

Supplementary information

Rehabilitation Physical, Mechanical, Antibacterial and Cell growth Properties of Bio-Rubber Polymers Based on Poly(Glycerol Sebacic acid) with Helping Curcumin and Hydroxyapatite Nanoparticles

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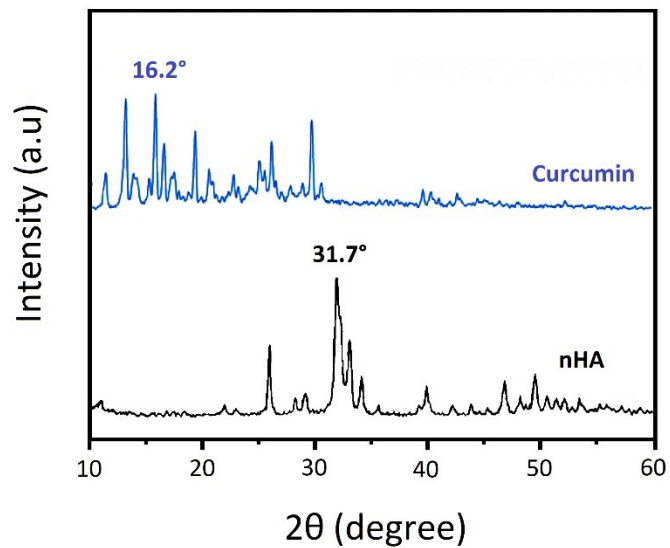


Figure S1. X-ray diffraction of curcumin powder and hydroxyapatite nanoparticles.

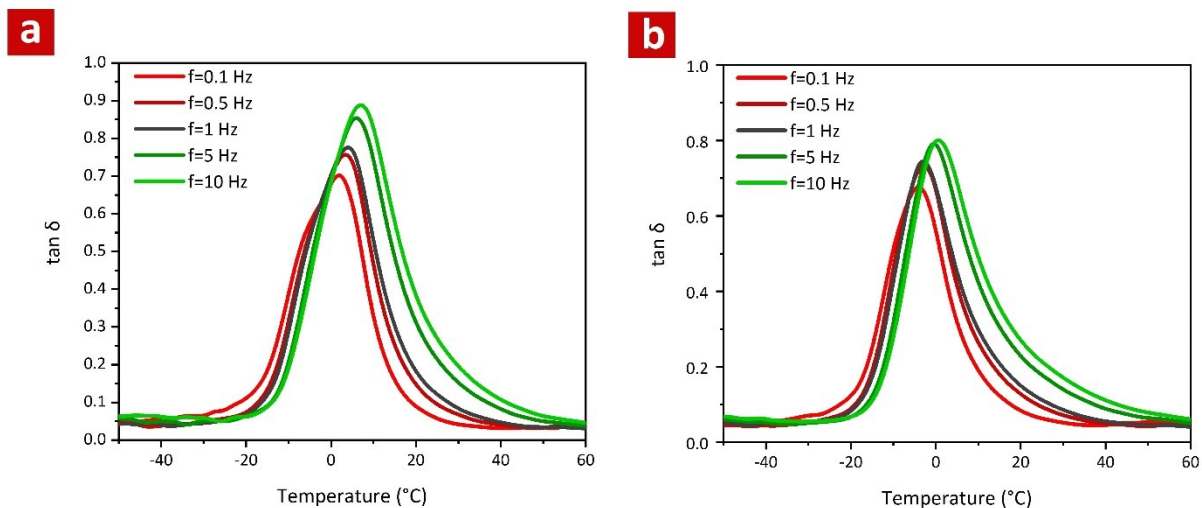


Figure S2. Effect of multi frequencies on loss factor (Tan δ) of investigated PGSU-based elastomers: **(a)** PGSU-HA and **(b)** PGSU-Cu

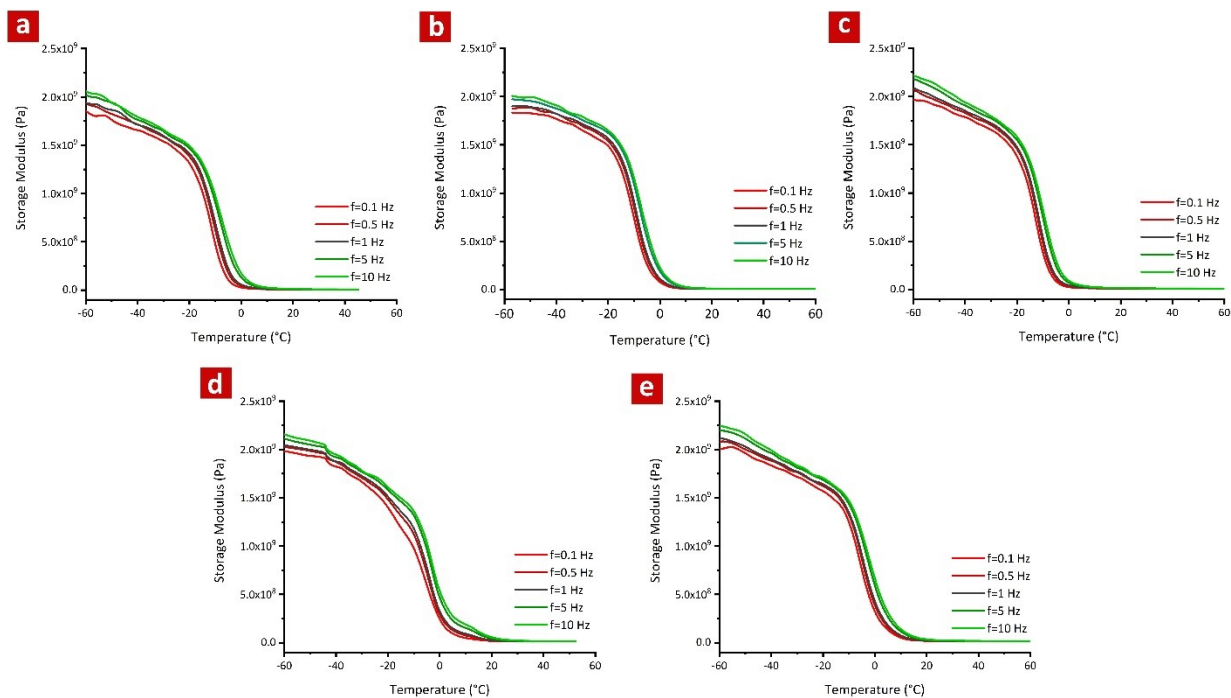


Figure S3. Effect of multi frequencies on storage modulus (E') of investigated PGSU-based elastomers: (a) PGSU, (b) PGSU-HA, (c) PGSU-Cu, (d) PGSU-HA-Cu5 and (e) PGSU-HA-Cu3

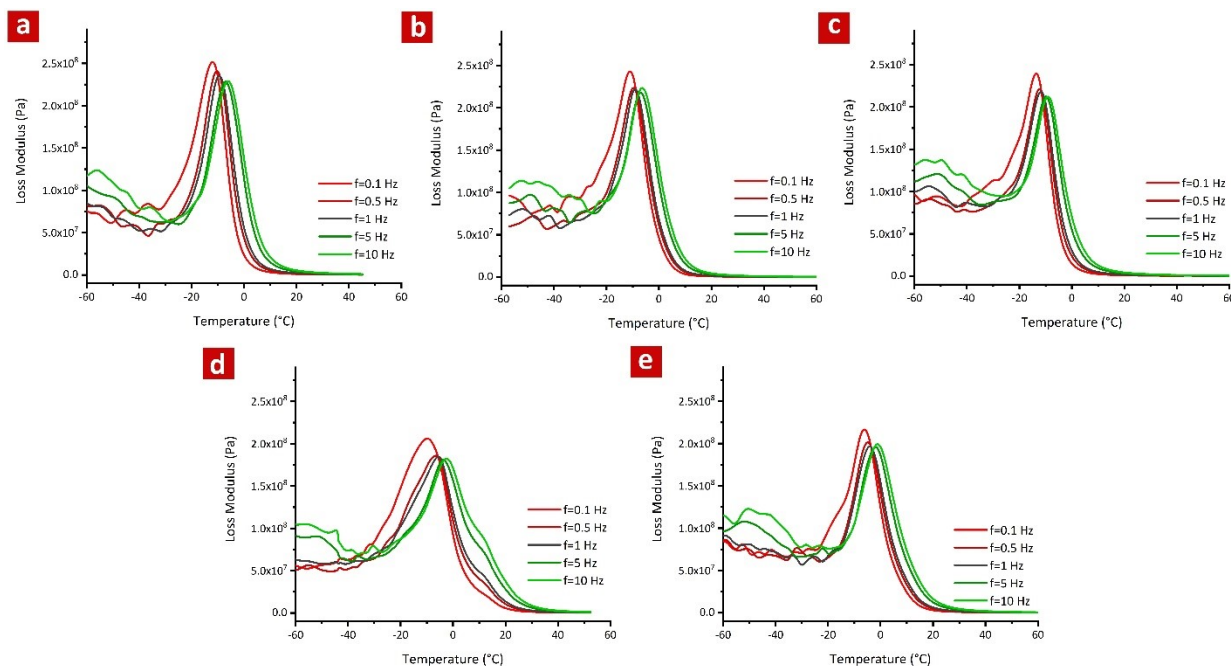


Figure S4. Effect of multi frequencies on loss modulus (E'') of investigated PGSU-based elastomers: (a) PGSU, (b) PGSU-HA, (c) PGSU-Cu, (d) PGSU-HA-Cu5 and (e) PGSU-HA-Cu3

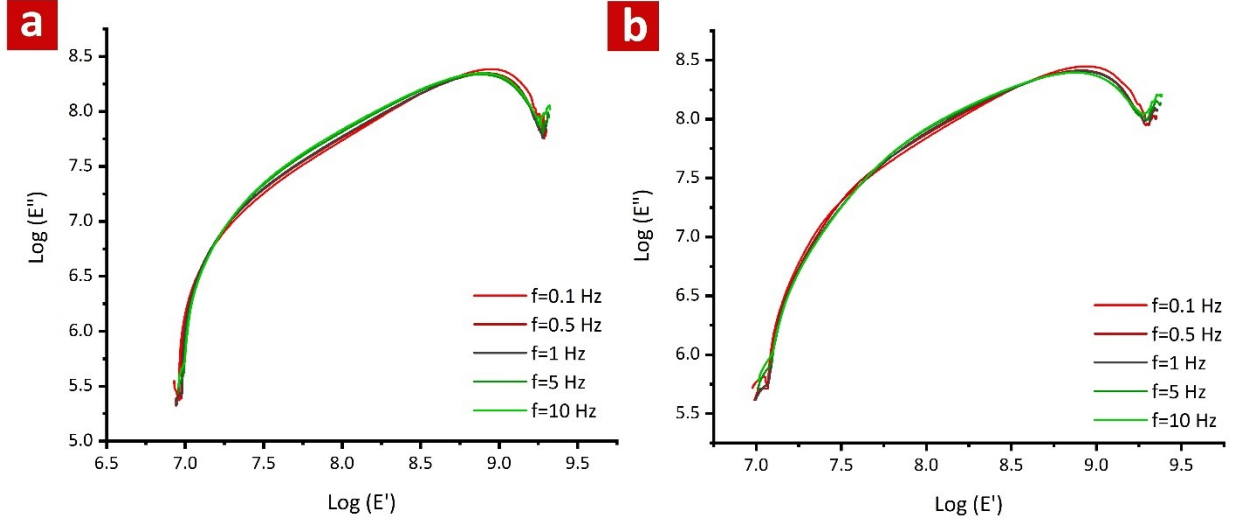


Figure S5. Cole-Cole plots at various frequencies: **(a)** PGSU-HA and **(b)** PGSU-Cu.

1. Generating Master curves

For storage modulus, TTS principle can be expressed by the equation S1:

$$E'(f a_T, T_r) = E'(f, T) \quad (S1)$$

Where a_T , f and T_r are the horizontal shift factor, frequency and the reference temperature, respectively.

In the temperature range of T_g to T_g+100 °C, the shift factor (a_T) can be calculated by the Williams-Landel-Ferry (WLF) equation expressed as:¹

$$\text{Log}(a_t) = \frac{-C_1(T - T_0)}{C_2 + (T - T_0)} \quad (S2)$$

Where T_0 is the reference temperature and C_1 and C_2 are WLF constants. If T_g is taken as T_0 , the C_1 and C_2 are equal to 17.4 and 51.6, respectively. For other reference temperatures the WLF constants (C_1^0 and C_2^0) can be calculated by the following equations:¹

$$C_1^0 = \frac{C_1^g C_2^g}{C_1^g + T_0 - T_g} \quad (S3)$$

$$C_2^0 = C_2^g + T_0 - T_g \quad (S4)$$

Where C_1^g and C_2^g are WLF constant at T_g .

Table S1. WLF constants and calculated $\log(a_T)$ for all samples at a reference temperature of 37°C.

Sample	T_g (°C)	WLF Constant (C_1)	WLF Constant (C_2)	$\log(a_T)$									
				0(°C)	5(°C)	10(°C)	15(°C)	20(°C)	25(°C)	30(°C)	35(°C)	45(°C)	55(°C)
PGSU	-9.5	14.0742	98.1	8.523	6.814	5.345	4.069	2.950	1.962	1.081	0.293	-1.061	-2.182
PGSU-HA	-9	14.1851	97.6	8.661	6.920	5.425	4.128	2.992	1.989	1.096	0.297	-1.075	-2.209
PGSU-Cu	-11.5	13.6473	100.1	8.002	6.413	5.041	3.844	2.792	1.859	1.026	0.278	-1.010	-2.080
PGSU- HA-Cu5	-5.5	15.0134	94.1	9.728	7.736	6.041	4.581	3.310	2.194	1.207	0.326	-1.176	-2.411
PGSU- HA-Cu3	-4	15.3988	92.6	10.247	8.131	6.338	4.798	3.463	2.293	1.259	0.340	-1.225	-2.506

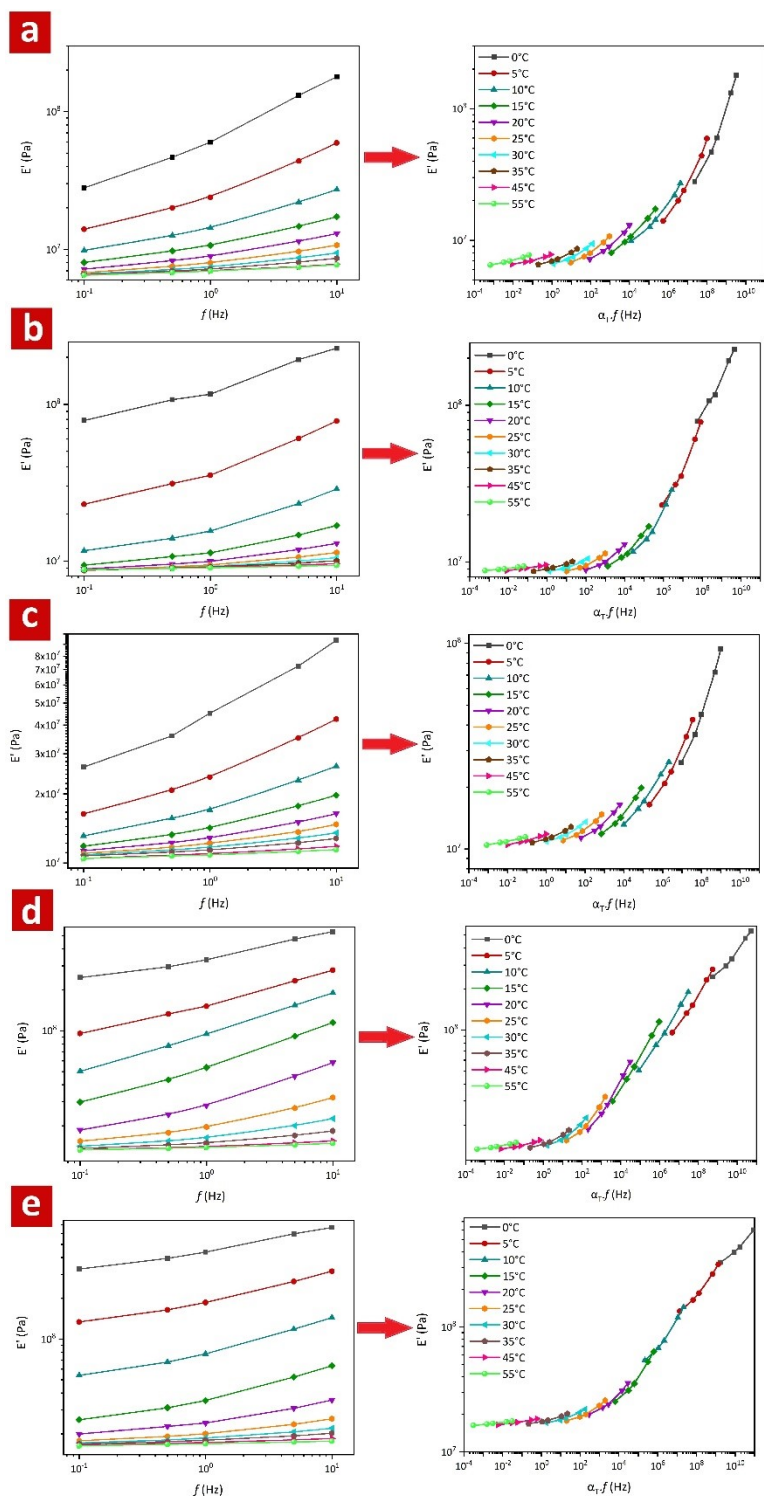


Figure S6. Frequency sweep data versus storage modulus and transferred plot of storage modulus of (a) PGSU, (b) PGSU-HA, (c) PGSU-Cu, (d) PGSU-HA-Cu5, and (e) PGSU-HA-Cu3 at a reference temperature of 37°C.

2. Calculating surface tension

Wetting phenomena on a macroscopic scale can be shown by Young's equation.²

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} \quad (S5)$$

Where θ is the contact angle, γ_{sl} is solid-liquid interfacial free energy, γ_{lv} is liquid surface tension and γ_{sv} is solid surface free energy.

The solid surface free energy of an unknown material can be calculated through Owens-Wendt method:^{2,3}

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 2(\sqrt{\gamma_{sv}^D \gamma_{lv}^D} + \sqrt{\gamma_{sv}^P \gamma_{lv}^P}) \quad (S6)$$

Where γ_{sv}^D and γ_{lv}^D are dispersive portions and γ_{sv}^P and γ_{lv}^P are polar portions of solid and liquid surface energies, respectively. By combining Eq.S5 and Eq.S6:

$$\sqrt{\gamma_{sv}^D \gamma_{lv}^D} + \sqrt{\gamma_{sv}^P \gamma_{lv}^P} = 0.5[\gamma_{lv}(1 + \cos \theta)] \quad (S7)$$

The solid surface free energy of an unknown material can also be calculated through Wu- harmonic-mean equation:³

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 4\left(\frac{\gamma_{sv}^d \gamma_{lv}^d}{\gamma_{sv}^d + \gamma_{lv}^d} + \frac{\gamma_{sv}^p \gamma_{lv}^p}{\gamma_{sv}^p + \gamma_{lv}^p}\right) \quad (S8)$$

By combining Eq.S8 and Eq.S5:

$$\frac{\gamma_{sv}^d \gamma_{lv}^d}{\gamma_{sv}^d + \gamma_{lv}^d} + \frac{\gamma_{sv}^p \gamma_{lv}^p}{\gamma_{sv}^p + \gamma_{lv}^p} = 0.25[\gamma_{lv}(1 + \cos \theta)] \quad (S9)$$

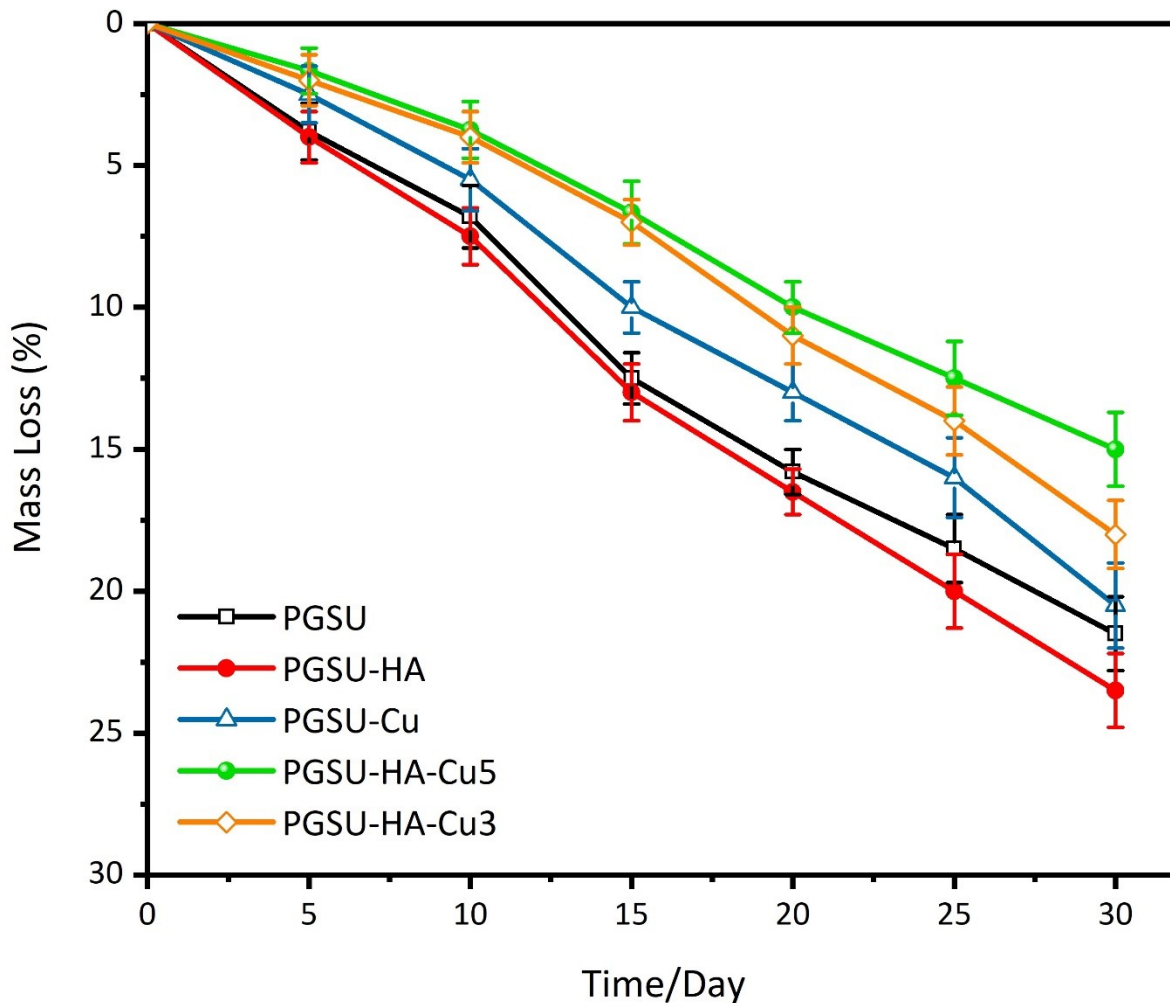


Figure S7. *In-vitro* enzymatic degradations profile of the bioelastomers in PBS solution (pH=7.4) at 37 °C

References:

1. Landel RF, Nielsen LE. *Mechanical Properties of Polymers and Composites*. CRC Press; 1993. doi:10.1201/b16929
2. Annamalai M, Gopinadhan K, Han SA, et al. Surface energy and wettability of van der Waals structures. *Nanoscale*. 2016;8(10):5764-5770. doi:10.1039/C5NR06705G
3. Fakhri V, Monem M, Mir Mohamad Sadeghi G, Khonakdar HA, Goodarzi V, Karimpour-Motlagh N. Impact of poly(ϵ -caprolactone) on the thermal, dynamic-mechanical and crystallization behavior of polyvinylidene fluoride/poly(ϵ -caprolactone) blends in the presence of KIT-6 mesoporous

particles. *Polym Adv Technol.* 2021;n/a(n/a). doi:<https://doi.org/10.1002/pat.5444>