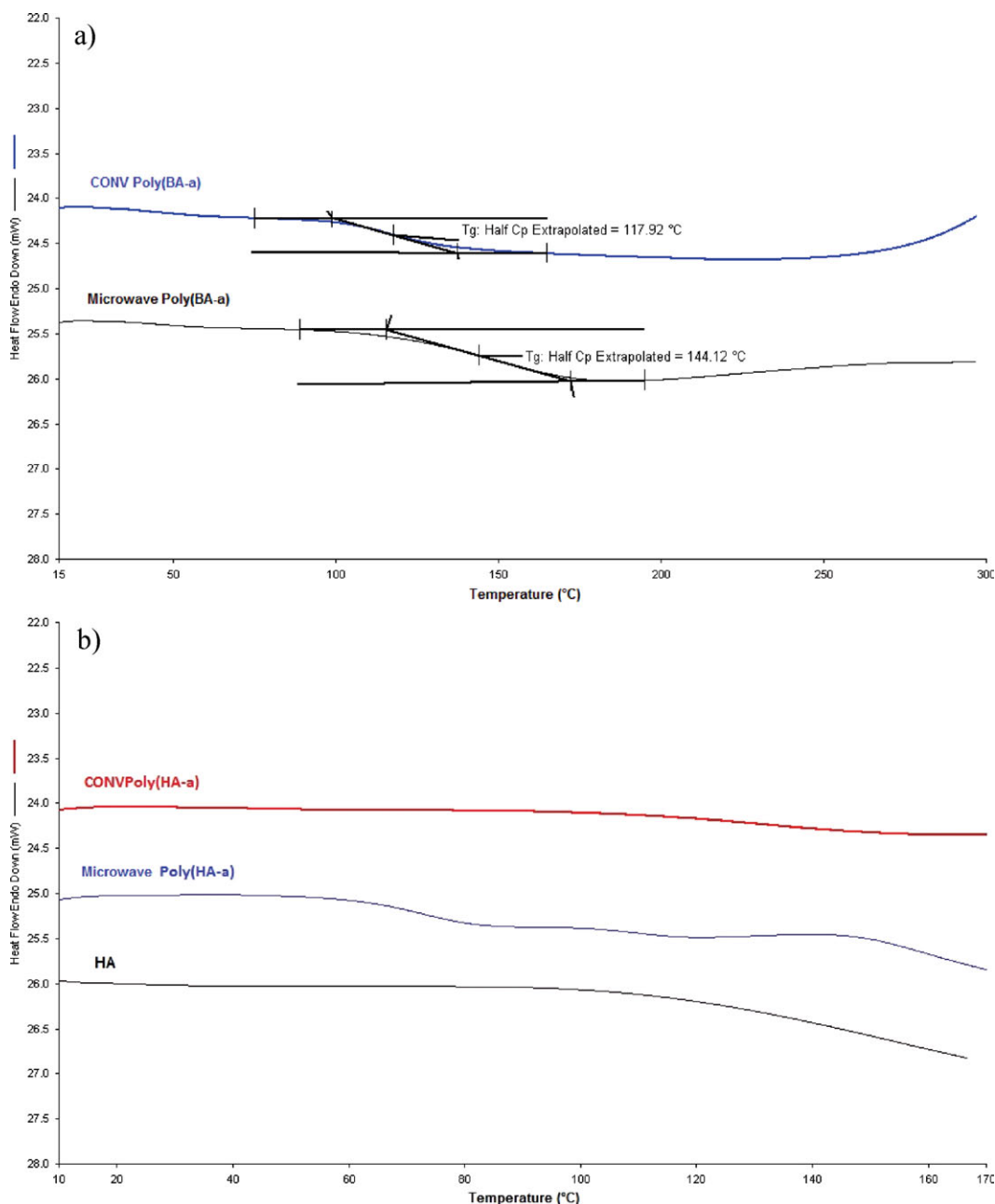


Figure 3. DSC thermograms of polybenzoxazines (a) Poly(BA-a), (b) Poly(HA-a). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

together and heated in microwave system at 120°C for 5 min until the mixture became viscous transparent pale yellow color for BisA-based precursors and viscous black color for HA precursors. Conventional and microwave heat-treated poly(benzoxazine) precursors are taken into the aluminum plates to further obtain polybenzoxazines [Figure 1(I,II)].

Preparation of the Polymeric Benzoxazines

Solvent-Less Conventional Heat Process. Benzoxazine solutions were prepared from poly(benzoxazine) precursors with BisA and HA, [Figure 1(II)].⁹ The precursor's concentrations were kept at 20 and 40%. After that, the mixtures were transferred into vials

and sealed. The temperature was slowly raised to 130°C and then held at 130°C for an additional 96 h in an oven. The attained products were partially cured by drying at ambient temperature and pressure for 2 days to remove the xylene from their matrices. They were step-cured in an oven at 160, 180°C for an hour at each temperature and 200°C for 2 h. The specimens were finally left to cool to room temperature and were then ready for further characterization [Figure 1(II)]. The synthetic reactions of polybenzoxazine from BisA and HA precursors are shown in Schemes 3 and 4, respectively. Transparent, brownish specimens were obtained for BisA-based polybenzoxazines and black specimens were obtained for HA-based polybenzoxazines as shown in Figure 1(II).

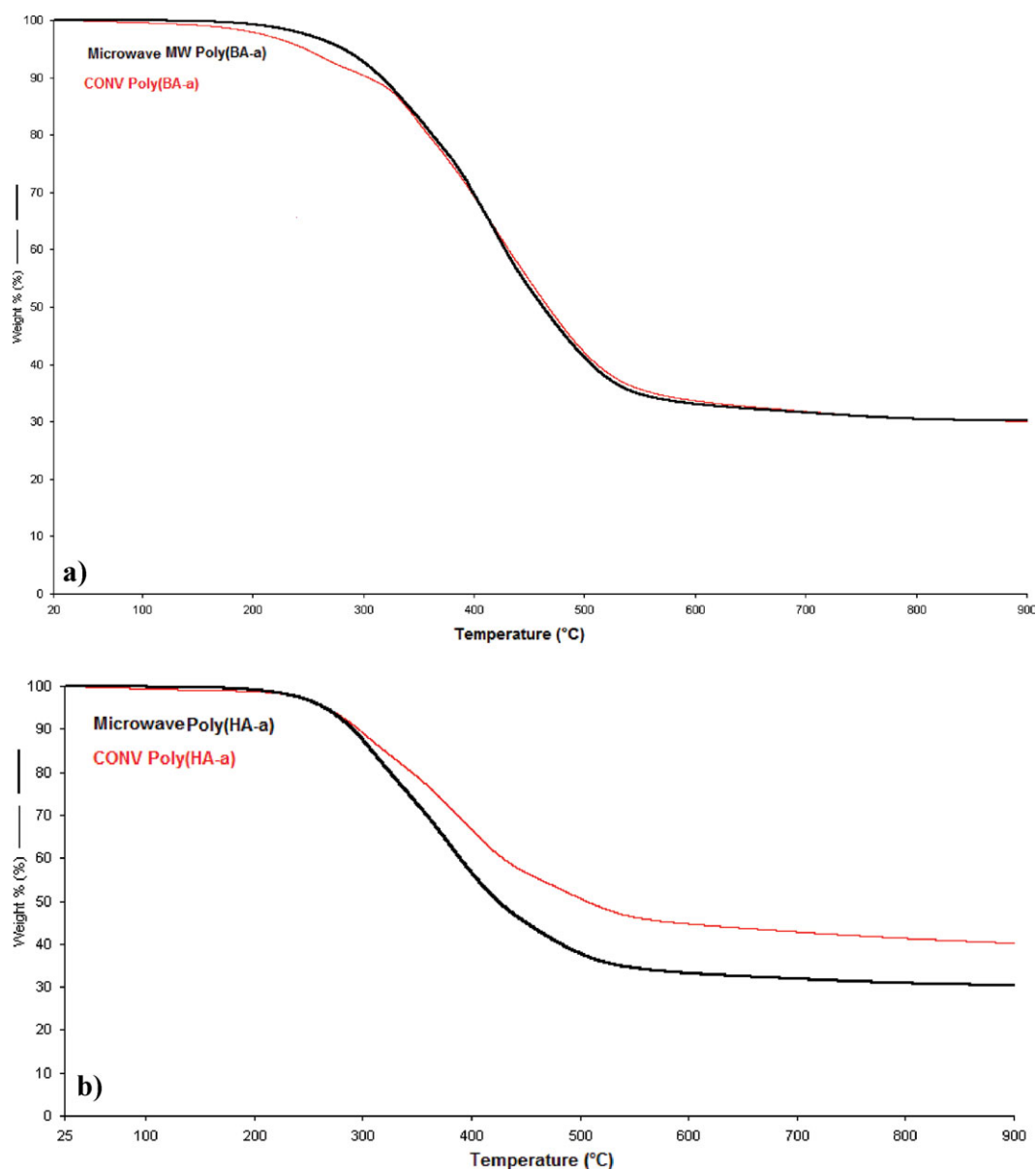


Figure 4. TGA thermograms of polybenzoxazines (a) Poly(BA-a), (b) Poly (HA-a). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The produced poly(benzoxazine) precursors and polybenzoxazines were denoted as BA-a and HA-a and Poly(BA-a) and Poly(HA-a), where BA represents bisphenol A and HA represents HA, respectively. Conventional (CONV) and microwave applications were added in front of the names.

Analytical Procedures

FTIR spectra of the KBr discs of the samples were taken by a Perkin Elmer Spectrum One FTIR spectrometer. Glass transition temperatures were determined by Perkin Elmer Pyris 1 differential scanning calorimeter (DCS). Scans were run at a heating rate of $10^{\circ}\text{C min}^{-1}$ under nitrogen purge at a rate of $30\text{ cm}^3\text{ min}^{-1}$. Reported values were obtained from a second heating after a quick cooling. Thermogravimetric analyses (TGA) were performed by Perkin Elmer Pyris 1 thermogravimetric analyzer

with a heating rate of $10^{\circ}\text{C min}^{-1}$ in air. Scanning electron micrographs (SEM) of the samples were taken with a JEOL JSM-6335 F “field emission scanning electron” microscope. Microwave-assisted reactions were conducted by using ETHOS D Microwave Labstation by Milestone. Gel content of the cured samples was determined by Soxhlet extraction for 12 h using acetone–toluene mixture (1/1, v/v). About 5 g samples were used (m_0), insoluble gel fraction was dried under vacuum for 24 h at 80°C and was weighed after drying (m_1) to calculate the gel content. The gel content w_1 was thus

$$\%w_1 = (m_1/m_0)100$$

To determine extraction time pre-experiment studies performed. For this aim, three extraction set was used. One of them

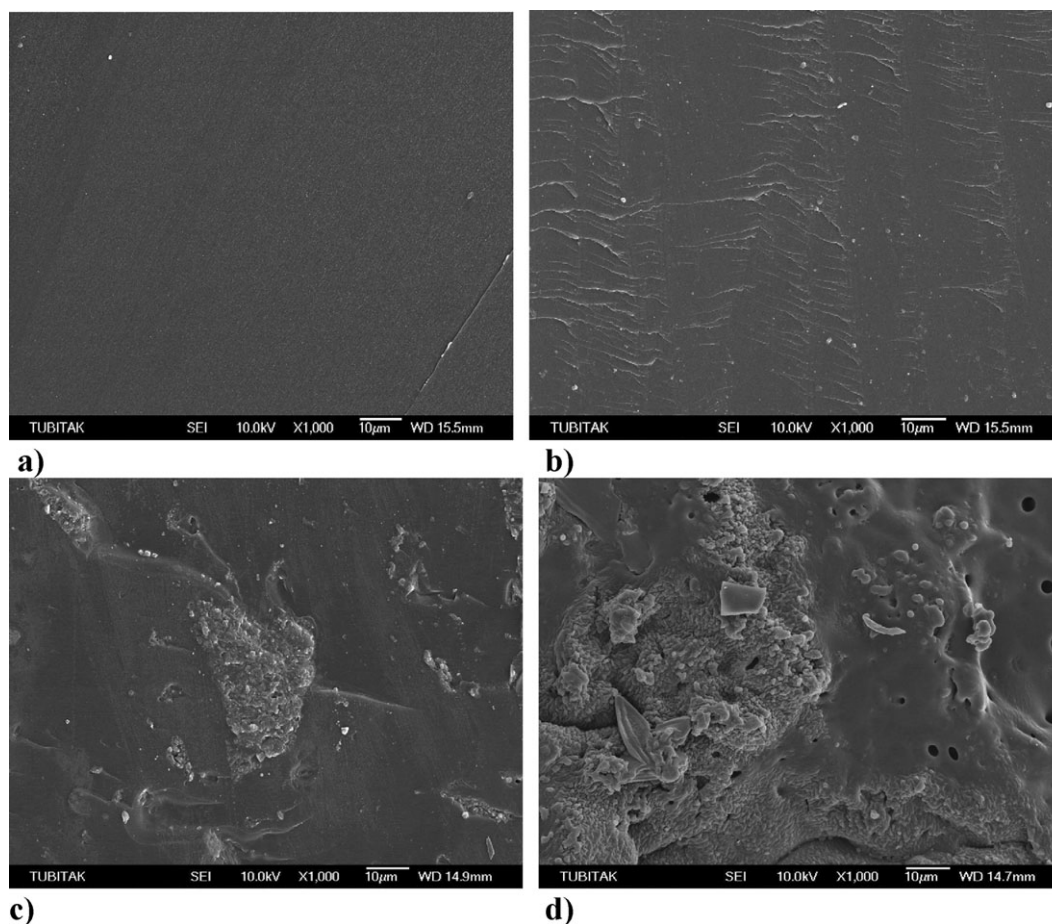


Figure 5. SEM images of polybenzoxazines (a) MWpoly(BA-a), (b) CONVPoly(BA-a), (c) MWPoly(HA-a), (d) CONVPoly(HA-a).

terminated after 6 h, the other one after 10 h and the last one ended after 12 h. Although 8-h results were very close to the 12-h extracted results, we decided to choose the extraction time as 12 h and all extractions were performed with two samples.

Samples were analyzed by X-ray diffraction (XRD, 600 SHI-MADZU). The radiation was Cu K α of wavelength 1.5405 Å.

RESULTS AND DISCUSSION

Synthesis methods of two different poly(benzoxazine) precursors have been used for the production of polybenzoxazine, namely solvent-less conventional and microwave heating process with a phenol source of BisA and renewable source of HA. Solvent-less poly(benzoxazine) precursors synthesis that was faster than a benzoxazine synthesis employing a solvent in the reaction mixture was provided. In this study, it was shown that novel microwave heating process for the synthesis of polybenzoxazine precursors was easy and relatively cheap and more efficient than the solvent-less conventional heat process. In addition, more homogeneous heating was obtained. Conventional and microwave heat-treated poly(benzoxazine) precursors are then taken into the aluminum plates to further obtain polybenzoxazines [Figure 1(II)].

The obtained precursors from two different methods were then step cured in an oven at 160, 180°C for an hour at each

temperature and 200°C for 2 h. Aldehyde and primary amine were used for the synthesis of benzoxazines and HA and BisA were used as phenol source.

FTIR spectrophotometer is one of the method for the characterization of poly(benzoxazine) precursors and polybenzoxazines. Figure 2(a,b) shows that the FTIR spectra confirmed the characteristic absorption peaks of benzoxazine structure for both bisphenol A and HA precursors (microwave (BA-a) and CONV(BA-a) and HA-a microwave (HA-a) and CONV(HA-a)) and polymers (microwavePoly(BA-a), CONVPoly(BA-a) and microwavePoly(HA-a), CONVPoly(HA-a)) at 1230–1236 cm^{-1} (asymmetric stretching of C–O–C), at 1028–1036 cm^{-1} (symmetric stretching of C–O–C), at 1327–1340 cm^{-1} (CH_2 wagging), and at 920–950 and 1491–1500 cm^{-1} (trisubstituted benzene ring). It is also seen from Figure 2(b) that in addition to the band corresponding to C–O–C oxazine ring mode at 1390 cm^{-1} and aromatic C–H stretching vibration over 3000 cm^{-1} , O–H stretching bands at 3391 cm^{-1} are also present for microwave treated samples. The presences of oligomers also show the OH band due to the phenolic groups. For the conventional solvent-less process, it was also observed that some polymerization has started before step curing procedure. Furthermore, the band at 931 cm^{-1} for the benzene ring to which oxazine ring is attached was also observed. Region of 1350–1000 cm^{-1} , arising from the CH_2 wagging mode (1327 and 1305 cm^{-1}), C–O–C

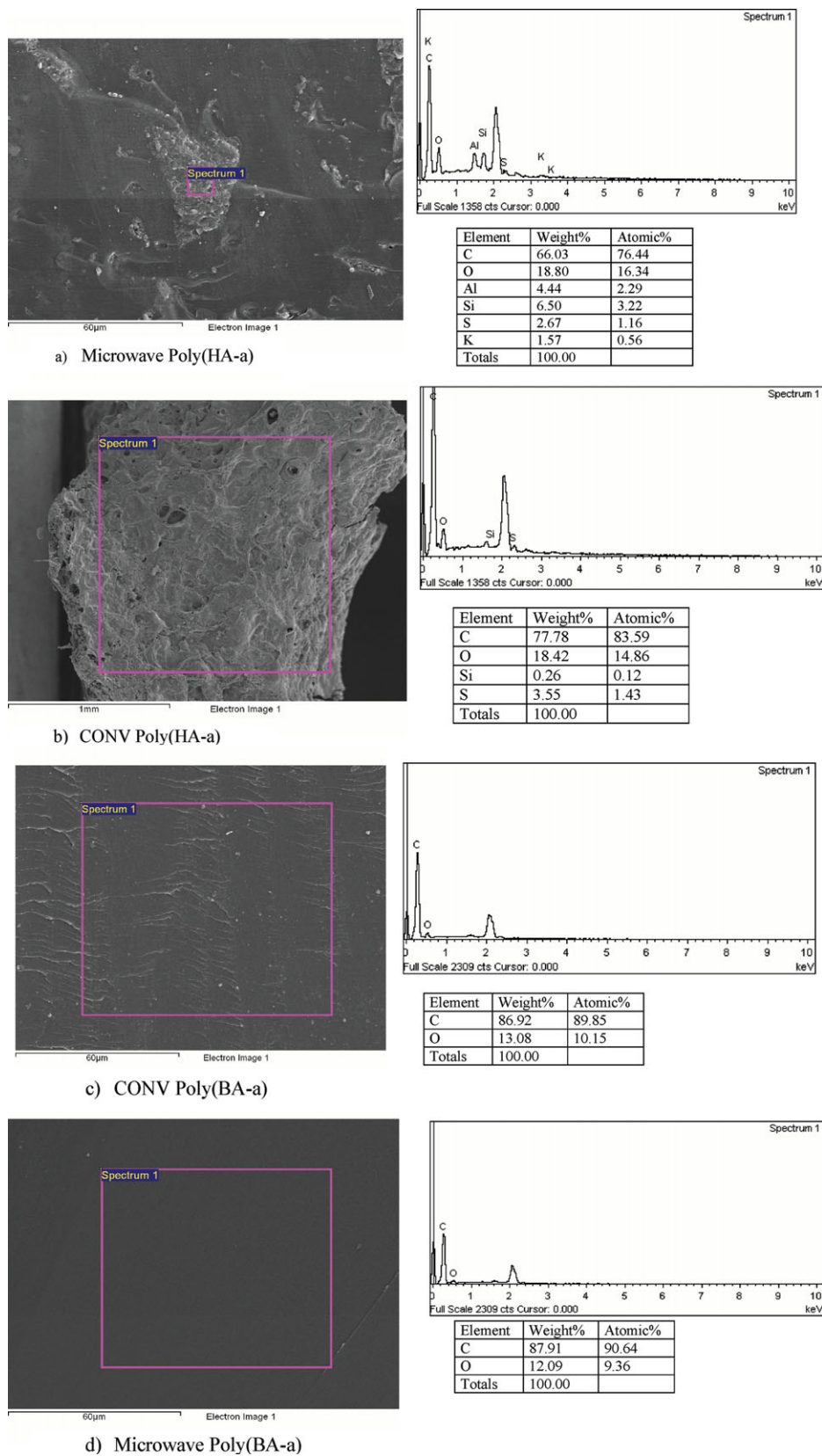


Figure 6. SEM EDS analysis results of polybenzoxazines (a) MWPoly(HA-a), (b) CONVPoly(HA-a), (c) CONVPoly(BA-a), (d) MWPoly(BA-a). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

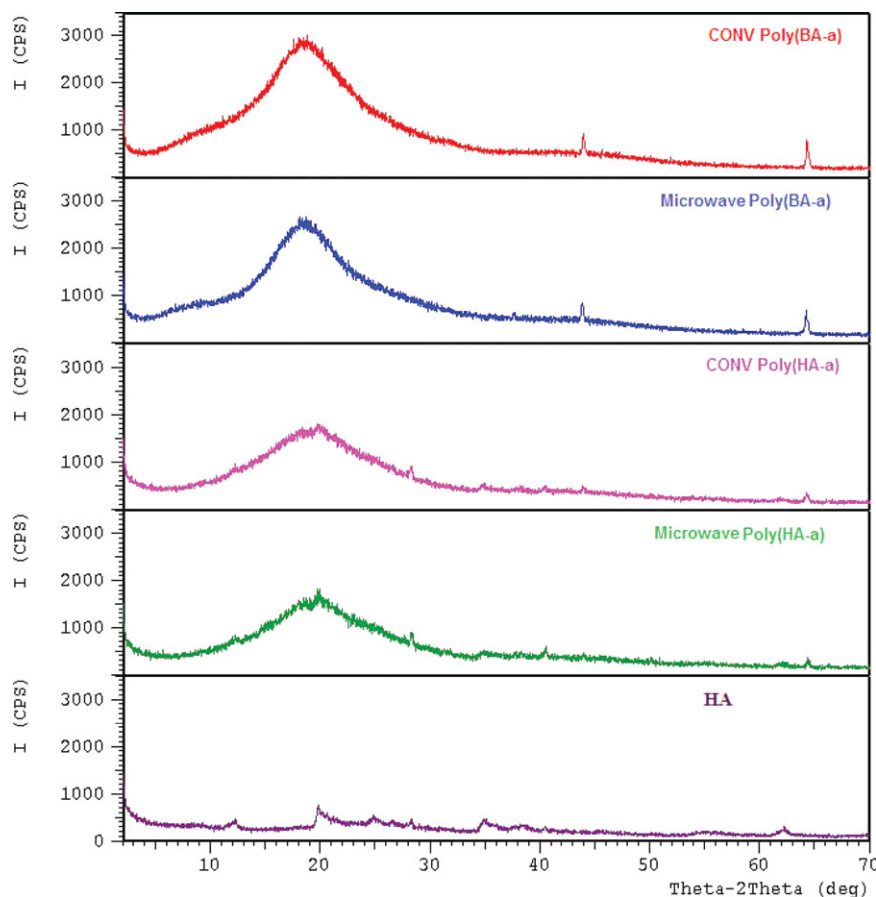


Figure 7. XRD patterns of polybenzoxazines (Poly(BA-a), Poly(HA-a), and HA). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

asymmetric stretching mode (1233 cm^{-1}), C—N—C asymmetric stretching mode (1159 cm^{-1}), and C—O—C symmetric stretching mode (1031 cm^{-1}) of the oxazine ring, as well as the decrease of the peak resolution, indicate the opening of the oxazine ring and the polymerization of the monomers into oligomers and polymers.

Insoluble inorganic structures existing in HA prevented to take ^1H NMR data for the synthesized precursors.

Gel contents of microwavePoly(BA-a) and CONVPoly(BA-a) were found to be 97.5 and 82.7%, respectively. This means that the crosslinking degree of Bis A-based resins is better for microwave heating than conventional. On the other hand, gel contents of microwave Poly(HA-a) and CONVPoly(HA-a) were obtained as 85.2 and 85.5%, respectively. The crosslinking degrees for both Poly(HA-a) samples have almost the same values. The lower crosslinking density of microwavePoly(HA-a) than microwavePoly(BA-a) may be because of the higher molecular weight and lower —OH degree of HA than BisA and non homogeneous distribution of the inorganic content of HA.

The glass transition temperatures of polybenzoxazines were measured by using DSC. As shown in Figure 3(a), T_g s of benzoxazine polymers for CONVPoly(BA-a) and microwavePoly(BA-a) were observed to be 117 and 144°C, respectively.

The T_g of CONVPoly(HA-a) [Figure 3(b)] shows well cross-linked polymer. This was attributed to the incorporation of larger molecules with inorganics that cause increase in T_g . Also pure HA starts to decompose after 100°C because of the small molecules in its structure while the others decompose later because of the crosslinked structures of the both polybenzoxazines.

A very important property of polybenzoxazine is its high thermal stability. This property along with its other prominent features such as high char yield, near zero shrinkage or even slight volumetric expansion upon polymerization provides polybenzoxazines high potential for structural applications.^{2–5} To check the thermal properties of the polymers obtained from different systems, TGA up to 900°C were performed on these polymers to test the weight loss. Microwave and conventional heat treatment applied polymers for (BA-a) gave very similar decompositions as shown in Figure 4(a). The onset degradation temperature of these polymers is almost the same (about 250°C) and char yield at 900°C under nitrogen environment is about 30%. The obtained results are parallel with the values obtained in literature.^{6,10} Microwave assisted polybenzoxazine have higher T_g and higher decomposition temperatures than conventional polybenzoxazines and gel content value for microwavePoly(BA-a) was higher than CONVPoly(BA-a) supporting this higher temperature decomposition value. The T_g of these all polymers

support the results obtained from TGA. Microwave assisted polybenzoxazines have higher T_g s. Because of the inorganic content of the HA and applied polymerization differences there are some differences for the char yields. Microwave application provides more homogeneous heat than conventional heat treatment. HA-based polybenzoxazines of Poly(HA-a) are given in Figure 4(b). The onset degradation temperatures of these polymers are almost same about 300°C^{6,10} and char yield at 900°C under nitrogen environment is about 30 and 40% for microwavePoly(HA-a) and CONVPoly(HA-a), respectively. The high char yield value and high residue percentage may show lower —OH degree of HA than BisA and non homogeneous distribution of the inorganic content of HA.

SEM micrographs of the cross-sections of the pure Poly(BA-a) systems indicate rough and glassy microstructures [Figure 5(a,b)]. This supports the brittle nature of the pure Poly(BA-a) for two systems. The micrograph of the cross section for microwave heat treated (microwavePoly(BA-a)) sample indicates more homogeneous structure than conventional heat treated sample (CONVPoly(BA-a)). Figure 5(c,d) shows SEM micrographs of the natural humic acid-based hybrid composites (microwavePoly(HA-a) and CONVPoly(HA-a)). MicrowavePoly(HA-a) shows mostly smooth and homogeneous surface morphology. However, the inorganic materials in humic acid have some agglomerated structure over the full volumes of Poly(HA-a) matrixes. Inorganic and organic phases are heterogeneous and thermodynamically immiscible due to their dissimilar structures.

SEM EDS analysis of Poly(HA-a) [Figure 6(a,b)] proved the existence of inorganic phases by showing inorganic elements of Al, Si, K, Ca, C, and O in the structure while EDS analysis of the Poly(BA-a) [Figure 6(c,d)] show only C and O elements in the structure proving the totally organic phase in the structure as expected. The unlabelled peaks at 2.122 and 2.838 are Au and Pd respectively that was used for coating samples as an Au-Pd alloy.

The structure of polybenzoxazines was also characterized by X-ray diffractogram. The pattern of humic acids shows intense peaks at ~19.84°, 20.50°, and 35.01°, as shown in Figure 7. These peaks are a reflection of the content of silica-based inorganic materials.¹⁴ The XRD spectra of the Poly(HA-a) composites exhibited the highest peak at 19.82°. All the patterns for Poly(BA-a) and Poly(HA-a) show a single amorphous halo arising from the presence of amino and benzoxazine group substitution isomers, respectively. The similar results were obtained with the literature.¹⁵

CONCLUSION

Novel composite polybenzoxazine materials were successfully prepared by using polymeric HA from renewable source of coal-based products called HA containing about 43% of inor-

ganic material including kaolin, illite, gypsum, and magnetite and Bis A by economical, time-saving solvent-less conventional and microwave heat application.

The microwave heat application is very time saving, solvent-less method for the synthesis of polybenzoxazines. The —OH sources used were BisA and novel renewable coal based HA for the production of polybenzoxazines which is a candidate as a new, cheap composite material. Conventional and microwave heat assisted model compounds of BisA-based polybenzoxazines gave higher T_g with the solvent-less microwave method than solvent-less conventional synthesis method while HA-based polybenzoxazine synthesis was more effective with the method of solvent-less conventional method. It was showed that humic acid as a phenolic source and microwave heating as alternative heating system can be used for polybenzoxazine synthesis.

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REFERENCES

- Allen, D.; Ishida, H. *J. Appl. Polym. Sci.* **2006**, *101*, 2798.
- Ning, X.; Ishida, H. *J. Polym. Sci. A Polym. Chem.* **1994**, *32*, 1121.
- Ishida, H.; Low, H. Y. *Macromolecules* **1997**, *30*, 109.
- Ishida, H.; Allen, D. *J. Polym. Sci. Polym. Phys.* **1996**, *34*, 1019.
- Hatsuo, I. Patent No WO 9,531,447, **1995**.
- Kiskan, B.; Koz, B.; Yagci, Y. *J. Polym. Sci. A Polym. Chem.* **2009**, *47*, 6955.
- Stevenson, F. J. *Humus Chemistry: Genesis, Composition, Reactions*; Wiley: New York, **1994**.
- Novák, J.; Kozler, J.; Jano, P.; Cezíková, J.; Tokarová, V.; Madronová, L. *React. Funct. Polym.* **2001**, *47*, 101.
- Erdogan, S.; Baysal, A.; Akba, O.; Hamamci, C. *Polish J. Environ. Stud.* **2007**, *16*, 671.
- Wang, Y.-X.; Ishida, H. *Polymer* **1999**, *40*, 4563.
- Caddick, S. *Tetrahedron* **1995**, *51*, 10403.
- Faustino, E.; Morán, V.; Palazzi, V. I.; Sanchez de Pinto, M. I.; Claudio, D. *Geoderma* **2009**, *151*, 61.
- Chin, Y.-P.; Aiken, G.; O'Loughlin, E. *Environ. Sci. Technol.* **1994**, *28*, 1853.
- Naidja, A.; Huang, P. M.; Anderson, D. W.; Van Kessel, C. *Appl. Spectrosc.* **2002**, *56*, 318.
- Zhang, J.; Xu, R.; Yu, D. *Eur. Polym. J.* **2007**, *43*, 743.