Disulfide Exchange Assisted Self-healing Epoxy/PDMS/Graphene Oxide Nanocomposites

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Preparation of graphene oxide:

Hummers method was followed to synthesis graphene oxide(GO) sheets. The sulfuric acid (23ml) was added in the mixture of graphite flakes (1g) and sodium nitrate ($NaN0_3$) (0.5g) at 0^0C (ice bath). After 10 -15 mins, the Potassium permanganate ($KMnO_4$) (3mg) was slowly added in the reaction mixture at 20^{o}c, then it was allowed at 35^{0}C for 7h. Furthermore, Potassium permanganate ($KmnO_4$) (3g) was added slowly in the reaction and it was stirred at 35^{0}C for 10-12h. Then after, reaction mixture was cooled at room temperature and then cold water (133ml) was added with 30% hydrogen peroxide(H_2O_2) (3ml). Finally, after certain time precipitated layer was washed with ethanol, HCl and water 3 times respectively by centrifuge.

Calculation for epoxy and amine hardener ratio:

$$\text{Parts by weight of amine to be used with 100 parts by weight of BADGE resin (phr)} =$$

$$\left(\frac{\text{amine hardener molecular weight / number of hydrogens per molecule}}{\text{BADGE equivalent weight}}\right) * 100\%$$

The equivalent weight of BADGE resin is 176 g/mole (mentioned by manufacture) and an active hydrogen in 2-AFD is FOUR.

=> $\left(\frac{248/4}{176}\right) * 100$ %= 35.6%

So, 35.6 g of AFD is needed to cure the 100 g of BADGE resin.

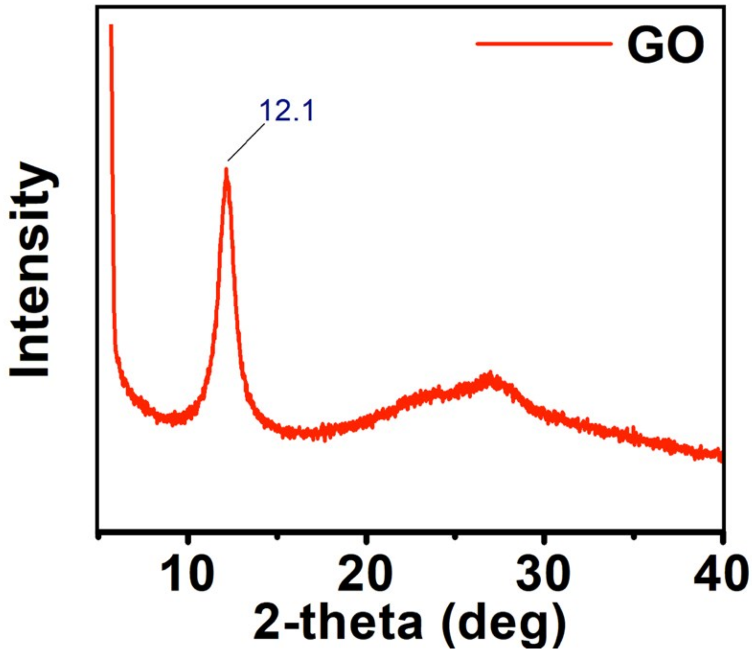
Table S1. Different (a) Epoxy composite and (b) Epoxy/PDMS/GO nanocomposite

(a) Epoxy/PDMS composites

Sample Code	Epoxy (m g)	DG-PDMS	
		PDMS Weight (mg)	Weight percentage (wt%)
EP-pristine	500	0	0
EP-1	500	5	1
EP-2	500	10	2
EP-3	500	15	3
EP-5	500	25	5

(b) Epoxy/PDMS/GO Nanocomposites

Epoxy-2-GO (EP-2-y)	Epoxy (mg)	DG-PDMS (mg)		Graphene oxide (mg)		Graphene oxide dispersed solution (mL)
		Weight (mg)	Weight percentage (wt%)	Weight (mg)	Weight percentage (wt%)	
EP-2-0.1	600	12	2	0.6	0.1	0.04
EP-2-0.2	600	12	2	1.2	0.2	0.08
EP-2-0.5	600	12	2	3	0.5	0.20
EP-2- 1	600	12	2	6	1	0.40
EP-2- 2	600	12	2	12	2	0.80



XRD

Figure S1. X-Ray Diffraction spectroscopy analysis for graphene oxide

FTIR

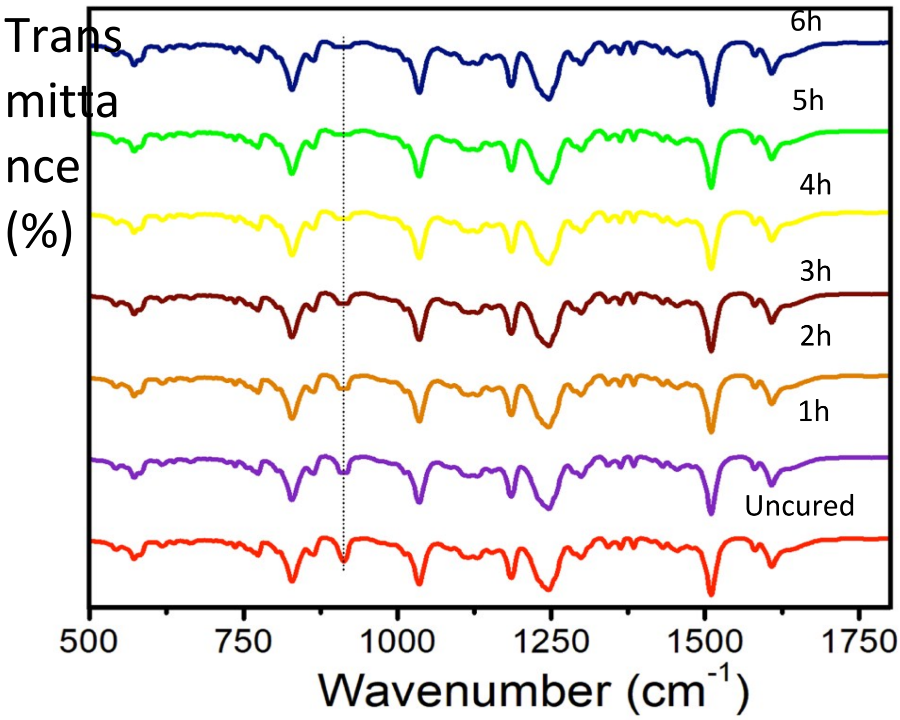
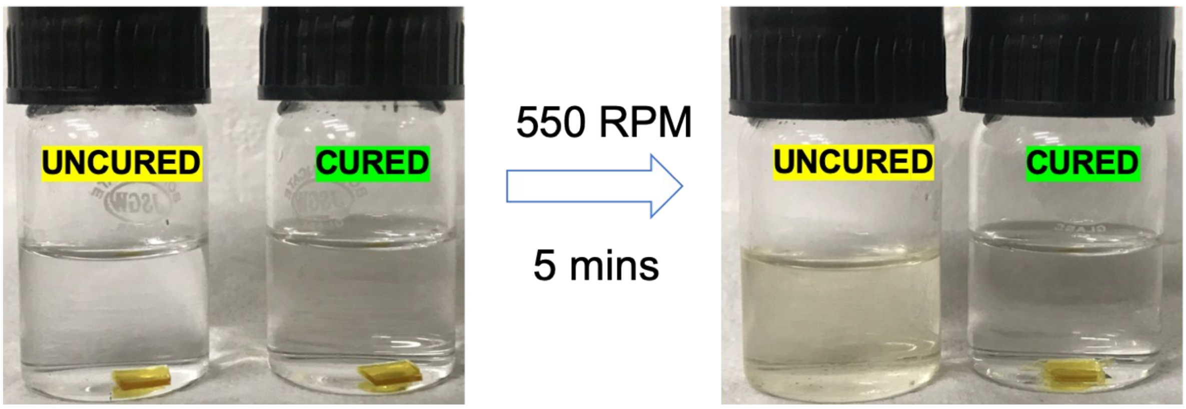
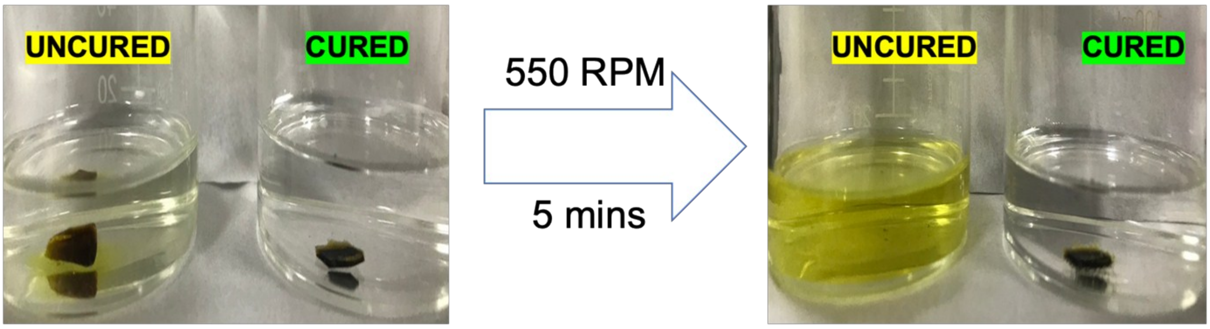


Figure S2. FTIR results for EP-pristine curing with respect to time

THF swelling test:



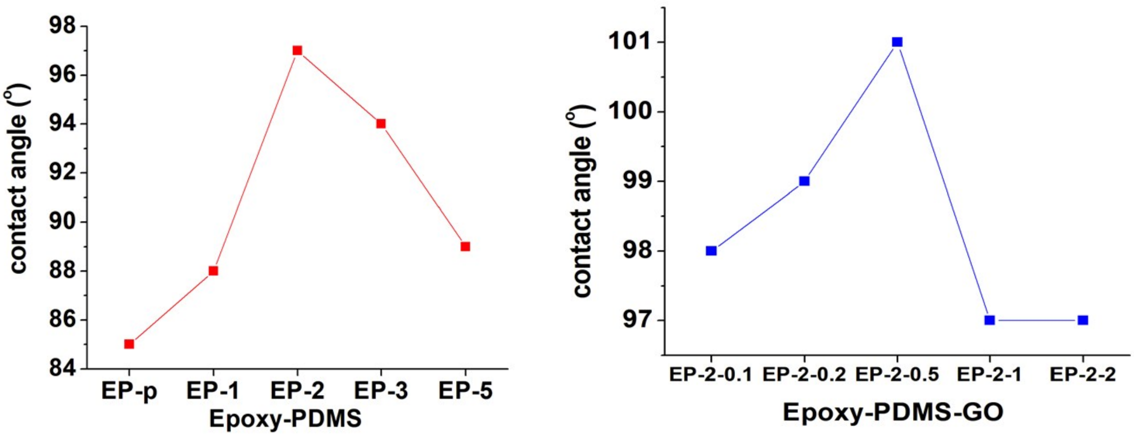
(i)



(ii)

Figure S3. THF swelling test for (i) EP-p (ii) EP-2-0.5

Contact angle measurements



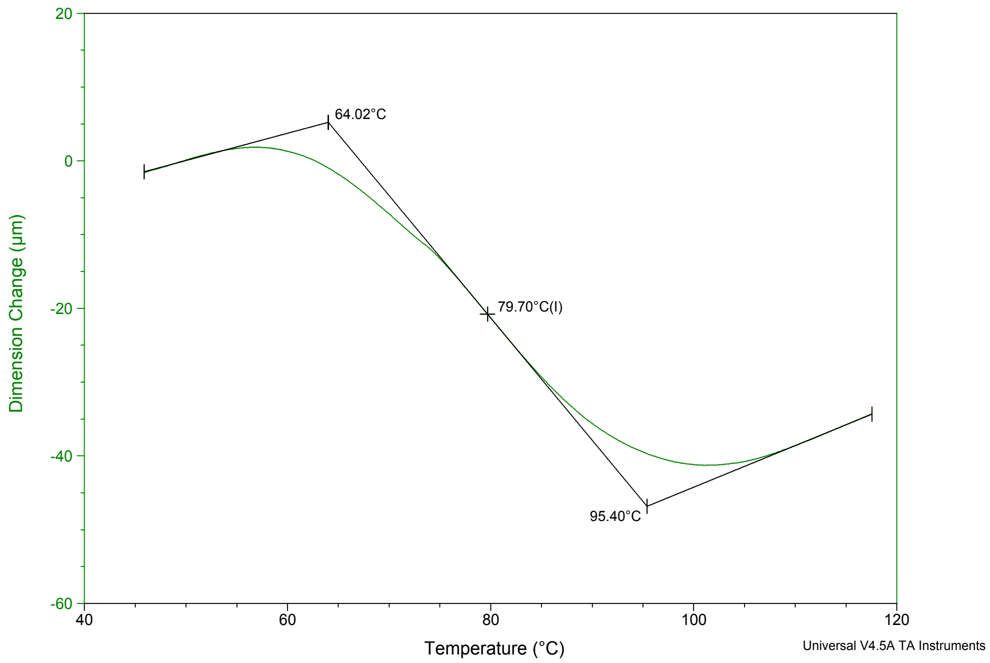
(a) (b)

Figure S4. Contact angle measurements of different samples.

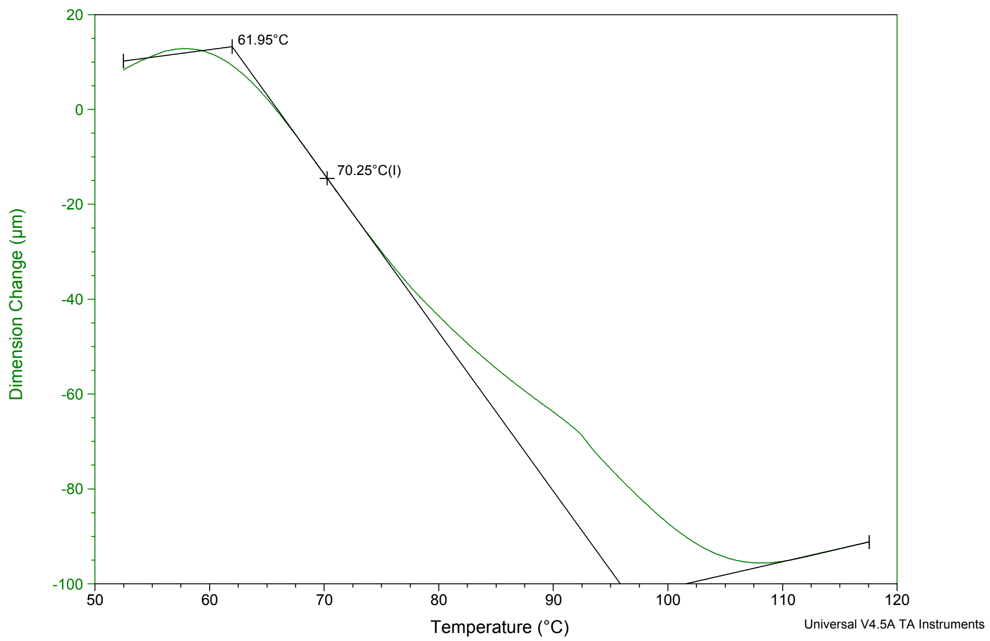
Glass transition temperature:

The different nano fillers contained epoxy vitrimer glass transition was analyzed through TA-Q400 em dimension change experiments.

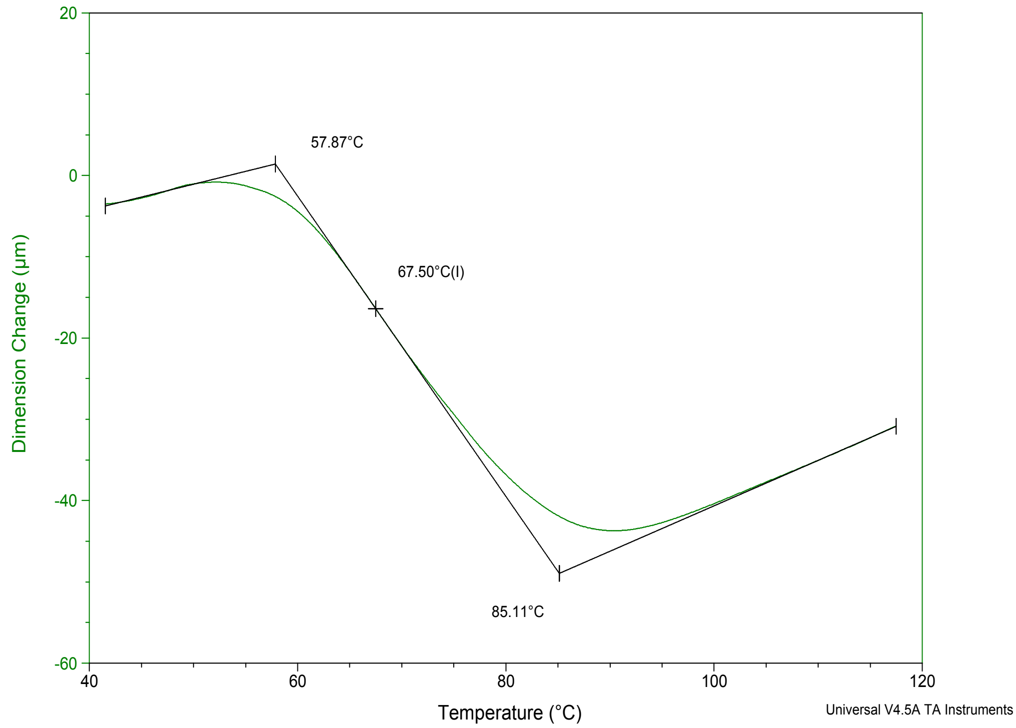
a) EP-pristine



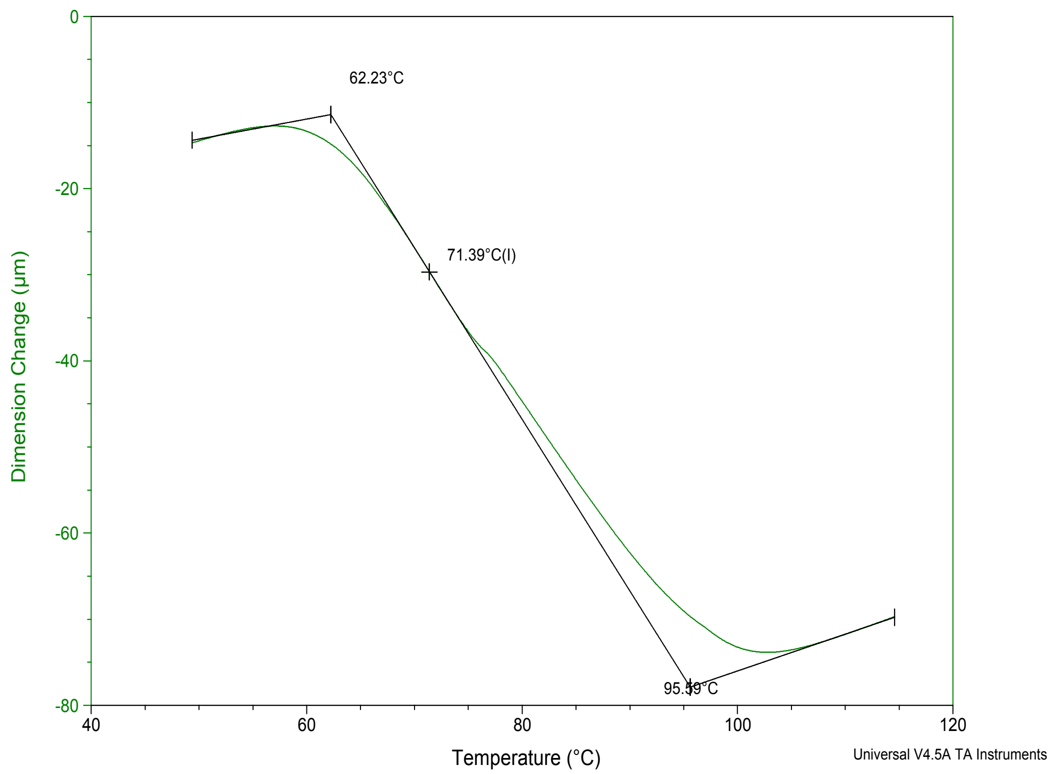
b) EP-1



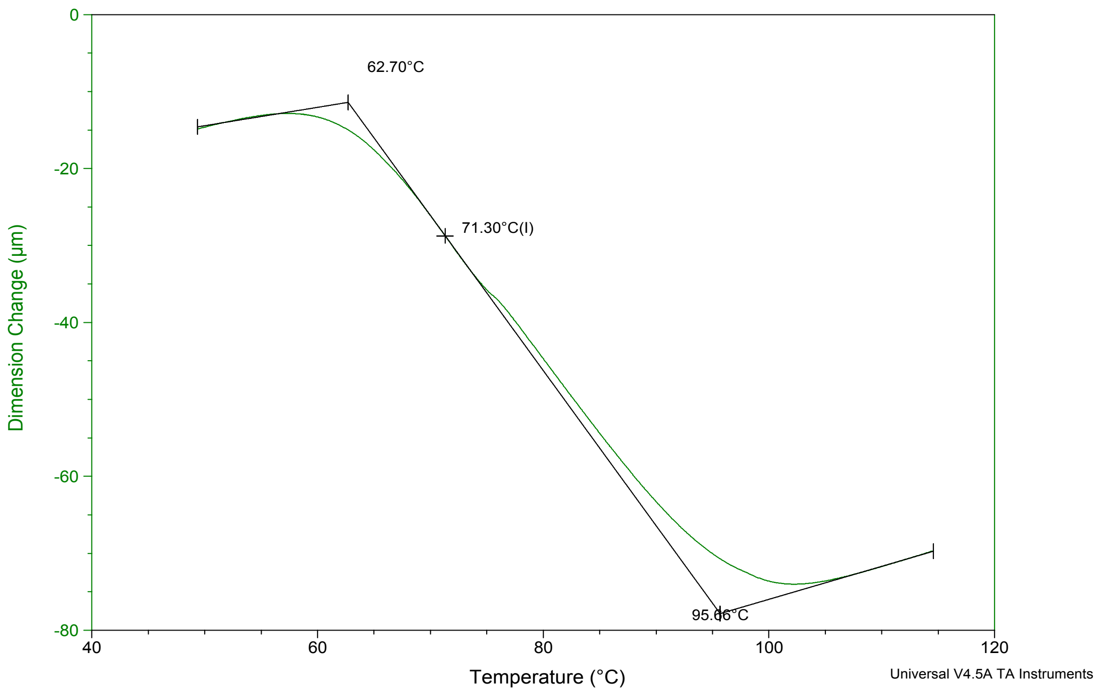
c) EP- 2


57.87°C
67.50°C(I)
85.11°C
Dimension Change (µm)
Temperature (°C)
Universal V4.5A TA Instruments

d) EP-3

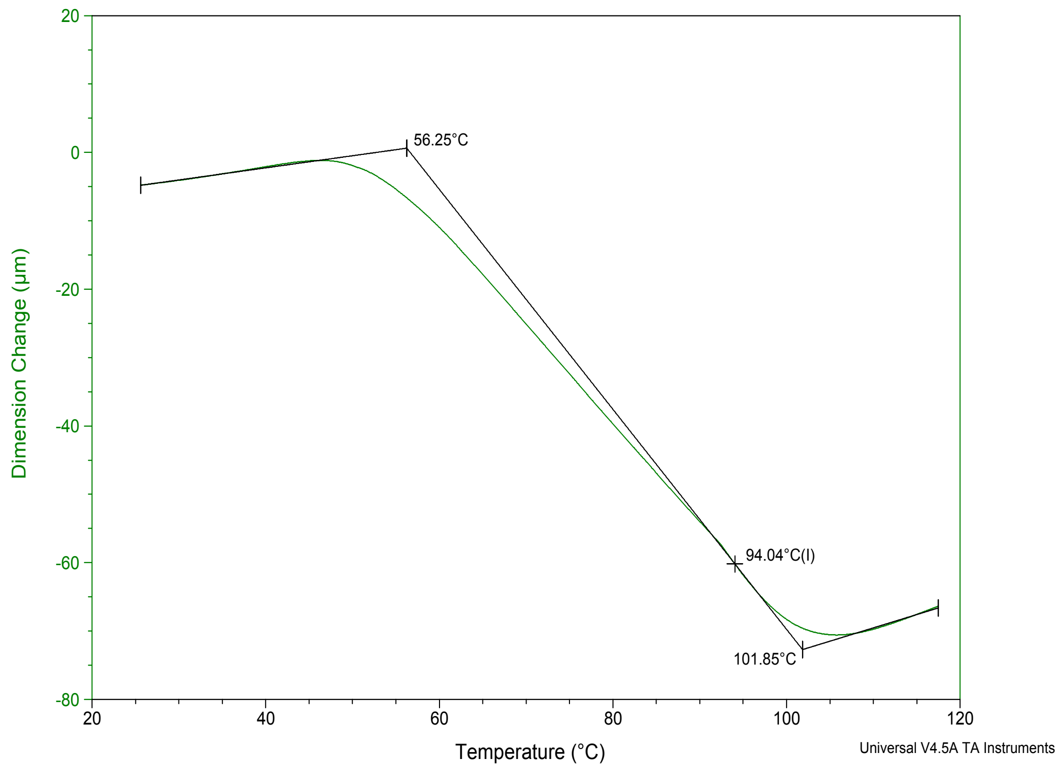

62.23°C
71.39°C(I)
95.59°C
Dimension Change (µm)
Temperature (°C)
Universal V4.5A TA Instruments

e) EP- 5



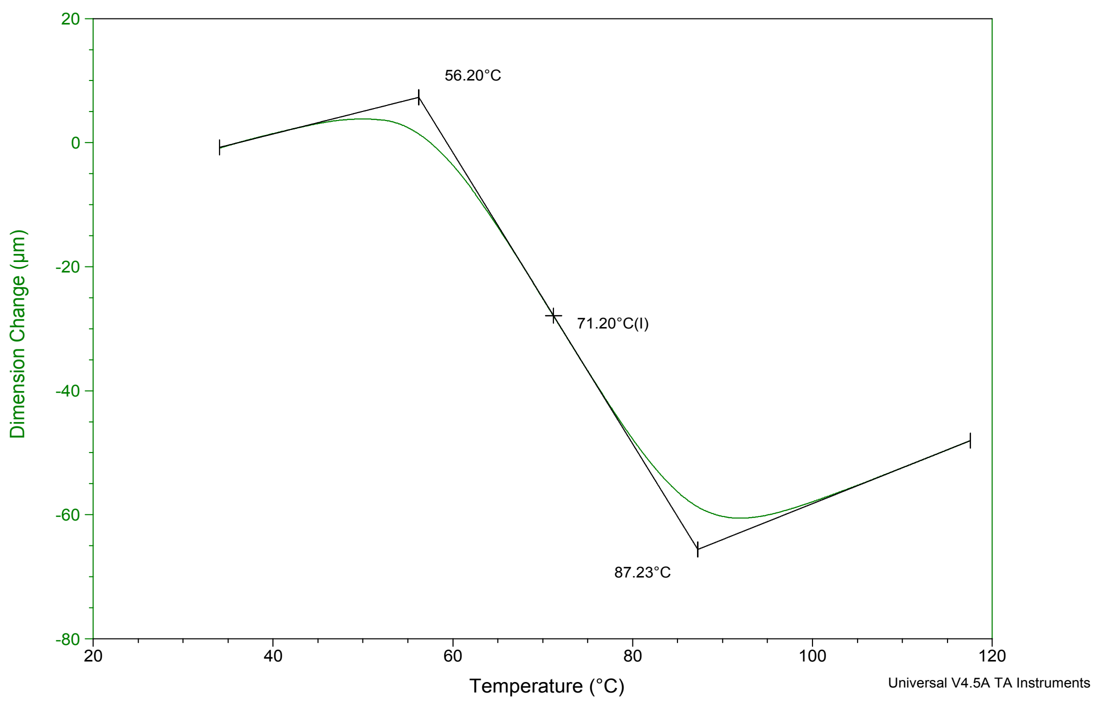
62.70°C
71.30°C(I)
95.66°C
0
-20
-40
-60
-80
Dimension Change (µm)
40
60
80
100
120
Temperature (°C)
Universal V4.5A TA Instruments

f) EP-2-0.1



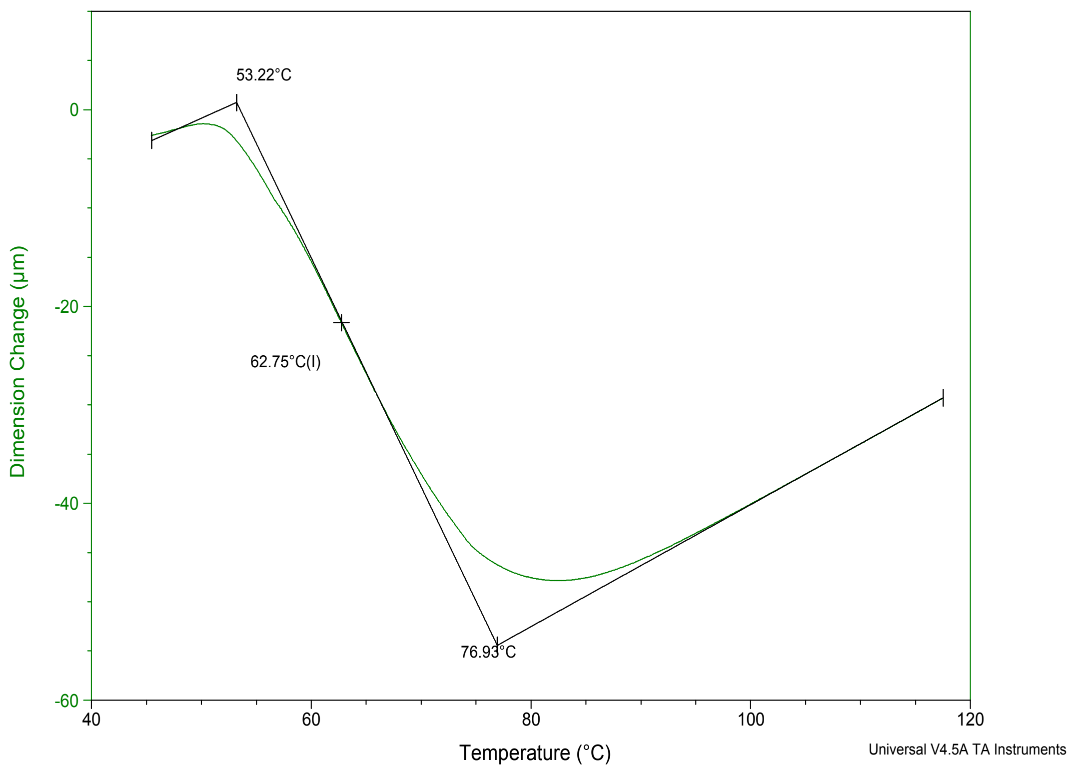
20
0
-20
-40
-60
-80
Dimension Change (µm)
56.25°C
94.04°C(I)
101.85°C
20
40
60
80
100
120
Temperature (°C)
Universal V4.5A TA Instruments

g) EP-2-0.2

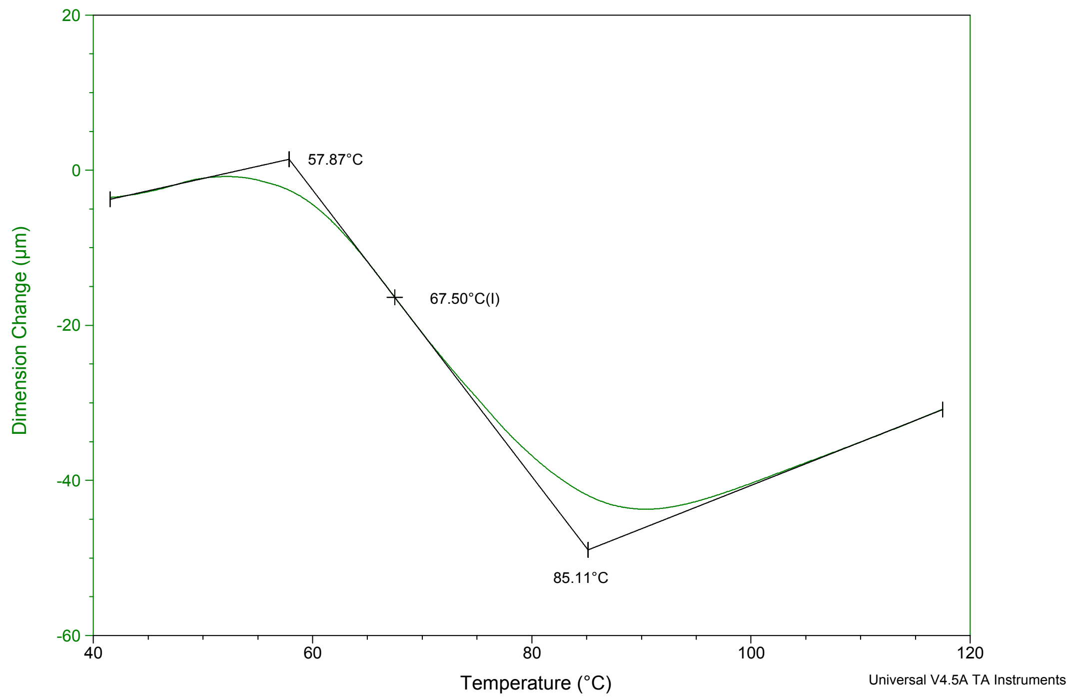


20
0
-20
-40
-60
-80
Dimension Change (µm)
56.20°C
71.20°C(I)
87.23°C
20
40
60
80
100
120
Temperature (°C)
Universal V4.5A TA Instruments

h) EP-2-0.5



i) EP-2-1



j) EP-2-2

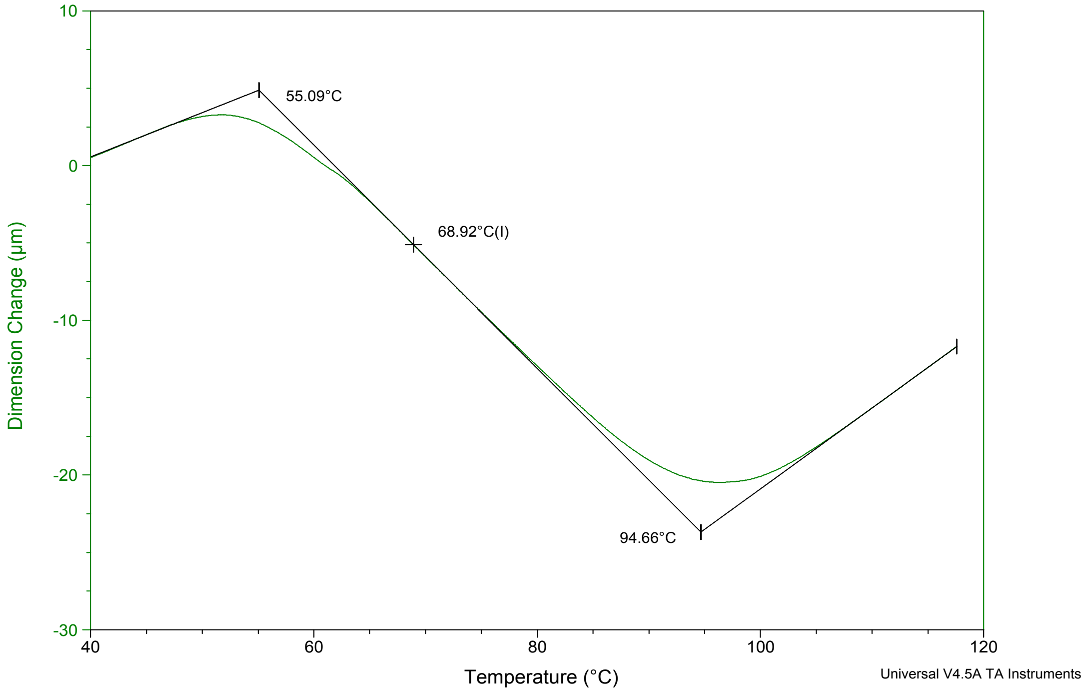
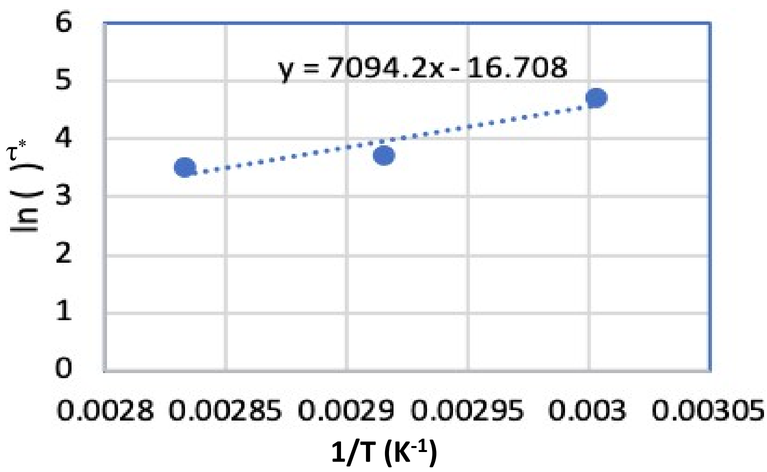


Figure S5. Glass transition temperature through TA-Q400em dimensional change experiments

Calculations for stress relaxation derived activation energy



i) EP-p :

Equation obtained from Arrhenius law: y = y = 7094.2x - 16.708

Which corresponds to: $\ln(\tau^*) = 7094.2 * 1/T – 16.708$

The Arrhenius law related to the activation energy is:

$\tau^* = \tau_0 \exp (E_a/RT)$ (S1)

Identifying this to the experimental equation: $E_a/R = 7094.2$

E_a = 7094.2 * 8.314 = 59 kJ/mol Therefore: $\ln(\tau^*) = \ln(\tau_0) + E_a/RT$

Calculation for T_v:

To calculate T_v , we used Maxwell equation (S2),

$\eta = G.\ \tau^*$ (S2)

G- Shear viscosity modulus;

Relation between shear modulus and tensile modulus,

$G = E'/\ 2(1+\upsilon)$ (S3)

Generally, υ- Poisson's ratio is 0.5 for rubbery materials. From the storage modulus (Figure 5a), average tensile modulus was observed at 80^{o}c- 120^{o}c temperature range and the obtained value 1504 MPa denoted the rubbery plateau modulus of vitrimer network.

So , $G=1504/3= 501$MPa (or) $501*10^6$ Pa

To find T_v, viscosity value arbitrary has been taken as: $\eta=10^{12}$ Pa.s.

$\tau^*= 10^{12}/(501*10^6) = 1996$ s.

$\ln(\tau^*) = \ln(1996) = 7.59$

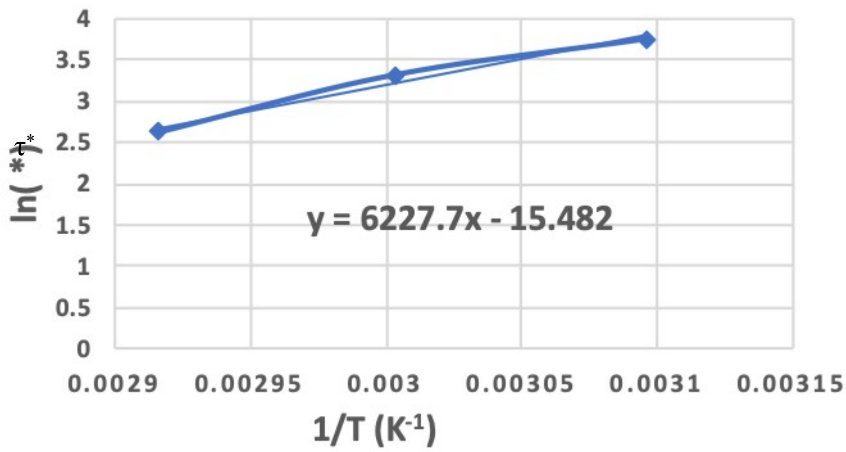
Equation obtained from Arrhenius law: $\ln(\tau^*) = 7094.2x - 16.708$

$x=1/T= (\ln(\tau^*)+16.708)/7094.2 =0.003426$

So, $T= 1/0.003426$

T_v=292 K (or) 19^{0}C .

ii) EP-2 :



Equation obtained from Arrhenius law: y = y = 6227.7X-15.482

Which corresponds to: $\ln(\tau^*) = 6227.7 * 1/T – 15.482$

The Arrhenius law related to the activation energy is:

$$\tau^* = \tau_0 \exp (E_a/RT) \quad \text{(S1)}$$

Therefore: $\ln(\tau^*) = \ln(\tau_0) + E_a/RT$

Identifying this to the experimental equation: $E_a/R = 6227.7$

E_a = 6227.7 * 8.314 = 51.7 kJ/mol

Calculation for T_v:

To calculate T_v , we used Maxwell equation (S2),

$$\eta = G.\ \tau^* \quad \text{(S2)}$$

G- Shear viscosity modulus;

Relation between shear modulus and tensile modulus,

$$G = E' / 2(1+\upsilon) \quad \text{(S3)}$$

Generally, υ- Poisson's ratio is 0.5 for rubbery materials. From the storage modulus (Figure 5a), average tensile modulus was observed at 70°c- 120°c temperature range and the obtained value 1795 MPa denoted the rubbery plateau modulus of vitrimer network.

So , $G=1795/3= 598.3$ MPa (or) $598.3*10^6$ Pa

To find T_v, viscosity value arbitrary has been taken as: $\eta=10^{12}$ Pa.s.

$\tau^*= 10^{12}/(598.3*10^6) = 1671.42$ s.

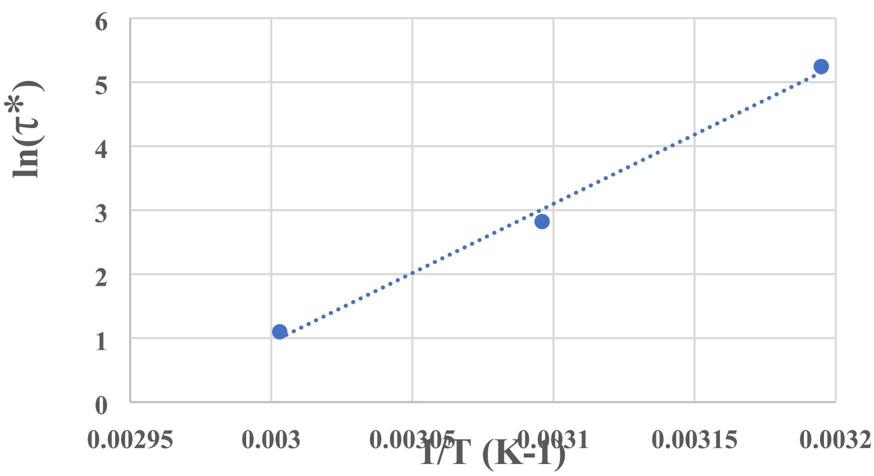
$\ln(\tau^*) = \ln(1671.42) = 7.42$

Equation obtained from Arrhenius law: $\ln(\tau^*) = 6227.7X-15.482$

$x=1/T= (\ln(\tau^*)+15.482)/6227.7 =0.003677$

So, $T= 1/0.003677$

T_v=272 K (or) -1^{0}C .



iii) **EP-2-0.5 :**

Equation obtained from Arrhenius law: y = y = 21639x-63.982

Which corresponds to: $\ln(\tau^*) = 21639 * 1/T - 63.982$

The Arrhenius law related to the activation energy is:

$\tau^* = \tau_0 \exp (E_a/RT)$ (S1)

Therefore: $\ln(\tau^*) = \ln(\tau_0) + E_a/RT$

Identifying this to the experimental equation: $E_a/R = 21639$

E_a = 21639 * 8.314 = 179.9 kJ/mol

Calculation for T_v:

To calculate T_v , we used Maxwell equation (S2),

$\eta = G. \tau^*$ (S2)

G- Shear viscosity modulus;

Relation between shear modulus and tensile modulus,

$G = E'/ 2(1+\upsilon)$ (S3)

Generally, υ- Poisson's ratio is 0.5 for rubbery materials. From the storage modulus (Figure 5a), average tensile modulus was observed at 60°c- 120°c temperature range and the obtained value 2452 MPa denoted the rubbery plateau modulus of vitrimer network.

So , $G=2452/3= 817.3$ MPa (or) $817.3*10^6$ Pa

To find T_v, viscosity value arbitrary has been taken as: $\eta=10^{12}$ Pa.s.

$\tau^*= 10^{12}/(817.3*10^6) = 1223.5$ s.

$\ln(\tau^*) = \ln(1223.5) = 7.1$

Equation obtained from Arrhenius law: $\ln(\tau^*) = 21639x-63.982$

$x=1/T= (\ln(\tau^*)+63.982)/21639 =0.00328$

So, $T= 1/0.00328$

T_v=304 K (or) 31⁰C .

Supporting videos:

1. EP-p self-healing