Supporting Information

Influence of Dodecyl Surfactants on the Cross-Linking, Plasticization and Damping Behavior of Epoxy Novolac Resin

Sathiadasan Minu¹, Ramasubbu Ramani¹*, Ramakrishna Indu Shekar¹, Teggina Math Kotresh¹ and Naveen Vijay Padaki²

1. Defence Bio-Engineering and Electromedical Laboratory (DEBEL), Defence Research and Development Organization (DRDO), ADE Campus, C. V. Raman Nagar, Bangalore - 560 093.

2. Central Silk Technological Research Institute (CSTRI), Central Silk Board (CSB), BTM Layout, Bangalore – 560 068.

* Corresponding author: R. Ramani

E-mail: <u>rramani.debel@gov.in</u>

Orchid ID: 0000-0003-2861-9502

Table-S1: Curing results from DSC

SI. No.	Sample	T _i (°C)	Т _{мсР} (°С)	T _f (°C)	ΔT (°C)	ΔH (J g ⁻¹)	Enthalpy change %	ΔH *	Δ T *	CI
1.	ENR	63.3	105.4	159.9	96.6	498.6	-	1.00	1.00	1.00
2.	DDA-E	66.6	108.1	148.9	82.3	439.4	11.9	0.88	0.85	0.75
3.	LA-E	65.5	100.3	137.8	72.3	386.2	22.5	0.77	0.75	0.58
4.	DP-E	64.9	101.6	145.3	80.4	469.5	8.6	0.94	0.83	0.78
5.	DR-E	62.2	104.6	139.7	77.5	455.5	5.8	0.91	0.80	0.73
6.	DBSA-E	69.6	101.5	176.3	106.7	488.5	2.0	0.98	1.10	1.08



Fig-S1: Plots showing curing conversion (α) versus time for pristine and surfactant added ENR samples isothermally cured at 70 °C.

SI.	Sample	d (Å)
No.	Name	
1.	ENR	4.49
2.	DDA-E	4.51
3.	LA-E	5.06
4.	DP-E	4.98
5.	DR-E	4.59
6.	DBSA-E	4.80

Table-S2: The 'd' spacing from XRD results

Table-S3: DSC Results

SI.	Sample	DSC	TOPEM	
No.		Т _g (°С)	Т _g (°С)	
1	ENR	126.1	124.4	
2	DDA-E	119.0	118.2	
3	LA-E	114.4	113.4	
4	DP-E	115.6	114.3	
5	DR-E	120.0	117.9	
6	DBSA-E	122.7	122.4	

Table-S4: DMTA Results

SI. No.	Sample	E' (GPa) @100 °C	E' (Mpa) @160 °C	T _g from E" (°C)	Ve x 10 ³ (mol/m ³)	Tan-δ Max value	Tan-δ T _g (°C)
1.	ENR	5.9	63.2	127.8	5.85	2.25	163
2.	DDA-E	5.4	52.4	120.2	4.86	1.53	155
3.	LA-E	5.8	49.0	113.6	4.54	2.98	149
4.	DP-E	5.6	49.5	114.2	4.58	2.89	150
5.	DR-E	5.6	49.3	121.7	4.67	1.25	153
6.	DBSA-E	5.5	51.6	123.1	4.78	0.80	161

S1. CHARACTERIZATION:

Thermogravimetric Analysis (TGA): The thermal stabilities of the samples were found using a Thermogravimetric analyzer (TA Instruments; model TGA Q-500). Samples of ca. 5 mg were placed in platinum pans and heated up to 800 °C at the heating rate of 20 °C/min both in non-oxidative (nitrogen) and oxidative (air)

atmospheres. The purge gas in each case was maintained at a flow rate of 50 mL/min.

S2. RESULTS AND DISCUSSION:

Thermal stability by TGA :





Thermogravimetry is the most widely used technique to characterize the thermal decomposition of polymers. The TGA curve of normalized mass and the

derivative mass of all samples at a heating rate of 20 °C/min in nitrogen and air media are presented in Fig. S2. The onset temperature (T_{onset}), the maximum degradation temperature (T_{max}) and % of residue at 800 °C (R_{800}) for all the samples in nitrogen and air media are tabulated in Table-S5.

SI No	Sample	Nitrogen			Air				
		T _{onset} (°C)	T _{max} (°C)	R ₈₀₀ (%)	T _{onset} (°C)	T _{max 1} (°C)	T _{max 2} (°C)	T _{max 3} (°C)	R ₈₀₀ (%)
1	ENR	326.0	344.5	8.9	327.2	343.8	436.4	594.0	0.05
2	DDA-E	325.8	342.2	9.7	327.6	343.0	436.4	611.6	0.08
3	LA-E	325.6	342.2	7.6	325.0	342.2	443.2	610.8	0.09
4	DP-E	331.2	347.4	10.0	332.6	347.4	435.2	591.7	0.10
5	DR-E	327.8	343.8	9.5	327.9	344.7	439.2	622.7	0.05
6	DBSA-E	330.9	347.4	8.0	329.5	345.9	436.7	614.4	0.06

Table-S5: TGA Results

 T_{onset} (°C) = Onset temperature, T_{max} (°C) = Maximum degradation temperature, R_{800} (%) = Residue at 800°C

First let us discuss regarding the decomposition behavior of pure ENR as well as those incorporated with surfactants in nitrogen medium. Although the TGA curve of ENR in the inert atmosphere appears to suggest single decomposition, the derivative plot displays two additional mild decomposition stages at the shoulder in addition to the maximum mass loss at ca. 345 °C. This indicates that more than one process occurs during thermal degradation. Please note that the pyrolysis of novolac resins^{1,2} and epoxidized novolac resins^{3,4} have

been reported to exhibit three step decomposition in agreement with the present results.

The thermal decomposition of phenolic resins⁵ and the thermally initiated ring-opening homo polymerization of pure epoxy resins⁶ are reported to occur at ca. 300 °C. The first decomposition that occurs for ENR in the range 326 to 372 °C, with the maximum mass loss at ca. 345 °C could be related to breaking up of epoxide linkage/ glycidol ether side chain and cleave-off of methoxy groups present in them.^{5,7,8} This decomposition step results to toluene as the main volatile material.⁹

In the temperature range 370 to 410 °C, the second stage of decomposition occurs in which cross-links gradually begin to cleave-off and the methylene and N-methylene bridges break into methyl, phenol and cresol groups with traces of CO and CO₂ gases.^{9,10} The last stage of decomposition occurs between 420 to 550 °C, where the methylene bridges and the hydrogen and oxygen atoms from the aromatic structure further pyrolyze to release hydrocarbons, carbon oxides and hydrogen.^{2,4} The cleavage at the phenoxy oxygen could lead to decomposition products of phenolic mixtures such as cresols and phenols at the final stage of

decomposition.⁸ After the final decomposition step, the curve flattens to result a residue of 7 to 10 % in all these samples (please see Table S5).

The decomposition behavior of EPN in air medium is somewhat similar to that observed in nitrogen but is characterized by three distinct decomposition steps.¹¹ It has been reported that the TGA plots and derivative thermograms of all the samples do not significantly vary in terms of their T_{onset} and T_{max} in both nitrogen and air medium and our results are in accordance with this report.¹² The intensity of the second and third decomposition steps that are mild in inert medium becomes distinct and intense in air atmosphere owing to their good oxidation ability.

The first decomposition step is prominent in air medium and starts at ca. 327 °C and ends at 380 °C with a maximum rate of mass loss around 344 °C. This decomposition is followed by a mild degradation step which occurs between 411 and 517 °C with maximum mass loss at ca. 436 °C. The final decomposition step leads to a negligible residue (<1 %) that commences almost instantaneously after second step and ends at ca. 698 °C with maximum mass loss at 594 °C.

The type of evolved gases during thermal and thermo-oxidative decomposition of ENR are same but the intensity of the evolved products were

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more during thermo-oxidative process than during pyrolysis (thermal decomposition), which is attributed to the oxidation of the decomposition product.¹³ The thermo-oxidation process is distinct and starts to occur at ca. 550 °C which is in agreement with the earlier TGA results of epoxies.^{3,12,14,15} The decomposition behavior of all the other surfactant incorporated ENR samples follows similar pattern without any significant change in T_{onset} implying that the addition of surfactant (by 2 wt%) does not significantly affect the thermal decomposition behavior of ENR.

To summarize the TGA results, the ENR exhibited a major single step decomposition with mild additional two stages in inert medium with a char of 7 to 10 % while the decomposition in air showed a clear three step decomposition with almost no residue. The presence of dodecyl surfactants has not shown any significant change in the thermal and thermo-oxidative decomposition behavior as compared to pristine ENR.³

Table-S6: DETA Results

SI.	Samples	Т _. (°С)		
No.		5 1		
1.	ENR	113.6		
2.	DDA-E	107.2		
3.	LA-E	100.2		
4.	DP-E	101.7		
5.	DR-ENR	110.4		
6.	DBSA-E	112.1		

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