A fully bio-based Schiff base vitrimer with self-healing at room temperature

Lin Jiang[#], Yazhou Tian[#], Xiaomu Wang, Junying Zhang, Jue Cheng, Feng Gao**

Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

* Correspondence: Jue Cheng, Email: chengjue@mail.buct.edu.cn, Tel: +86 64425439

* Feng Gao, Email: gaofeng@mail.buct.edu.cn

#: These authors contributed equally to this work

Supporting Information:

The FDV and FCV samples were separated by HPLC (Prominence LC 20A, Shimadzu, Tokyo, Japan) with ZORBAXSB-C18 column (4.6×250 mm, 5 μm). The solution A (formic acid aqueous solution, 0.1% V/V) and B (methanol acetonitrile, 10% V/V). Samples were eluted via binary phase program which was demonstrated by Table S1. The elution velocity was set as 0.2 mL/min, the injection volume was set as 20 μL with the approximately concentration 5 mg/mL, and the wavelength of the UV detector was set as 280 nm. The temperature of the column was maintained as 30 °C during the test. The Electron Spray Ionization (ESI) was adopted with positive model with atomization pressure 1.5 Bar and atomization voltage 3500 V. The drying flow was set as 6 L/min with 180 °C. The collision energy was 10 eV, and the m/z scan rage was 50-1000. The TOF was calibrated using the sodium formate standard.

Table S1 The gradient elution program for HPLC

Time	A (%)	B (%)
0	90	10
1	90	10
5	80	20
16	80	20

Fig. S1(a) demonstrated the HRMS for FDV and SCV by HPLC-ESI-TOF. The elution time for FDV was 11.87 min. The details of the TOF characterization of the fragments from FDV peak was demonstrated by Table S2, where the FDV was abbreviated as M. The theoretical m/z ration of $[M+H]^+$ was 425.0868, and the main peak from the TOF was located at 425.0869, consistent with the prediction. The appearances of $[M+H-CO]^+$ indicated the monomer contained aldehyde groups [1]. Moreover, the $[M+H-2OCH_3+2H]^+$ peak indicated the existence of two methoxy groups [2, 3]. The fragments demonstrated by Table S2 confirmed the formation of FDV in this work.

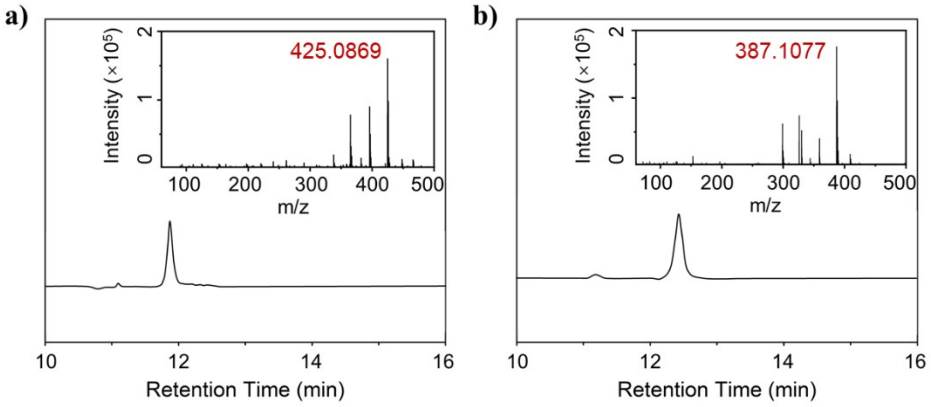

Fig. S1 The HRMS for FDV and SCV by HPLC-ESI-TOF, a) the spectrum for FDV; b) the spectrum for SCV.

Table S2 The analysis of the fragment of FDV peak.

No.	Tested m/z	Normalized intensity (1%)	Formula	Theoretical m/z	Structure
1	365.0656	43.1	$C_{20}H_{13}O_7$	365.0656	$[M+H-2OCH_3+2H]^+$
2	397.0919	54.7	$C_{21}H_{17}O_8$	397.0918	$[M+H-CO]^+$
3	425.0869	100	$C_{22}H_{17}O_9$	425.0868	$[M+H]^+$
4	447.0691	5.8	$C_{22}H_{16}O_9Na$	447.0687	$[M+Na]^+$

The HRMS spectrum for SCV was presented by Fig. S1(b), and the elution time for SCV was 12.36 min. The fragments of SCV peak were analyzed and presented in Table S3, where SCV was abbreviated as M. The result indicated the $[M+H]^+$ was 387.1077, consistent with the theoretical value which was 387.1075. The existence of $[M+H-CO]^+$ and $[M+H-CO-CHO]^+$ indicated that there were two aldehyde groups on the substance [1]. In addition, the appearance of $[M+H-CO-2OCH_3+2H]^+$ and $[M+H-2OCH_3+2H]^+$ demonstrated the existence of two methoxy groups [2, 3]. The HRMS result

confirmed the formation of SCV

Table S3 The analysis of the fragment of SCV peak.

No.	Tested m/z	Normalized intensity (1%)	Formula	Theoretical m/z	Structure
1	299.0917	25.3	$C_{17}H_{15}O_5$	299.0914	$[M+H-CO-2OCH_3+2H]^+$
2	327.0865	29.6	$C_{18}H_{15}O_6$	327.0864	$[M+H-2OCH_3+2H]^+$
3	330.1098	18.7	$C_{18}H_{18}O_6$	330.1098	$[M+H-CO-CHO]^+$
4	359.1130	22.6	$C_{19}H_{19}O_7$	359.1126	$[M+H-CO]^+$
5	387.1077	100	$C_{20}H_{19}O_8$	387.1075	$[M+H]^+$
6	409.0895	7.8	$C_{20}H_{18}O_8Na$	409.0894	$[M+Na]^+$

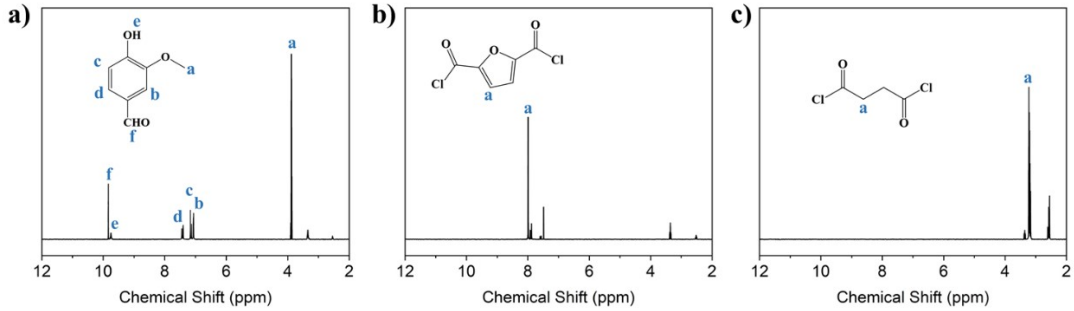

Fig. S2 The ^{1}H NMR spectra for the raw material in this work, a) vanillin; b) 2,5-Furandicarboxyl chloride; c) succinyl chloride.

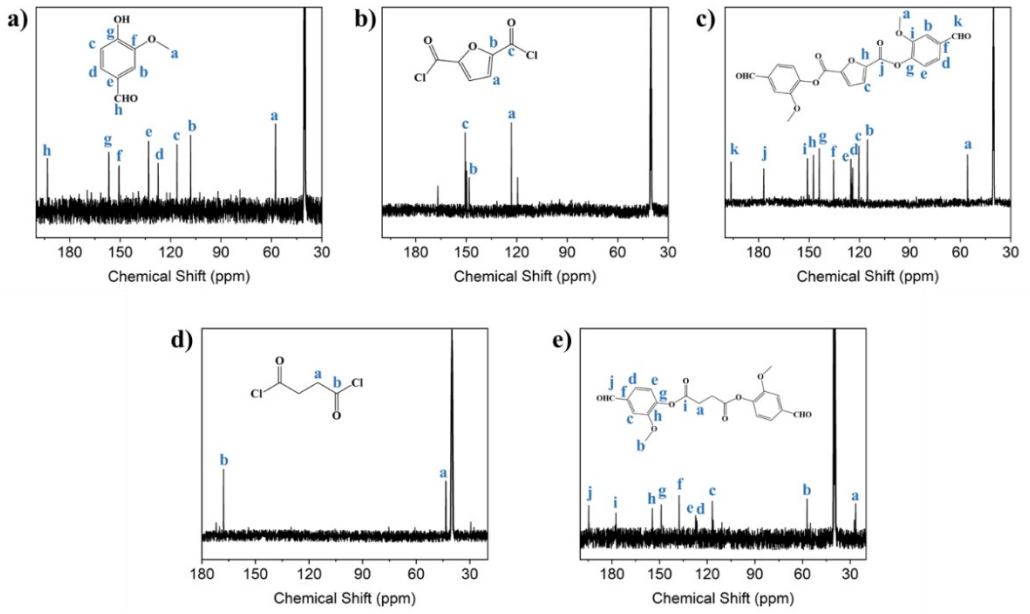

Fig. S3 The ^{13}C NMR for FDV, SCV and all the raw materials used in this work, a) vanillin; b) 2,5-Furandicarboxyl chloride; c) FDV; d) succinyl chloride; e) SCV.

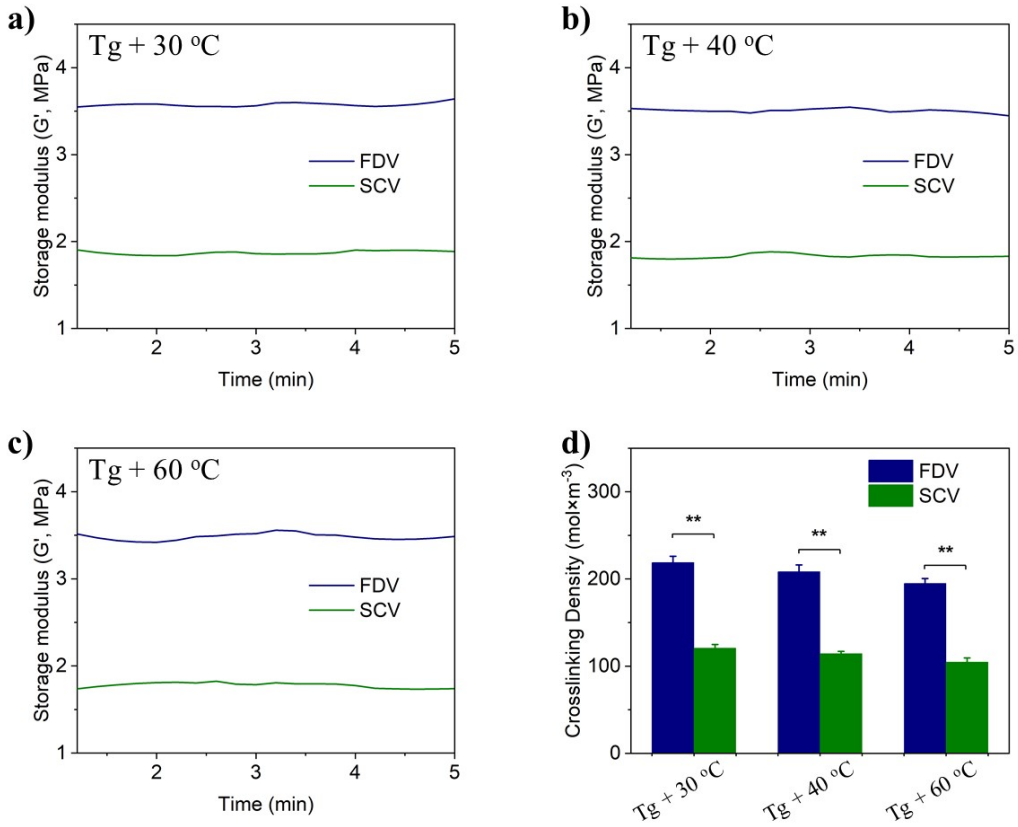

Fig. S4 The calculation of crosslinking degree of FDV and SCV, a) the plateau modulus values for the vitrimers at T_g + 30 °C; b) the plateau modulus values for the vitrimers at T_g + 40 °C; c) the plateau modulus values for the vitrimers at T_g + 60 °C; d) the calculation of the crosslinking degree for FDV and SCV.

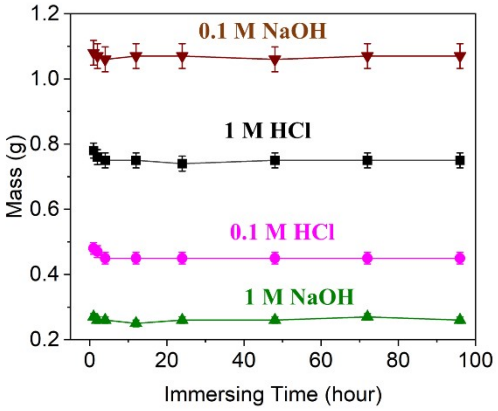

Fig. S5 The mass change of FDV-1071 with immersing time in acidic and basic aqueous solution with different pH values.

References:

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