Advances in Materials Research, *Vol. 9, No. 4 (2020) 311-321*
DOI: https://doi.org/10.12989/amr.2020.9.4.311

Sawdust reinforced polybenzoxazine composites: Thermal and structural properties

Ravi Krishna Swami Garigipati [a] and Ramakrishna Malkapuram*

Department of Mechanical Engineering, Vignan's Foundation for Science Technology and Research, Guntur, Andhra Pradesh-522213, India

(*Received August 21, 2020, Revised November 12, 2020, Accepted December 15, 2020*)

Abstract. In this study, *Mangifera Indica* tree sawdust reinforced bisphenol-A aniline based benzoxazine composites were prepared by varying the sawdust from 20 wt% to 45 wt%. Thermogravimetric analysis of composites revealed excellent compatibility between polybenzoxazine and sawdust from the remarkable growth in char yield from 22% (neat resin) to 36% (for highly filled) and glass transition temperature from 151 to 165°C. Ultimate weight loss of the composites evaluated from the Derivatives of TG plots. Limiting oxygen index values of the composites reported considerable growth i.e., from 28 to 32 along with the increase in filler content. Differential scanning calorimetry results showed that sawdust particles have an insignificant effect on curing temperature (219°C) for the raise in sawdust content. Structure of the sawdust, benzoxazine monomer, polybenzoxazine and composites were studied using Fourier transformation infrared spectroscopy. Overall, polybenzoxazine composites with sawdust as filler showed improved thermal properties when compared with pure polybenzoxazine.

Keywords: composite material; thermal properties; structural properties; sawdust; polybenzoxazine

1. Introduction

Sawdust (SD) is the waste generated from sawmills. It is a lignocellulosic material consists of hemicellulose, lignin, and cellulose. Abundant sawdust generated from sawmills which are either landfilled or burnt which in turn causes severe air pollution. Therefore, the concept of utilization of sawdust is increasing year by year for various purposes. Sawmill industry by-products were utilized as raw material to fabricate chip-sawdust boards (Radoslaw *et al*. 2020). Sawdust can be developed as fuel and adsorbents (Ravi *et al*. 2004, Ribeiro *et al*. 2000), filler in polymers (Hisham *et al*. 2011, Felix *et al*. 2013), fertilizer (Herai *et al*. 2006). Sawdust composites used in ceiling panels because of lightweight, interior, and exterior wall decors due to thermal insulation and good soundproof properties (Kolaitis *et al*. 2014), tiles (Moslemi 1988). Sawdust in combination with polyurethane foam acts as sound-absorbent material. Superhydrophobic pellets made of sawdust were used for oil water separation (Latthe *et al*. 2020).

Sawmill waste which is obtained by cutting the *Mangiferra Indica* trees was taken as filler. Usually, sawdust is using for the preparation of wooden pallets, wooden crates, and a wooden boxes

*Corresponding author, Ph.D., Professor, E-mail: professormramakrishnaa@gmail.com
[a] Research Scholar, E-mail: grkswami1@gmail.com

http://www.techno-press.org/?journal=amr&subpage=5 ISSN: 2234-0912 (Print), 2234-179X (Online)

for the transport industry. The sawdust may utilize in the making of advanced polymer composites. Sawdust reinforced polymeric composites gained advanced materials researchers attention in the last few decades. SD can be highly filled into polymer matrices and it shows less abrasiveness, low density when compared with synthetic fibers (Bettini *et al*. 2008, Correa *et al*. 2007, Kazayawoko *et al*. 1999, Zafeiropoulos *et al*. 2002). The higher volumes of sawdust affect the viscosity of the resin. Therefore, more machine power or pressure necessary, which is difficult sometimes (Li and Wolcott 2006).

The highly filling possibility of sawdust results in higher modulus and it is a biodegradable material (Bettini *et al*. 2008, Correa *et al*. 2007, Kazayawoko *et al*. 1999, Zafeiropoulos *et al*. 2002). SD reinforced bisphenol A aniline based polybenzoxazine (BPA-PBZ/SD) composites may exhibit superior properties compared to the pristine polybenzoxazine. These composites are inexpensive and easily producible materials because sawdust is very cheap and polybenzoxazine can synthesize easily. Sawdust may available free of cost or for very minimal price. Therefore, by using sawdust as filler in polybenzoxazine composites cost of the material can reduce effectively. Applications of these composites include composite panels and wall decors due to its thermal resistance. Hence these composites may come under the category of sustainable materials.

Benzoxazine resin having excellent molecular design flexibility, near-zero volumetric change upon curing, high heat resistance, chemical resistance, low dielectric constant, excellent thermal and mechanical properties, very low melt viscosity, low flammability (Ghosh *et al*. 2007, Yagci *et al*. 2009, Ishida 2011, Ohashi and Ishida 2017, Kiskan *et al*. 2011). All these properties of polybenzoxazines leading to many applications such as electronic packaging materials, coatings, composites, and adhesives. However, disadvantages like brittleness and high curing temperatures of polybenzoxazines restrict to further applications (Kiskan *et al*. 2011). The nature of the pure polybenzoxazine resin is brittle and one method of improving the performance of polybenzoxazine is to mix with filler (Dayo *et al*. 2018a).

Rimdusit et al. reported about the para rubber and *Hevea brasiliensis* wood flour reinforced polybenzoxazine composites (Rimdusit *et al*. 2013, 2007). Thermal, Mechanical, curing behavior, weathering effect on mechanical properties and water absorption of polybenzoxazine composites reinforced with hemp fiber was reported by (Dayo *et al*. 2017, 2018b, 2020). In recent year's polybenzoxazine composites with natural reinforcements got their importance due to many applications such as corrosion resistance, water oil-separation, and sound absorption (Hariharan *et al*. 2020, Nanna *et al*. 2015). The main purpose and objective of this study is to utilize the abundantly available sawdust of mangiferra indica trees in India as reinforcement material in polybenzoxazine matrix. Moreover, this particular natural filler was not reported as reinforcement in polybenzoxazine. Therefore, in this paper, thermal and structural properties of the BPA-PBZ/SD composites evaluated. The sawdust content in the resin was varied from 20 wt% to 45 wt%. Curing of the composites took place in a vacuum oven. The raw sawdust (without any treatment) was used as filler.

2. Materials and methods

2.1 Materials

Sawdust was obtained from a local sawmill located near University. Bisphenol-A benzoxazine resin based on aniline synthesized with bisphenol–A (BPA), paraformaldehyde, and aniline. Bisphenol-A was supplied by Antares Chem Private Limited, Mumbai, India. Paraformaldehyde for synthesis 96%, aniline for synthesis 99%, and 1,4-Dioxane pure 99% was procured from Amaravathi

Scientifics and Lab equipments, Guntur, India.

2.2 Preparation of sawdust/polybenzoxazine composites

The benzoxazine material prepared in the polymer composite lab, using BPA, Aniline, and paraformaldehyde at a stoichiometric molar ratio of 1:2:4 (Ohashi and Ishida 2017). The collected sawdust which is the dust obtained while sawing *Mangifera Indica* tree, sieved with 450 mesh size to maintain orderly particles and dried in an oven to remove moisture at 105°C. The oven-dried sawdust used as filler.

Benzoxazine monomer which is in solid form was taken into four round bottom flasks and dioxane of appropriate proportion added to it to dissolve the Benzoxazine. The dissolving of Benzoxazine happened properly by stirring the content for 30 minutes. Sawdust of four weight ratios such as 20, 30, 40, and 45 wt% were reinforced into the benzoxazine dioxane solution in four-round bottom flasks and stirred overnight for the homogeneous mixing and thereby wetting of the filler. The mixtures were gently poured into four different Petri dishes of 100 mm dia. The Petri dishes were kept in the vacuum oven overnight at 50°C, to evaporate dioxane. The curing of the samples was carried out from 100 to 220°C at the rate of 20°C/hour and then cooled to ambient temperature. The code names of bisphenol-A aniline based benzoxazine composites filled with 20, 30, 40, and 45 wt% of sawdust are BPA-PBZ/SD 20, BPA-PBZ/SD 30, BPA-PBZ/SD 40, and BPA-PBZ/SD 45 respectively.

2.3 Thermogravimetric analysis

Degradation of the composite samples concerning temperature investigated using thermogravimetric analyzer (TGA) model Hitachi STA-7200 instrument. The samples in the range of 10 to 20 mg were heated at 20°C /min under nitrogen purging of 20 ml/min from 30 to 800° C.

2.4 DSC analysis of BPA-BZ/SD composites

Thermal transitions and curing behaviors of the unfilled and filled composites were investigated using differential scanning calorimeter (DSC) model Hitachi EXSTAR DSC-7020 instrument. The composites samples of 2 to 5 mg were sealed in aluminum pans and tested immediately from atmospheric temperature to 300° C at the rate of 10° C/min, under purging of Nitrogen at 20 ml/min.

(a) (b) (c) (d)

Fig. 1 Sawdust reinforced polybenzoxazine composites, (a) 20 wt% of SD, 80 wt% of PBZ; (b) 30 wt% of SD, 70 wt% of PBZ; (c) 40 wt% of SD, 60 wt% of PBZ; and (d) 45 wt% of SD, 55 wt% of PBZ

2.5 Fourier Transformation Infrared Spectroscopy (FTIR)

FTIR spectra of the sawdust, polybenzoxazine and composite samples were recorded from 4000 to 400 cm^{-1} on an Agilent Cary 630 FTIR spectrometer instrument.

3. Results and discussions

3.1 Thermo Gravimetric Analysis (TGA)

Thermal stability, char yield, and degradation temperature of BPA-PBZ/SD composites analyzed using thermogravimetric analysis and the supporting plots depicted in Fig. 2. The 10% and 15% weight loss temperatures (T_{10} and T_{15}), char production (Y_c), or char yield at 800°C, LOI, and T_{max} are summarized in Table 1. The composite's char yield increased with an increase in SD material, which is 22% for the neat resin and 36% for the highly filled system whereas 16% for the filler. The higher char recorded for 45 wt% of SD/PBZ composite due to higher carbon percentage of sawdust

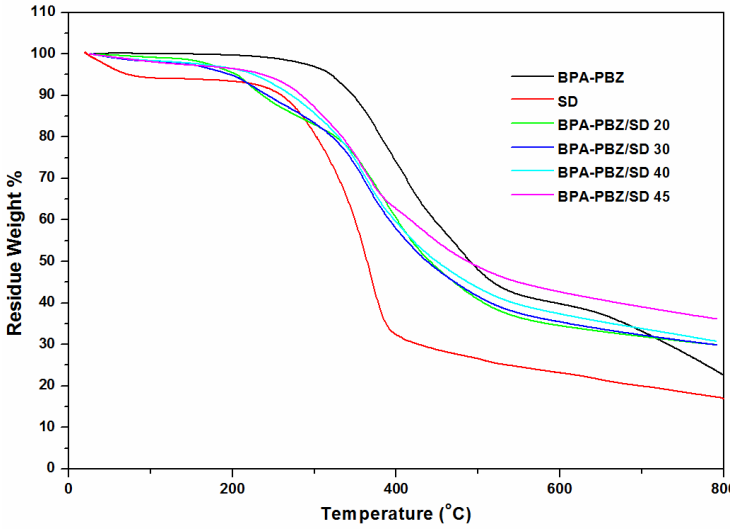

Fig. 2 TGA plots of BPA-PBZ/SD composites at various compositions and their values, PBZ, and SD

Table 1 Decomposition temperatures at 10 and 15% weight loss, char yield, LOI and maximum weight loss temperatures of BPA-PBZ/SD composites at various compositions and their values

Composite samples	T_{10} (°C)	T_{15} (°C)	Char Yield % at 800°C (Y_c)	LOI	T_{max} (°C)
BPA-PBZ	346	365	22	26.3	-
BPA-PBZ/SD20	236	278	30	29.5	380
BPA-PBZ/SD30	242	286	30	29.5	365
BPA-PBZ/SD40	272	304	31	30	364
BPA-PBZ/SD45	284	310	36	32	361
SD Particles	259	285	16	24	368

at 800°C. Sawdust and polybenzoxazine individually recorded less char yield whereas the SD/PBZ composites recorded an increase in char yield for the increase in SD content. From this, it was obvious that with the addition of sawdust char yield of the composites increasing substantially.

Derivatives of TG i.e., DTG also plotted as shown in Fig. 3. It was evident from the DTG results that maximum weight loss temperatures (T_{max}) decreased with increased filler content due to fewer degradation temperatures of cellulose filler. There was an increase in T_{max} from SD to the BPA-PBZ/SD20 due to high-temperature resistance characteristics of polybenzoxazine, but there was a fall in T_{max} of SD reinforced polybenzoxazine composites from 20 wt% to 45 wt% due to less T_{max} values of sawdust material. Limiting oxygen indices (LOI) of the composites at 800°C was calculated using the relation between LOI and char yield. i.e.

$$LOI = 0.4\ CY + 17.5 \tag{1}$$

Where CY is the char production or char yield of materials at 800°C

LOI values of the composites increased by increasing the amount of sawdust from 20% to 45%, i.e., from 29.5 to 32 whereas 26.3 for pure resin and 24 for sawdust. The increase in LOI values of composites was due to increase in char yield and raise in oxygen level for sustainable combustion along with raise in sawdust content. LOI values of these composites exhibited greater than 26, i.e., more than the self-extinguishable limit. Therefore, these materials best suited for fire risk applications.

3.2 DSC characterization of BA-a/SD composite materials

The curing behavior of polybenzoxazine in the presence of various weight ratios (20, 30, 40, and 45) of sawdust was evaluated by DSC and shown in Fig. 4**.** There was no significant variation in the curing temperature of the composites filled with various weight ratios of sawdust. The curing peaks at different sawdust content showed the curing temperature with a similar value of 219°C. For increased filler content, the energy needed to cure the composite decreases from 20 wt% to 45 wt%.

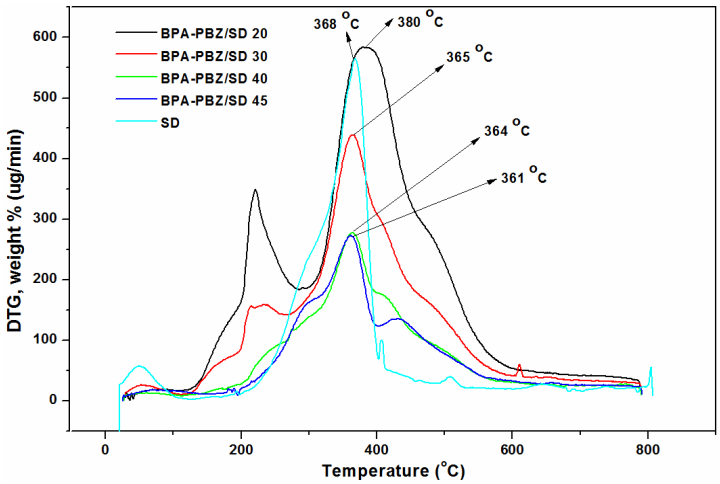

Fig. 3 DTG of sawdust and different compositions of BPA-PBZ/SD composites and their weight percentages

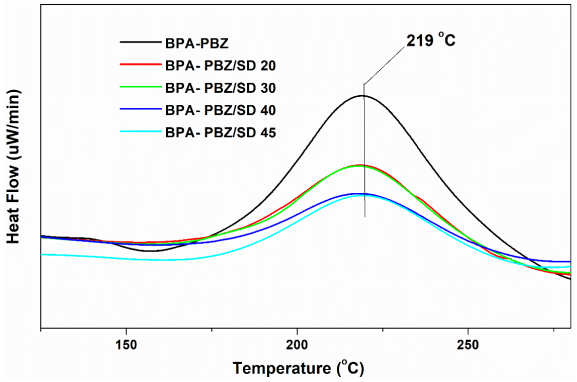

Fig. 4 DSC Thermograms of different compositions of BPA-PBZ/SD composites and their weight percentages

The composite's glass transition temperature (T_g) increased with the increase in the amount of sawdust as shown in Fig. 5. Nearly 10°C rise in T_g observed from BPA-PBZ/SD20 to BPA-PBZ/SD45, which is from 156°C to 165°C. There was no considerable change in glass transition temperature at higher loading levels of SD due to higher packing of filler. The T_g of pure BPA-PBZ was recorded at 151°C. Considerable increase in Tg was noticed from unfilled to 20, 30 and 40 wt% filled composites due to the excellent compatibility between sawdust filler and polybenzoxazine. Good interfacial adhesion was reported between the untreated SD/PBZ composite (Rimdusit *et al*. 2006). This can be attributed to the creation of a chemical bond between polybenzoxazine and SD by the formation of phenolic hydroxyl based polybenzoxazine structure by bisphenol A based benzoxazine ring-opening after heating.

3.3 Fourier Transformation Infrared Spectroscopy (FTIR)

The benzoxazine monomer structure was confirmed by FTIR. The FTIR plots of monomer and polymer were shown in Figs. 6 and 7. The characteristic absorption peak at 941 cm^{-1} indicates the oxazine ring (Dunkers and Ishida 1995). Also, 1230 cm^{-1} indicates the C-O-C asymmetric as well as

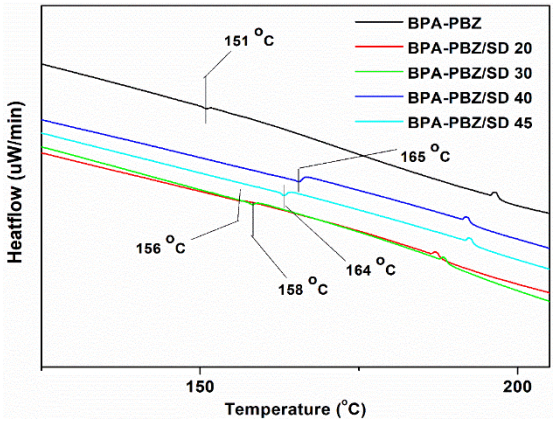

Fig. 5 DSC of BPA-PBZ/SD 20, 30, 40 and 45 wt%

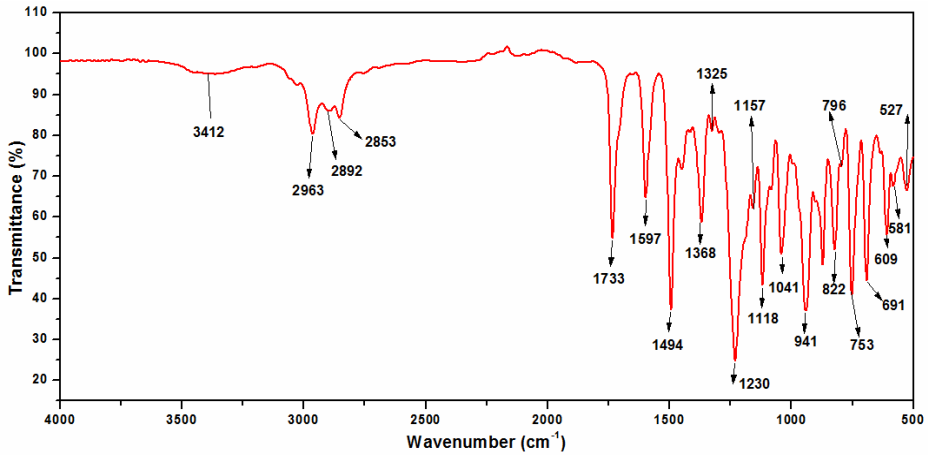

Fig. 6 FTIR of BPA aniline based benzoxazine monomer

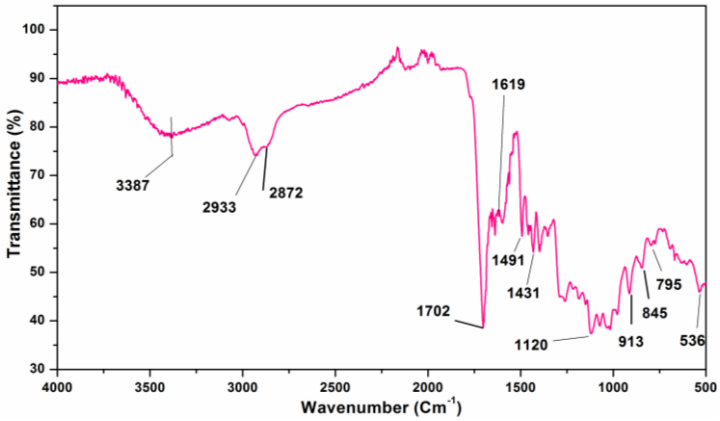

Fig. 7 FTIR of cured BPA aniline based benzoxazine

symmetric stretching vibrations. C-N-C asymmetric and symmetric stretching vibration observed at 1118-1157 cm^{-1} and around 822 cm^{-1} confirmed the structure of benzoxazine ring. The sharp and very strong bands at 1494 cm^{-1} and the bands with medium intensity at 1597 cm^{-1} correspond to the tri-substituted structure of the benzene ring with in-plane as well as the out-of-plane bending mode of C-H. The strong vibration peak at 1733 cm^{-1} correspond to C=O stretch of aldehydes. The bands at 753 and 691 cm^{-1} represent the monosubstituted benzene in the skeleton of bisphenol-A. There is an OH peak at 3412 cm^{-1}, it may due to the ring-opening mechanism of benzoxazine monomer on a small scale.

The cured benzoxazine was also analyzed by FTIR spectra. The characteristic absorption bands at 941 cm^{-1} due to the formation of benzoxazine structure, symmetric and asymmetric stretching of C-O-C, and CH_2 wagging at 1325 cm^{-1} and tri-substituted benzoxazine ring at 1494 and 822 cm^{-1} disappeared completely, due to complete opening of the ring. The strong absorption bands were due to the asymmetric stretching of the C-N-C shift around 1120 cm^{-1}. The new absorption bands visible around at 1619, 1491cm^{-1} were ascribed to intermolecular hydrogen-bonded phenolic OH and tetra-substituted benzoxazine ring (Garea *et al*. 2007, Yousefi and Lafleur 1997). These show that the

ring-opening cross-linking of the Bisphenol-A aniline based benzoxazine produced linkage of mannich bridge and phenolic hydroxyl groups.

FTIR spectra of sawdust and BPA-PBZ/SD composites

FTIR spectra of raw sawdust, 20 wt% filled and 20-45 wt% filled composites were represented in Figs. 8, 9 and 10. The FTIR spectra of the SD show the absorption bands at 3312 cm^{-1}, 2920 cm^{-1}, and 1725 cm^{-1} because of O-H, C-H, and C=O stretching vibrations. These absorption bands were because of the hydroxyl group, carbonyl group of acetyl ester, and carbonyl aldehyde groups in cellulose, hemicelluloses, and lignin respectively (Ismail *et al*. 2002). The band at 1600 cm^{-1} may be due to N–H groups in sawdust and the presence of band at 1454 cm^{-1} corresponds to deformation of –OH. The comparison of FTIR spectra of benzoxazine monomer, polymer and composites showed that 941 cm^{-1}, 1325 cm^{-1}, 1494 and 822 cm^{-1} also disappeared completely in Figs. 9 and 10 due to complete oxazine ring opening by formations of BPA-PBZ/SD composites.

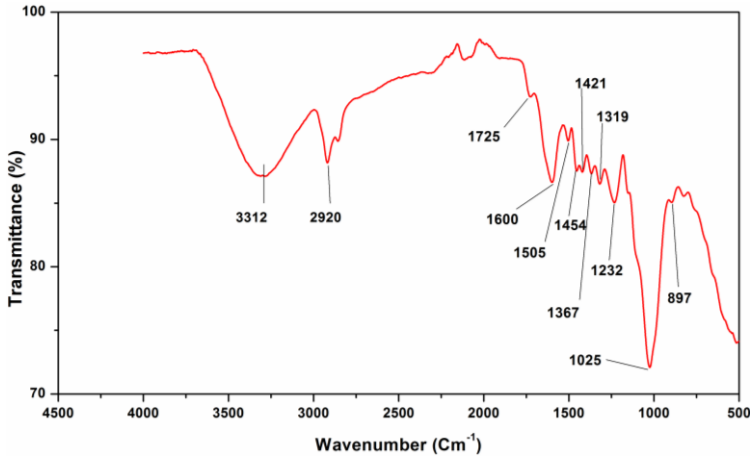

Fig. 8 FTIR spectra of raw sawdust

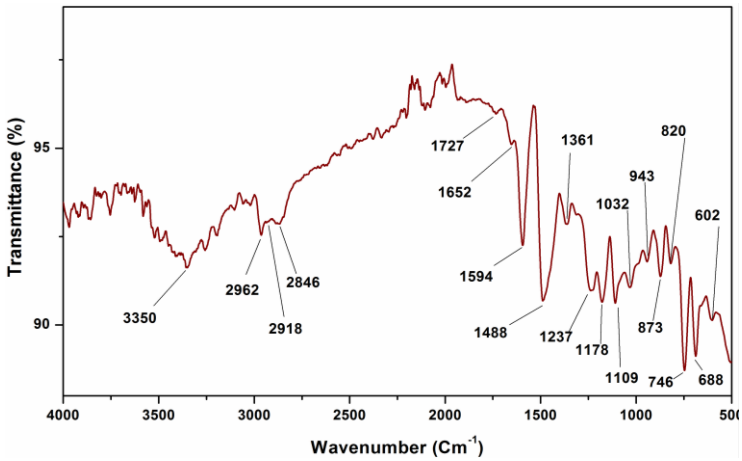

Fig. 9 FTIR of 20 wt% reinforced polybenzoxazine composite

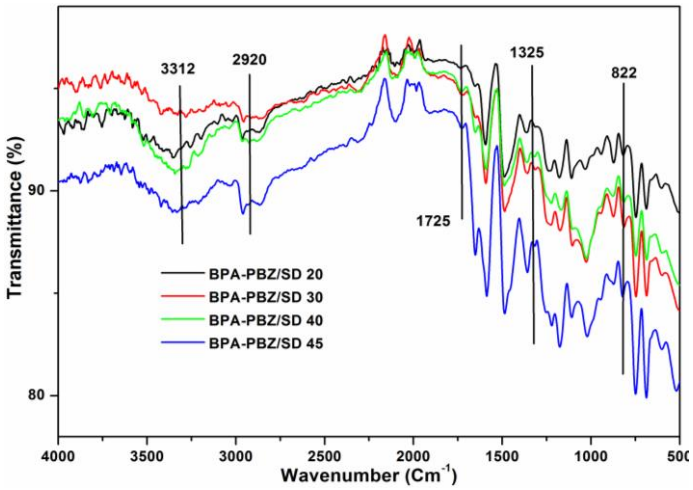

Fig. 10 FTIR Spectra of various weight ratios of sawdust reinforced polybenzoxazine composites

4. Conclusions

The preparation and properties of sawdust reinforced polybenzoxazine composites concluded as follows. The methodology and the preparation of the composite samples presented. There was no change in the curing temperature of the composites with the rise in filler content from zero to the maximum level. The T_g of the composites was found to rise with the sawdust content that is from 151°C in the case neat resin to 165°C at 45 wt% of filler. On the other hand, char yield increased with the rise in SD content that is 27% for the neat resin and 36% for the highly filled system due to higher carbon percentage of sawdust at 800°C, whereas 16% for the filler. From this, it was obvious that with the addition of sawdust char yield of the composites increasing substantially. Moreover, decomposition temperatures 10% and 15% weight loss reported. The maximum weight loss temperature of the composite materials lowered with the increase in SD content. The Limiting oxygen indices values also increased with an increase in sawdust. The structural properties of the sawdust, polybenzoxazine, and composites also analyzed and presented which gives great understanding of the composites.

Acknowledgments

The authors would like to acknowledge the funding given by management and the support given by Professors and research scholars of Chemical Engineering and Mechanical engineering departments. The Author would also like to thank the researchers/academicians those works have been cited directly or indirectly in this paper.

References

Bettini, S.H.P., Uliana, A.T. and Holzschuh, D. (2008), "Effect of process parameters and composition on mechanical, thermal, and morphological properties of polypropylene/sawdust composites", *J. Appl. Polym. Sci.*, **108**(4)**,** 2233-2241. https://doi.org/10.1002/app.27867

Correa, C.A., Razzino, C.A. and Hage, E. (2007), "Role of maleated coupling agents on the interface adhesion of polypropylene–wood composites", *J. Thermoplast. Compos. Mater.*, **20**(3), 323-339. https://doi.org/10.1177/0892705707078896

Dayo, A.Q., Gao, B.C., Wang, J., Liu, W.B., Derradji, M., Shah, A.H. and Babar, A.A. (2017), "Natural hemp fiber reinforced polybenzoxazine composites: Curing behavior, mechanical and thermal properties", *Compos. Sci. Technol.*, **144**, 114-124. https://doi.org/10.1016/j.compscitech.2017.03.024

Dayo, A.Q., Ma, R.K., Kiran, S., Zegaoui, A., Cai, W.A., Shah, A.H., Wang, J., Derradji, M. and Liu, W.B. (2018a), "Reinforcement of economical and environment friendly Acacia catechu particles for the reduction of brittleness and curing temperature of polybenzoxazine thermosets", *Compos. Part A Appl. Sci. Manuf.* **105**, 258-264. https://doi.org/10.1016/j.compositesa.2017.12.004

Dayo, A.Q., Zegaoui, A., Nizamani, A.A., Kiran, S., Wang, J., Derradji, M., Cai, W.A. and Liu, W.B. (2018b), "The influence of different chemical treatments on the hemp fiber/polybenzoxazine based green composites: Mechanical, thermal and water absorption properties", *Mater. Chem. Phys.*, **217**, 270-277. https://doi.org/10.1016/j.matchemphys.2018.06.040

Dayo, A.Q., Babar, A.A., Qin, Q.R., Kiran, S., Wang, J., Shah, A.H., Zegaoui, A., Ghouti, H.A. and Liu, W.B. (2020), "Effects of accelerated weathering on the mechanical properties of hemp fibre/ polybenzoxazine based green composites", *Compos. Part A Appl. Sci. Manuf.* **128,** 1-7. https://doi.org/10.1016/j.compositesa.2019.105653

Dunkers, J. and Ishida, H. (1995), "Vibrational assignment of N,Nbis (3,5-dimethyl-2-hydroxy-benzyl) methylamine in the fingerprint regine", *Spectrochim. Acta.*, **51**(5), 855-867. https://doi.org/10.1016/0584-8539(94)00187-G

Félix, J.S., Domeno, C. and Nerín, C. (2013), "Characterization of wood plastic composites made from landfill-derived plastic and sawdust: volatile compounds and olfactometric analysis", *Waste. Manage.*, **33**(3)**,** 645-655. https://doi.org/10.1016/j.wasman.2012.11.005

Garea, S.A., lovu, H., Nicolescu, A. and Calin, D. (2007), "Thermal polymerization of benzoxazine monomers followed by GPC, FT-IR and DETA", *Polym. Testing.*, **26**(2), 162-171. https://doi.org/10.1016/j.polymertesting.2006.09.011

Ghosh, N.N., Kiskan, B. and Yagci, Y. (2007), "Polybenzoxazines-new high performance thermosetting resins: synthesis and properties", *Prog. Polym. Sci.*, **32**(11), 1344-1391. https://doi.org/10.1016/j.progpolymsci.2007.07.002

Hariharan, A., Prabunathan, P., Kumaravel, A., Manoj, M. and Alagar, M. (2020), "Bio-based polybenzoxazine composites for oil-water separation, sound absorption and corrosion resistance applications", *Polym. Test.*, **86**, 1-23. https://doi.org/10.1016/j.polymertesting.2020.106443

Herai, Y., Kouno, K., Hashimoto, M. and Nagaoka, T. (2006), "Relationships between microbial biomass nitrogen, nitrate leaching and nitrogen uptake by corn in a compost and chemical fertilizer-amended regosol", *Soil. Sci. Plant. Nutr.* **52**(2), 186-194. https://doi.org/10.1111/j.1747-0765.2006.00031.x

Hisham, S., Faieza, A.A., Ismail, N., Sapuan, S.M. and Ibrahim, M.S. (2011), "Flexural mechanical characteristic of sawdust and chip wood filled epoxy composites", *Key Eng. Mater.*, **471**, 1064-1069. https://doi.org/10.4028/www.scientific.net/KEM.471-472.1064

Ishida, H. (2011), *Handbook of Benzoxazine Resins*, Elsevier, USA.

Ismail, H., Edyhan, M. and Wirjosentono, B. (2002), "Bamboo fibre filled natural rubber composites: the effects of filler loading and bonding agent", *Polym. Test.* **21**(2), 139-144. https://doi.org/10.1016/S0142-9418(01)00060-5

Kazayawoko, M., Balatinecz, J.J. and Matuana, L.M. (1999), "Surface modification and adhesion mechanisms in wood fiber polypropylene composites", *J. Mater. Sci.*, **34**, 6189-6199. https://doi.org/10.1023/A:1004790409158

Kiskan, B., Ghosh, N.N. and Yagci, Y. (2011), "Polybenzoxazine-based composites as high performance materials", Polym. Int., **60**(2), 167-177. https://doi.org/10.1002/pi.2961

Kolaitis, D.I., Asimakopoulou, E.K. and Founti, M.A. (2014), "Fire protection of light and massive timber elements using gypsum plaster boards and wood based panels: a large-scale compartment fire test", *Constr. Build. Mater.* **73**, 163-170. https://doi.org/10.1016/j.conbuildmat.2014.09.027

Latthe, S.S., Kodag, V.S., Sutar, R.S., Bhosale, A.K., Nagappan, S., Ha, C.S., Sadasivuni, K.K., Kulal, S.R., Liu, S. and Xing, R. (2020), "Sawdust-based superhydrophobic pellets for efficient oil-water separation", *Mater. Chem. Phys.*, **243**, 1-10. https://doi.org/10.1016/j.matchemphys.2020.122634

Li, T.Q. and Wolcott, M.P. (2006), "Rheology of wood plastics melt. Part 2. Effects of lubricating systems in HDPE/maple composites", *Polym. Eng. Sci.*, **46**(4), 464-473. https://doi.org/10.1002/pen.20505

Moslemi, A. (1988), "Inorganically bonded wood composites", *Chem. Tech.*, **18**(8)**,** 504-510.

Nannan, L., Hongqiang, Y., Lei, X., Lebo, M., Zhengping, F., Yihu, S. and Hao, W. (2015), "Flame retarding and reinforcing modification of ramie/ polybenzoxazine composites by surface treatment of ramie fabric", *Compos. Sci. Technol.*, **121**, 82-88. https://doi.org/10.1016/j.compscitech.2015.07.013

Ohashi, S. and Ishida, H. (2017), *Advanced and Emerging Polybenzoxazine Science and Technology*, Elsevier, USA.

Radoslaw, M., Dorota, D., Adam, D., Rafal, C. and Dorota, D. (2020), "By-Products of sawmill industry as raw materials for manufacture of chip-sawdust boards", *J. Build. Eng.*, **32**(1), 1-26. https://doi.org/10.1016/j.jobe.2020.101460

Ravi, M.R., Jhalani, A. Sinha, S. and Anjan, R. (2004), "Development of a semi-empirical model for pyrolysis of an annular sawdust bed", *J. Anal. Appl. Pyrol.*, **71**(1), 353-374. https://doi.org/10.1016/S0165-2370(03)00102-5

Ribeiro, A.B., Mateus, E.P., Ottosen, L.M. and Nielsen, G.B. (2000), "Electrodialytic removal of Cu, Cr, and As from chromated copper arsenate-treated timber waste", *Environ. Sci. Technol.*, **34**(5), 784-788. https://doi.org/10.1021/es990442e

Rimdusit, S., Tanthapanichakoon, W. and Jubsilp, C. (2006), "High performance wood composites from highly filled polybenzoxazine", *J. Appl. Polym. Sci.*, **99**(3), 1240-1253. https://doi.org/10.1002/app.22607

Rimdusit, S., Kampangsaeree, N., Tanthapanichakoon, W., Takeichi, T. and Suppakarn, N. (2007), "Development of wood-substituted composites from highly filled polybenzoxazine–phenolic novolac alloys", *Polym. Eng. Sci.*, **47**(2), 140-149. https://doi.org/10.1002/pen.20683

Rimdusit, S., Jubsilp, C. and Tiptipakoran, S. (2013), *Alloys and Composites of Polybenzoxazines*, Springer, Singapore.

Tiuc, A.E., Nemeş, O., Vermeşan, H. and Toma, A.C. (2019), "New sound absorbent composite materials based on sawdust and polyurethane foam", *Compos. B. Eng.*, **165**, 120-130. https://doi.org/10.1016/j.compositesb.2018.11.103

Yagci, Y., Kiskan, B. and Ghosh, N.N. (2009), "Recent advancement on polybenzoxazine-a newly developed high performance thermoset", *J. Polym. Sci. Part A*: *Polym. Chem.*, **47**(21), 5565-5576. https://doi.org/10.1002/pola.23597

Yousefi, A. and Lafleur, P.G. (1997), "Kinetic studies of thermoset cure reactions: a review", *Polym. Compos.*, **18**(2), 157-168. https://doi.org/10.1002/pc.10270

Zafeiropoulos, N.E., Baillie, C.A. and Hodgkinson, J.M. (2002), "Engineering and characterization of the interface in flax fibre/polypropylene composite materials. Part II. The effect of surface treatments on the interface", *Composites Part A.* **33**(9), 1185-1190. https://doi.org/10.1016/S1359-835X(02)00088-X

CC