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Heat-resistant and robust biobased benzoxazine resins developed with a green

synthesis strategy

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Fig. S1 HRM (ESI⁺) spectrum of IE-apa.



Fig. S2 HRM (ESI⁺) spectrum of V-apa.

Raw materials for synthesizing	Solvent	τ	τ.,	Storage	Tensile	Tensile	Elongation	
henzovazine monomer		(°C) ^a	/oc)d	Modulus	Strengt	modulus	at break	Ref
benzokazine monomen			(*C)*	(GPa) ^e	h (MPa)	(GPa)	(%)	
lessurenel 2 aminenhendesetulene	Nene	202h	205	2 00	66.7	2.20	5.16	This work
isoeugenoi, s-aninophenyiacetyiene	None	295~	395	5.69	±2.2	±0.12	±0.2	THIS WOLK
Vanillin 2 aminanhanylaastulana	None 304 ^b	202	2.65	59.0	1.89	3.98	This work	
vaniiin, 3-aminophenylacetylene		3045	393	3.65	±3.2	±0.18	±0.2	THIS WULK
Guaiacol, furfurylamine	None	82	329	NR	NR	NR	NR	S1
Guaiacol, stearylamine	None	148	352	NR	NR	NR	NR	S1
Arbutin, furfurylamine	None	190	NR	NR	NR	NR	NR	S2
Guaiacol, dehydroabietylamine	Dioxane	124	321	NR	NR	NR	NR	S3
4-methylumbelliferone,	Diavana	207	262	ND	ND	ND	ND	63
dehydroabietylamine	Dioxane	207	362	NK	INK	INK	INK	53
Sesamol, furfurylamine	Ethanol or ethyl acetate	NRc	374	NR	NR	NR	NR	S4
Eugenal stearylamine	None	101	313 Around 2.60	Around ^f	ND	NR	NR	55
Eugenoi, stear yiannie		101		212	2.60	INIX	IND	INIX
Eugenol furfurvlamine	None	1/18	361	Around	NR	NR	ND	55
	None	140	501	3.21	INIX	INIX	INIX	33
Eugenol, furfurylamine	None	183 ^b	338	NR	NR	NR	NR	S6
Isoeugenol, furfurylamine	None	179 ^b	375	NR	NR	NR	NR	S6
Cardanol, furfurylamine	None	NR	374	NR	NR	NR	NR	S7
Cardanol, stearylamine	None	NR	342	NR	NR	NR	NR	S7
Umbelliferone, aniline	Toluene	183	320	NR	NR	NR	NR	S8
Umbelliferone, furfurylamine	None	NR	420	NR	NR	NR	NR	S9
Eugenol, dehydroabietylamine	Dioxane	135	341	NR	NR	NR	NR	S10

Table S1 Thermal performances of biobased benzoxazine resins from mono-phenols in this work and literatures.

Eugenol, stearylamine	Dioxane	101	316	NR	NR	NR	NR	S10
Eugenol, furfurylamine	Dioxane	148	375	NR	NR	NR	NR	S10
Vanillin, furfurylamine	None	270	351	NR	NR	NR	NR	S11
Rosin, maleic anhydride, aniline	N,N-Dimethylformamide	NR	353	NR	NR	NR	NR	S12
Rosin, maleic anhydride, 4- amiobenzoic acid	N,N-Dimethylformamide	NR	321	NR	NR	NR	NR	S12
Urushiol, aniline	Dioxane	140 ^b	325	Around 0.60	15.3	0.0879	17.4	S13
Eugenol, chitosan	Dimethyl sulfoxide	135 ^b	239	Around 3.5	NR	NR	NR	S14
4-Hydroxyphenyl-10-undecenoate, 10-undecenyl amine	Tetrahydrofuran/dimethyl sulfoxide	87 ^b	317	Around 1.69	NR	NR	NR	S15
Guaiacol, aniline	Ethyl acetate/methanol/chloroform /hexane	NR	296	NR	NR	NR	NR	S16
Guaiacol, furfurylamine	Ethyl acetate/ chloroform/hexane	NR	298	NR	NR	NR	NR	S16
Guaiacol, aniline	Ethyl acetate/chloroform/hexane	NR	301	NR	NR	NR	NR	S16
Phloretic acid, stearylamine	Toluene	NR	250	NR	NR	NR	NR	S17
Phloretic acid, furfurylamine	Toluene	NR	303	NR	NR	NR	NR	S17

(a) T_q was determined by DSC with heated at a rate of 10 °C/min under a N₂ atmosphere.

(b) T_a was assigned as the temperature at the maximum of tan δ -temperature curve from DMA except otherwise stated.

(c) NR = Not reported.

(d) T_{di} is assigned as the temperature when the weight loss is 5 wt% except otherwise stated.

(e) Storage modulus was tested at 40 °C except otherwise stated.

(f) The datum was estimated from the

References

- [S1] C. Wang, J. Sun, X. Liu, A. Sudo and T. Endo, Green Chem., 2012, 14, 2799.
- [S2] L. Dumas, L. Bonnaud, M. Olivier, M. Poorteman and P. Dubois, Green Chem., 2016, 18, 4954-4960.
- [S3] X. Liu, R. Zhang, T. Li, P. Zhu and Q. Zhuang, ACS Sustain. Chem. Eng., 2017, 5, 10682-10692.
- [S4] M. L. Salum, D. Iguchi, C. R. Arza, L. Han, H. Ishida and P. Froimowicz, ACS Sustain. Chem. Eng., 2018, 6, 13096-13106.
- [S5] P. Thirukumaran, A. Shakila Parveen and M. Sarojadevi, ACS Sustain. Chem. Eng., 2014, 2, 2790-2801.
- [S6] N. Amarnath, S. Shukla and B. Lochab, ACS Sustain. Chem. Eng., 2018, 6, 15151-15161.
- [S7] P. Thirukumaran, R. Sathiyamoorthi, A. Shakila Parveen and M. Sarojadevi, *Polym. Composite.*, 2016, **37**, 573-582.
- [S8] P. Froimowicz, C. Rodriguez Arza, S. Ohashi and H. Ishida, J. Polym. Sci. Part A: Polym. Chem., 2016, 54, 1428-1435.
- [S9] P. Froimowicz, R. A. C, L. Han and H. Ishida, ChemSusChem, 2016, 9, 1921-1928.
- [S10] Y. T. Zhang, X. Y. Liu, G. Z. Zhan, Q. X. Zhuang, R. H. Zhang and J. Qian, Eur. Polym. J., 2019, 119, 477-486.
- [S11] N. K. Sini, J. Bijwe and I. K. Varma, J. Polym. Sci. Part A: Polym. Chem., 2014, 52, 7-11.
- [S12] S. Li, T. Zou, X. Liu and M. Tao, Des. Monomers. Polym., 2013, 17, 40-46.
- [S13] H. Xu, Z. Lu and G. Zhang, *RSC Adv.*, 2012, **2**, 2768-2772.
- [S14] P. Thirukumaran, A. Shakila Parveen, R. Atchudan and S.-C. Kim, Eur. Polym. J., 2018, 109, 248-256.
- [S15] A. Tüzün, G. Lligadas, J. C. Ronda, M. Galià and V. Cádiz, Eur. Polym. J., 2015, 67, 503-512.
- [S16] J. R. Oliveira, L. R. V. Kotzebue, F. W. M. Ribeiro, B. C. Mota, D. Zampieri, S. E. Mazzetto, H. Ishida and D. Lomonaco, J. Polym. Sci. Part A: Polym. Chem., 2017, 55, 3534-3544.
- [S17] R. Kirubakaran, P. Sharma, A. Manisekaran, J. Bijwe and L. Nebhani, J. Therm. Anal. Calorim, 2020, DOI: 10.1007/s10973-019-09228-y.