Supplementary Information (SI) for RSC Applied Polymers.

SUPPLEMENTARY INFORMATION

Hydroxyl-Functional Acrylic Adhesives: Leveraging Polysilazane Chemistry for Curing

Amrita Chatterjee [¥a], Shashank Jha[¥b], Sushmit Sen [a], Keshav Dev[c], Chayan Das[b], Pradip K. Maji[*a],

[a] Department of Polymer and Process Engineering, Indian Institute of Technology Roorkee, Saharanpur Campus, Saharanpur- 247001, India

[b] Department of Chemistry, Visvesvaraya National Institute of Technology, Nagpur, Maharashtra 440010, India

[c] Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee, 247667, India

*Corresponding Author: Pradip K. Maji (Email ID: pradip@pe.iitr.ac.in)

[¥] Equal Contributions (AC and SJ have contributed equally to this work)

1. Viscosity of the synthesized polymers:

The percentage of monomers employed was based on their offered properties. The MMA segment is responsible for imparting hardness to the resin because of its short chain length, whereas the SMA segment provides flexibility to the resin due to its longer chain length. The functional monomer HEA offers plasticity as well as provides the crosslinking site for the copolymer. Initially, three batches of copolymer were synthesized with three different percentages of monomers, as given below. The copolymer with monomers ratio as MMA: SMA: HEA = 40%:40%:20% by weights offered the most suitable viscosity for the copolymer, to be applied as adhesives without any requirement of the addition of external solvent.

Sample A: MMA: SMA: HEA = 60%:20%:20%

Sample used: MMA: SMA: HEA = 40%:40%:20%

Sample B: MMA: SMA: HEA = 30%:50%:20%

The viscosity vs. shear rate was determined at room temperature up to maximum shear rate of 100 s^{-1} using an MCR101 rheometer. The initial monomer mixture had a low viscosity of 0.75 Pa.s. The final batches were tested for viscosity once the polymerization was completed.

It can be seen that viscosity decreased with an increase in shear rate. Hence, the prepared acrylic copolymers showed shear thinning behavior.

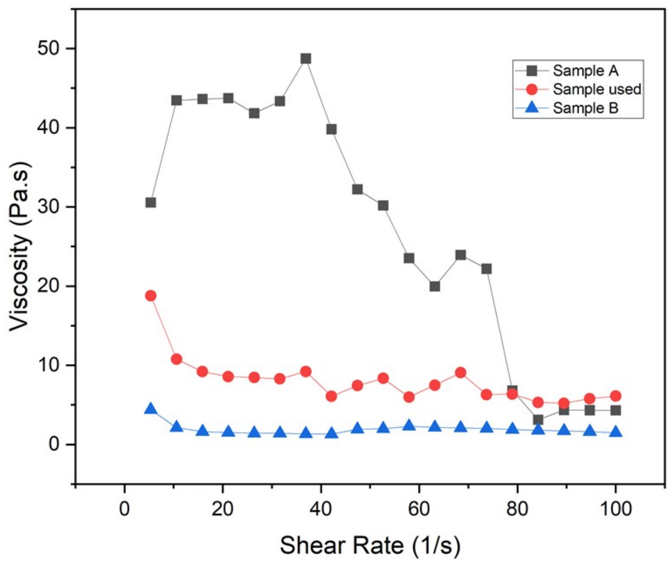

Fig. 1S: Change of viscosity with shear rate at room temperature

2. **Table 1S: Adhesive performance of polysilazane-cured resin and conventional diisocyanate-cured system**

Resin taken (g)	*Type of crosslinker used (5 wt. % of the resin)*	*Strength (MPa)*		*Avg. Strength (MPa)*
		Sam 1	*Sam 2*	
3	Cyamel	0.9	0.8	0.9
3	Polysilazane	0.9	1.1	**1.1**

3. **Table 2S: Adhesive performance of polysilazane-cured acrylic polymer on wood substrates**

Amount of Resin (g)	*Amount of Polysilazane (g)*	*PSZ amount in wt. % of the resin*	*Strength (MPa)*		*Strength Average (MPa)*	*Type of Failure*
			Sam-1	*Sam-2*		

3	1.5	50	1.6	1.8	1.7	Adhesive
3	1	30	2.3	2.6	2.5	Adhesive
3	**0.6**	**20**	**4.0**	**4.7**	**4.4**	**Substrate**
3	0.5	16	2.3	2.4	2.2	Adhesive
3	0.3	10	1.6	1.2	1.4	Adhesive

4. **Table 3S: Adhesive performance of polysilazane-cured acrylic polymer on aluminum substrates**

Amount of Resin (g)	*Amount of polysilazane (g)*	*Strength*		*Avg. Strength (MPa)*
		Sample 1	*Sample 2*	
3	0.3	1.4 MPa	1.6 MPa	1.5
3	0.6	**4.1 MPa**	**3.9 MPa**	**4.0**
3	1.5	0.9 MPa	0.8 MPa	0.9

5. **Stress-strain graphs of the adhesives with different Copolymers:**

The molecular weights (M_n) of the two copolymer samples. Sample A, synthesized with MMA: SMA = 60%:20%, exhibited an M_n of 1.263× 10^4 g/mol, while Sample B, prepared with MMA: SMA = 30%:50%, demonstrated an M_n of 2.145× 10^3 g/mol.

Adhesive formulations were subsequently prepared using both samples. Since the percentage of HEA (a hydroxyl-providing component) was kept constant across all copolymers, the required amount of crosslinker was also predetermined. Adhesion tests were performed with 20 wt.% PSZ, as this concentration yielded optimal performance in prior experiments. The results revealed that the low molecular weight copolymer (Sample B) achieved an adhesion strength of approximately

3 MPa. This relatively low performance is attributed to its lower molecular weight and reduced MMA content, which led to weaker polymer chain interactions and, consequently, diminished strength. In contrast, the higher molecular weight copolymer (Sample A) delivered results (~3.7 MPa) comparable to those obtained with our previously tested copolymer (MMA: SMA = 40%:40%). However, the significantly higher viscosity of Sample A's resin posed challenges during adhesive formulation, as it hindered smooth application onto the substrate and resulted in patchy coverage. The elevated viscosity is likely due to the increased MMA segment, which contributes to reduced resin flow. The results of GPC and tensile stress-strain are shown below in **Fig. 2S**.

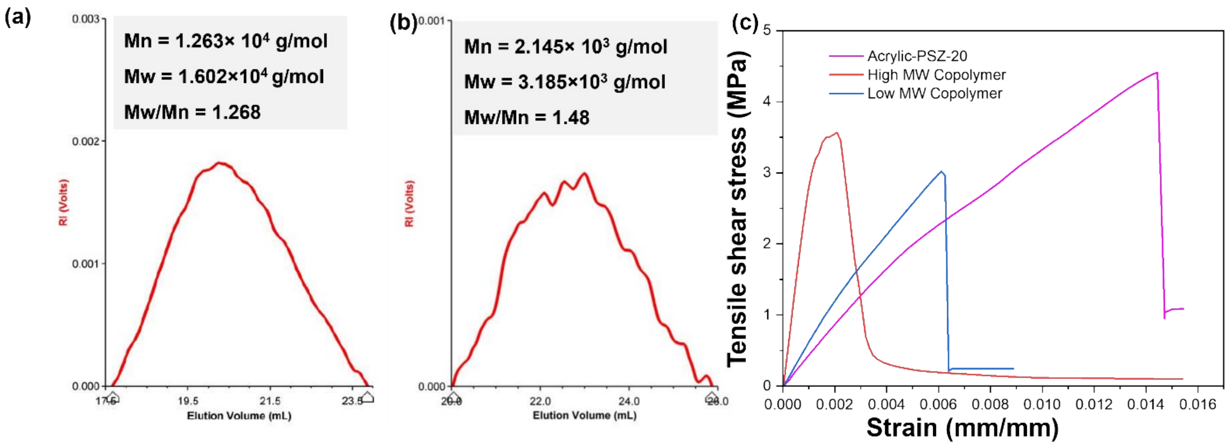

Fig. 2S: (a) Molecular weight of Sample A with higher MMA content, (b) Molecular weight of Sample B with lower MMA, higher SMA content, (c) adhesive strength of the samples with 20 wt.% of PSZ.