Supporting Information

A New Class of Bio-elastomers Based on β-Myrcene and a Glycomonomer; Its Application in Sustainable Adhesives

Tuhin Subhra Pal,[‡a] Uddhab Kalita,[‡a] Suman Pradhan,[a] Koushik Bhattacharya,[a] and Nikhil K. Singha[*a,b]

[a] *Rubber Technology Centre, Indian Institute of Technology Kharagpur, Kharagpur, West Bengal 721302, India.*

[b] *School of Nano Science and Technology, Indian Institute of Technology Kharagpur, Kharagpur, West Bengal 721302, India.*

[*] *Corresponding author email: nks@rtc.iitkgp.ac.in*

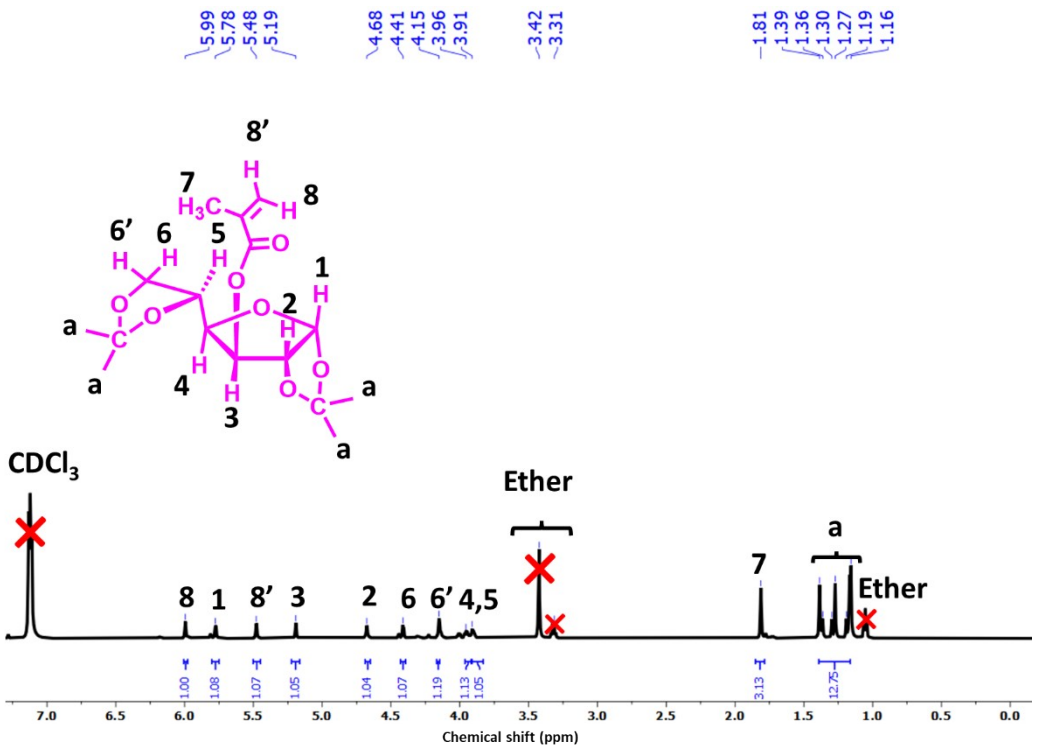


Fig. S1 ^{1}H NMR of 3-O-methacryloyl-1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (MAIpGlc).

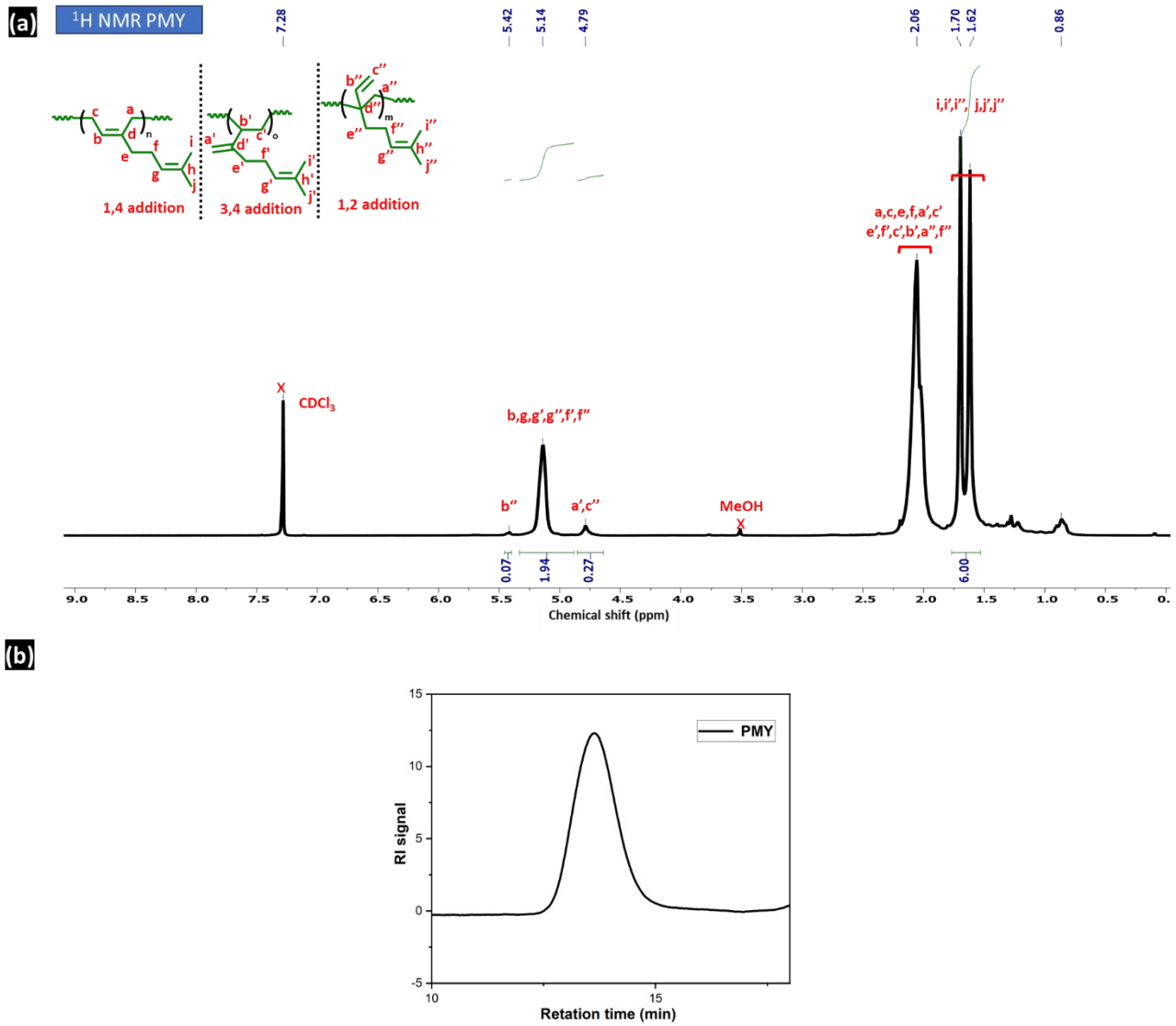


Fig. S2 (a) ^{1}H NMR of Poly(β-myrcene) (PMY), (b) GPC traces of PMY

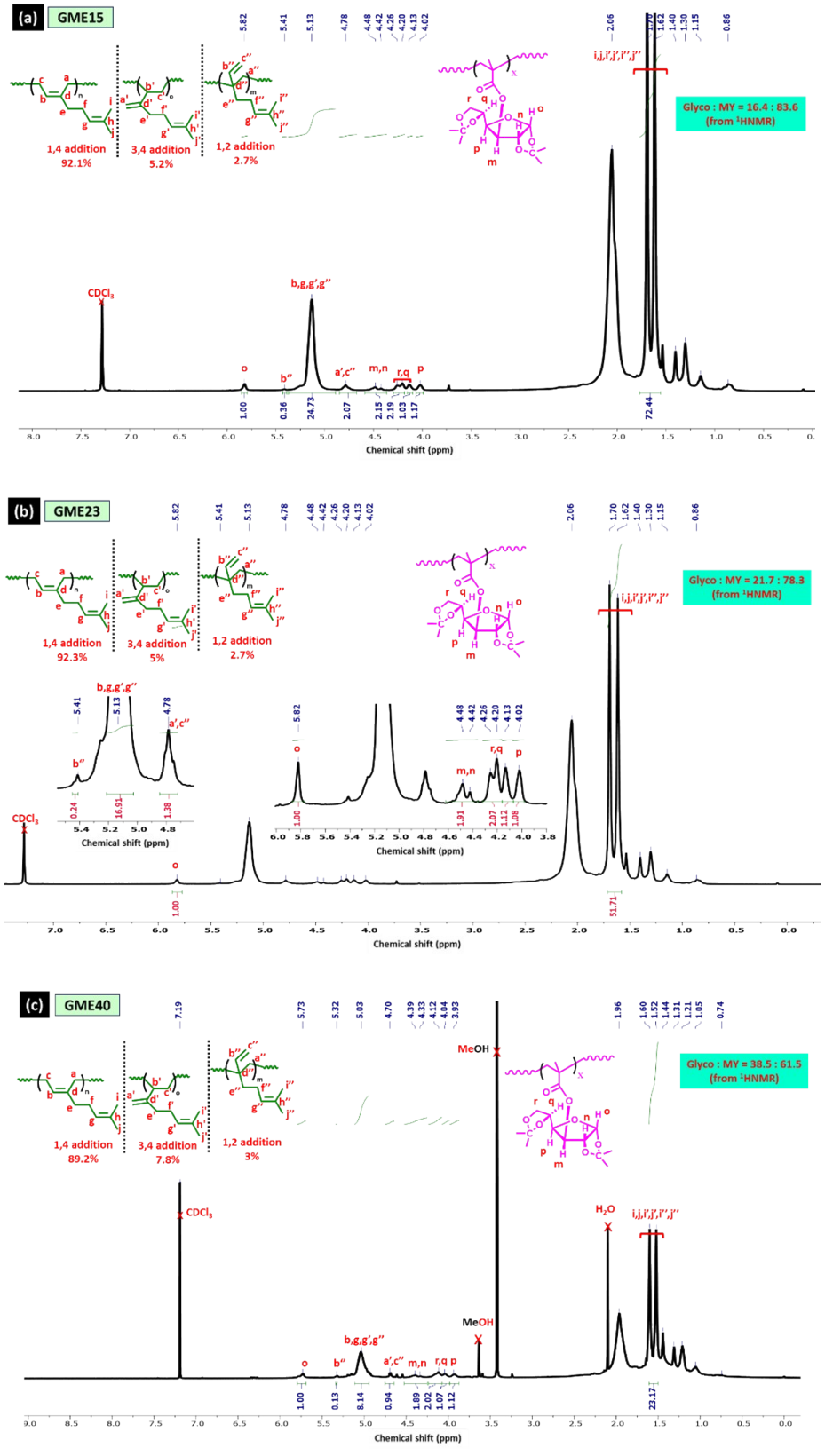


Fig. S3 ^{1}H NMR spectra of the synthesized GME copolymers in $CDCl_3$: (a) GME15, (b) GME23, and (c) GME40 exhibiting the content of Glyco in each of the GMEs. From ^{1}H NMR spectra, it was observed that the content of Glyco is 16.4, 21.7, and 38.5% respectively in GME15, GME23 and GME40. To determine the copolymerization composition and different microstructures of myrcene, the integral area of "o" proton (at 5.73 ppm) for sugar moiety and other vinyl protons of myrcene unit at (4.7-5.33 ppm) have been utilized using the formula-

% 1,2 addition = [Integral area of ^{1}H (1,2) / {Integral area of ^{1}H (1,2) + Integral area of ^{1}H (1,4) + Integral area of ^{1}H (3,4)}] *100%

= [^{1}H (1,2) / {^{1}H (1,2) + ^{1}H (1,4) + ^{1}H (3,4)} * 100]

% 3,4 addition = [^{1}H (3,4) / {^{1}H (1,2) + ^{1}H (1,4) + ^{1}H (3,4)}

% 1,4 addition = [100 - (%1,2 addition + 3,4 addition)]

% MAIpGlc= {^{1}H MAIpGlc / (^{1}H MAIpGlc+ ^{1}H β-myrcene)*100}

% β-myrcene =100-% MAIpGlc.

For example, in the ^{1}H NMR spectra of GME15 (Fig.S3a): peak area of one proton is - ^{1}H MAIpGlc = 1, ^{1}H (1,2) = 0.36, ^{1}H (3,4) = 0.675, ^{1}H (1,4) = 11.84, ^{1}H (β-myrcene)=12.

% 1,2 addition = [^{1}H (1,2) / {^{1}H (1,2) + ^{1}H (1,4) + ^{1}H (3,4)} *100]

=2.7%

% 3'4 addition = [^{1}H (3,4) / {^{1}H (1,2) + ^{1}H (1,4) + ^{1}H (3,4)}]

= 5.2%

% 1,4 addition =100-(%1,2 addition+3,4 addition)

=92.1%

% MAIpGlc = {^{1}H MAIpGlc / (^{1}H MAIpGlc+ ^{1}H β-myrcene) *100}]

=7.6%

% β-myrcene = (100-% MAIpGlc)

=92.4%

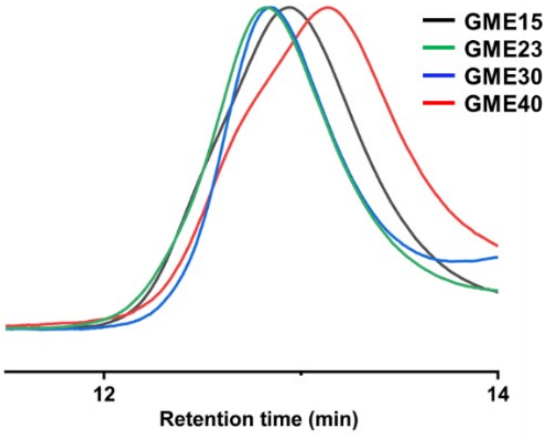
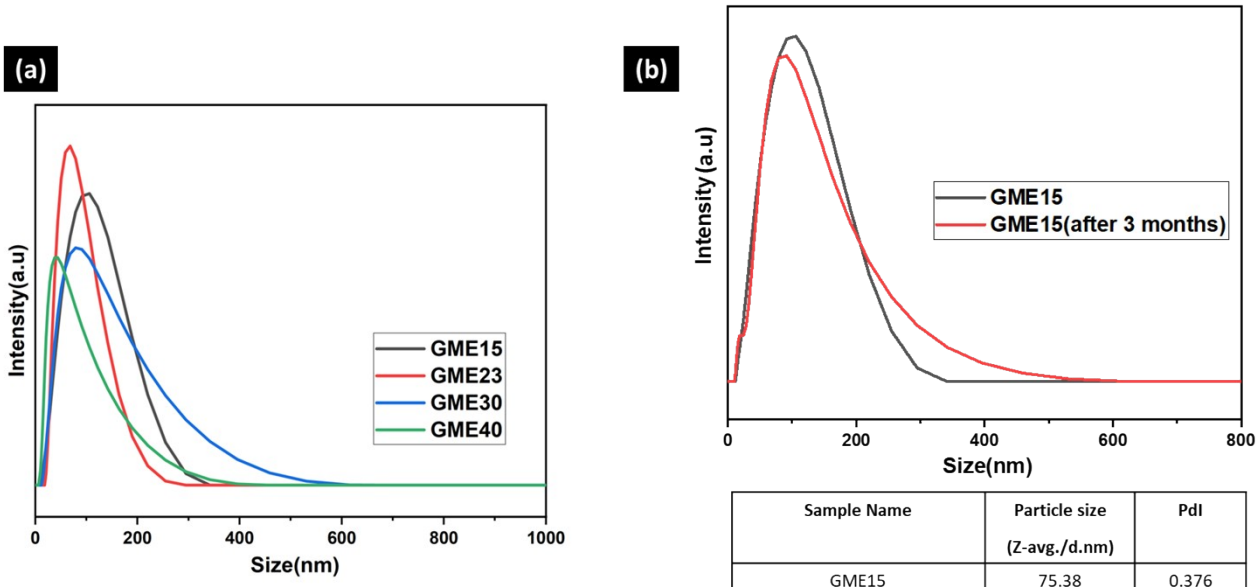


Fig. S4 GPC traces of the GME copolymers.



Sample Name	Particle size (Z-avg./d.nm)	PdI
GME15	75.38	0.376
GME15 (after 3 months)	78.71	0.409

Fig. S5 (a) Particle size distribution of the GME copolymers, (b) Particle size distribution of the GME15 and GME15 (after 3 months).

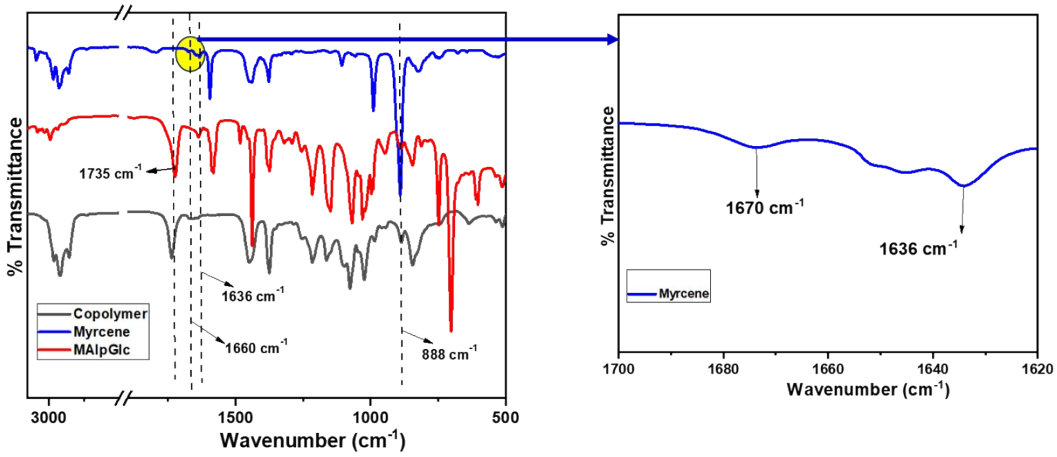


Fig. S6 FTIR spectra of MY, MAIpGlc and their copolymers (GME23).

Table S1 Summary of the copolymer of Glycomonomer and MY Synthesized via Emulsion Polymerization.

Sample ID	Monomers	Molecular weight (gm/mol)	Weight taken (mg)	Mol of monomers	Feed ratio of Glyco: MY (molar ratio)	Copolymer composition Glyco: MY from NMR (molar ratio)	Feed ratio of Glyco: MY (wt% ratio)	Copolymer composition Glyco: MY from NMR (wt% ratio)	Conversion (%)
GME15	Glyco	328	150	4.57×10^{-4}	6.8 : 93.2	7.6 : 92.4	15 : 85	16.4 : 83.6	92
	MY	136	850	6.25×10^{-3}					
GME23	Glyco	328	230	7.01×10^{-4}	11 : 89	10.3 : 89.7	23 : 77	21.7 : 78.3	91
	MY	136	770	5.66×10^{-3}					
GME30	Glyco	328	300	9.14×10^{-4}	14.9 : 85.1	14.85 : 85.15	30 : 70	29.6 : 70.4	89
	MY	136	700	5.14×10^{-3}					
GME40	Glyco	328	400	1.21×10^{-3}	21.5 : 78.5	20.6 : 79.4	40 : 60	38.5 : 61.5	94
	MY	136	600	4.41×10^{-3}					

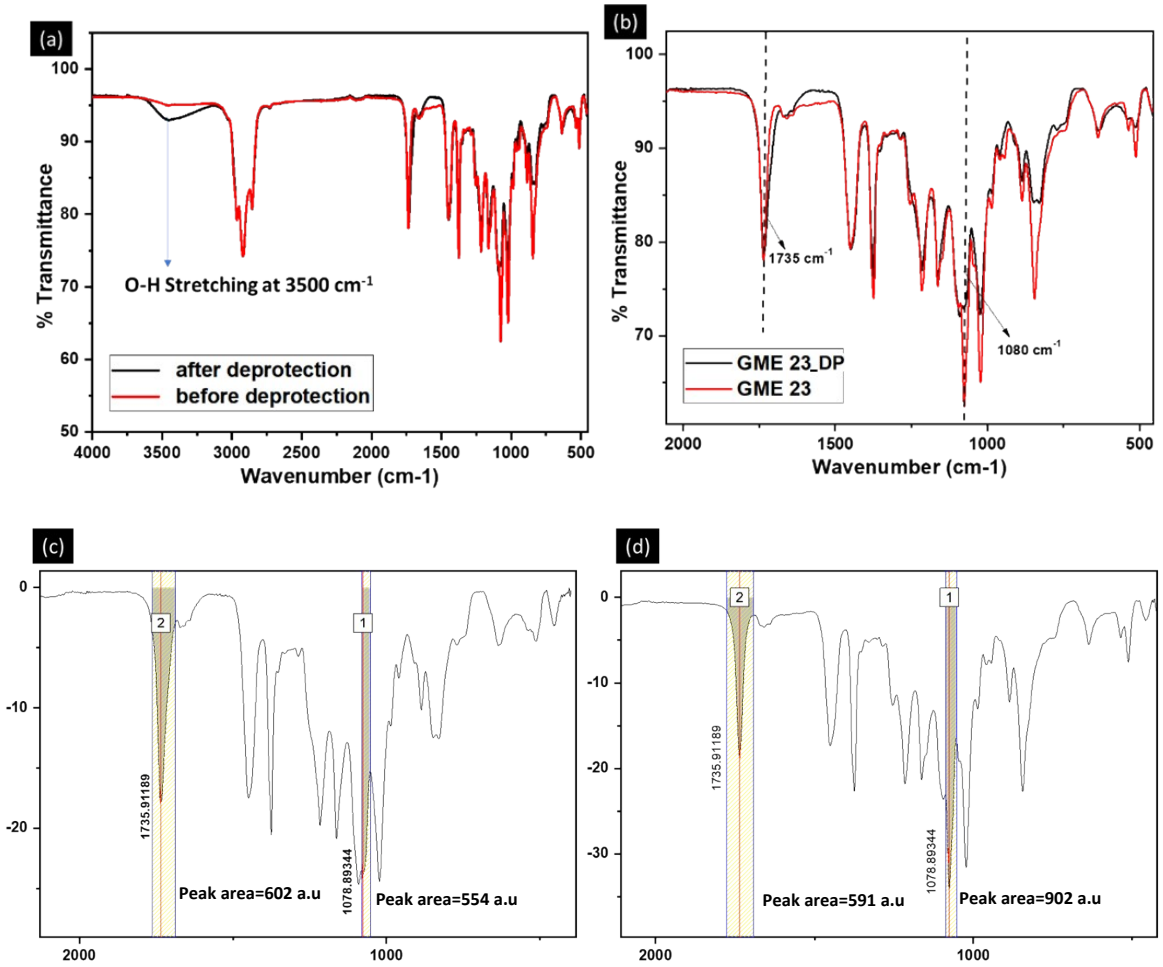


Fig. S7 (a), (b)FTIR Spectra before and after deprotection of copolymers (GME23) **(c)** Determination of Peak area under the peak for GME23 after deprotection **(d)** Determination of Peak area under the peak for GME23 before deprotection. % of deprotection was calculated using the formula: **% Deprotection (DP)** = [**(R_b -R_a)/R_b**] ***100**, where R_b= (area under the curve at 1080 cm^{-1} /area under the curve at 1735 cm^{-1}) before deprotection. R_a = (area under the curve at 1080 cm^{-1} /area under the curve at 1735 cm^{-1}) after deprotection. for example, in GME-23, R_b = (902/591) = 1.52, R_a = (554/602) = 0.92 **% DP** = [**(R_b -R_a)/R_b**] ***100= [**(1.52-0.92)/1.52]*100 =40.4%

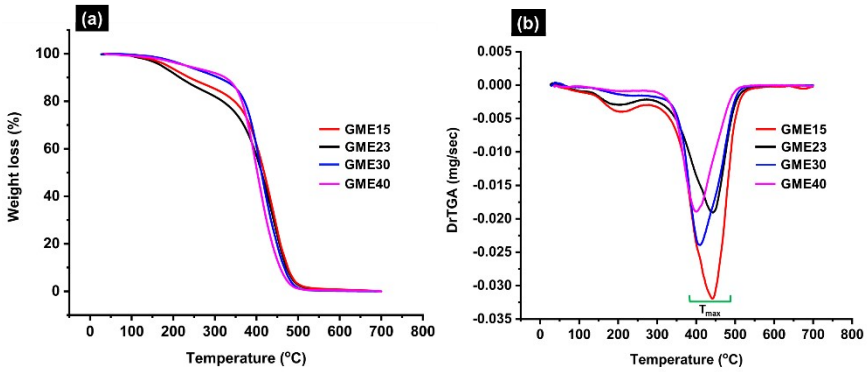


Fig. S8 (a) TGA and (b) DTG curves of GME copolymers.

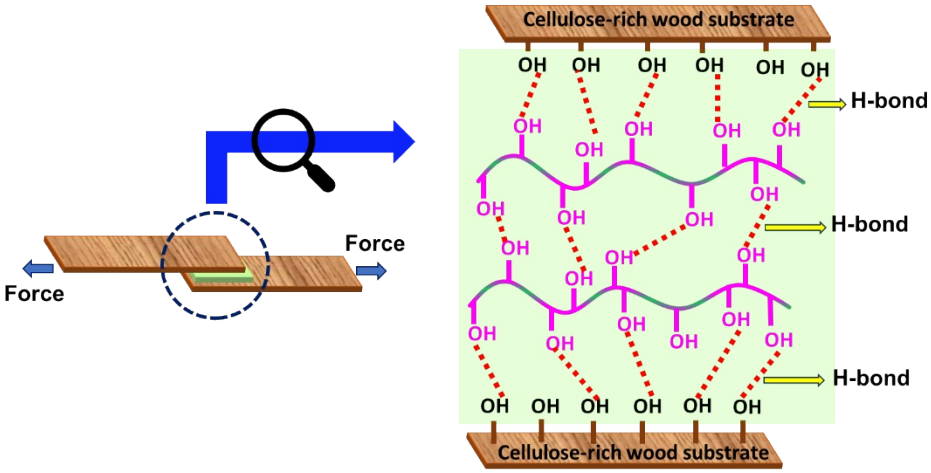


Fig. S9 Schematic illustration of hydrogen bonding between free hydroxyl (−OH) groups in the deprotected copolymers and hydroxyl groups in the cellulose-rich wood substrate.