Supporting Information

Renewable resource derived aliphatic hyperbranched polyurethane/aluminium hydroxide-reduced graphene oxide nanocomposites as robust, thermostable material with multi-stimuli responsive shape memory features

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Table S1 Compositions of the reactants (mmol) in polyurethanes

Composition	HPU-AH-rGO0.3	HPU-AH-rGO0.5	HPU-AH-rGO1.0	HPU-AH-rGO2.0
PCL	1.0	1.0	1.0	1.0
MGE	2.0	2.0	2.0	2.0
COMP	1.0	1.0	1.0	1.0
IPDI	4.5	4.5	4.5	4.5
Hard Segment %	36	36	36	36
Soft Segment %	59	59	59	59
Branching Unit %	4.7	4.7	4.7	4.7
Renewable source %	19.3	19.3	19.3	19.3

Table S2 Thermal degradation temperature of nanocomposites

Parameter	HPU-AH-rGO 0.3	HPU-AH-rGO 0.5	HPU-AH-rGO 1.0	HPU-AH-rGO 2.0
Onset decomposition temperature, T_{on} (°C)	300	306	308	315
Maximum decomposition temperature, T_{max} (°C)	375	375	377	378
End-decomposition temperature, T_{end} (°C)	430	437	442	446

Table S3 Transition temperature of nanocomposites

Parameter	**HPU-AH-rGO 0.3**	**HPU-AH-rGO 0.5**	**HPU-AH-rGO 1.0**	**HPU-AH-rGO 2.0**
Glass transition temperature of soft segments, T_g (°C)	-52.0	-52.3	-52.0	-52.1
Glass transition temperature of hard segments, $T_{g'}$ (°C)	-4.0	-0.5	1.5	2.0
Melting transition temperature, T_m (°C)	56.7	62.0	63.5	68.7

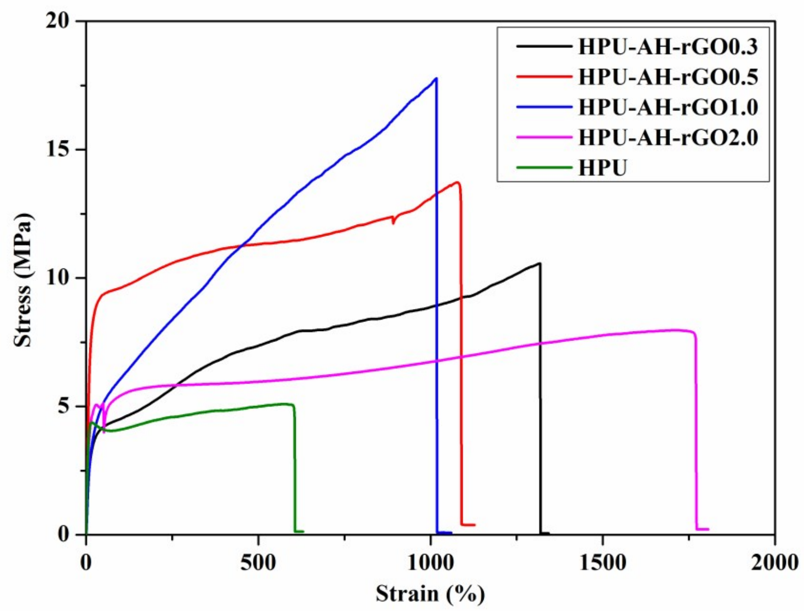

Figure S1 Stress-strain profile of HPU-AH-rGO nanocomposites

Comparison of performance of HPU-AH-rGO and HPU-GO

In order to distinguish between hyperbranched polyurethane nanocomposites based on AH-rGO nanohybrid and GO, bio-based hyperbranched nanocomposites with GO was fabricated and its mechanical, thermal properties, along with shape memory behaviour were evaluated. In a typical experiment, HPU-GO nanocomposite with 1wt% of GO was prepared by following the as-reported fabrication technique. The performance of the HPU-GO nanocomposite was compared with its AH-rGO counterpart to judge the superiority of the latter.

Mechanical performance

From the mechanical performance study as tabulated in **Table S4**, it can be seen that the effect of rGO and GO are different in terms of tensile strength, elongation at break and toughness of the nanocomposites.

Table S4 Mechanical properties of HPU-AH-rGO1.0 and HPU-GO1.0

Parameter	HPU-AH-rGO1.0	HPU-GO1.0
Tensile strength, σ (MPa)	17.7	14.23
Elongation at break, ε(%)	1018.7	1178.5
Toughness[a], T (MJm^{-3})	123.02	101.55

[a]Calculated by integrating the stress-strain curves.

This was also reflected in the stress-strain profile of nanocomposites (**Figure S2)**. The reason for this dissimilarity can be attributed to lesser re-inforcing effect of the HPU matrix by GO, in comparison to AH-rGO. GO contains large number of polar functionalities and hence more structural defects in their graphitic domains, due to which it causes difficulty in fabrication process. As a result, the extent of urethane reaction is less, as it is stopped before gel formation. Further, it is necessary to mention that the amount of rGO is less than 1 wt%, as AH is also present in the nanohybrid.

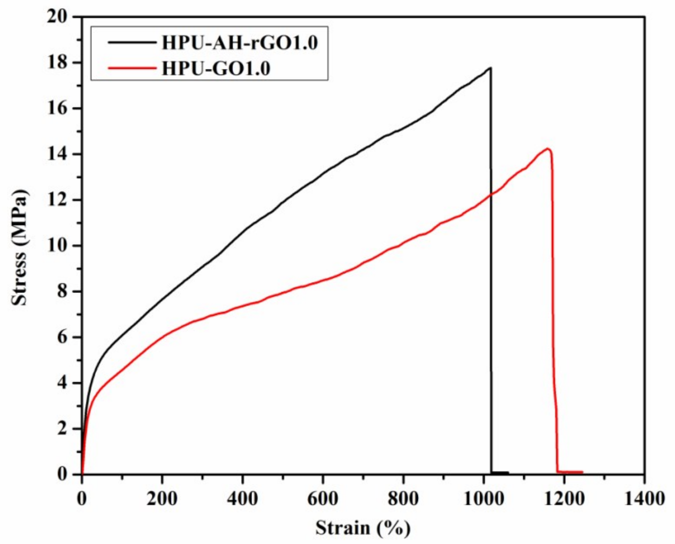

Figure S2 Stress-strain profile of HPU-AH-rGO1.0 and HPU-GO1.0

Thermal properties

From the thermal study of the nanocomposites, it is evident that HPU-AH-RGO nanocomposite is thermally more stable than HPU-GO nanocomposite (**Table S5**).

Table S5 Thermal properties of HPU-AH-rGO1.0 and HPU-GO1.0

Parameter	HPU-AH-rGO 1.0	HPU-GO 1.0
Onset decomposition temperature, T_{on} (°C)	308	300
Maximum decomposition temperature, T_{max} (°C)	375	370
Endset-decomposition temperature, T_{end} (°C)	437	450

As seen in **Figure S3**, the HPU-AH-rGO nanocomposite shows enhanced initial degradation temperature than HPU-GO due to the better re-inforcement of the polymer matrix, provided by the rGO sheets, and insulating property of AH. GO with its structural defects in the graphitic domains could not strengthen the HPU matrix as much as AH-rGO.

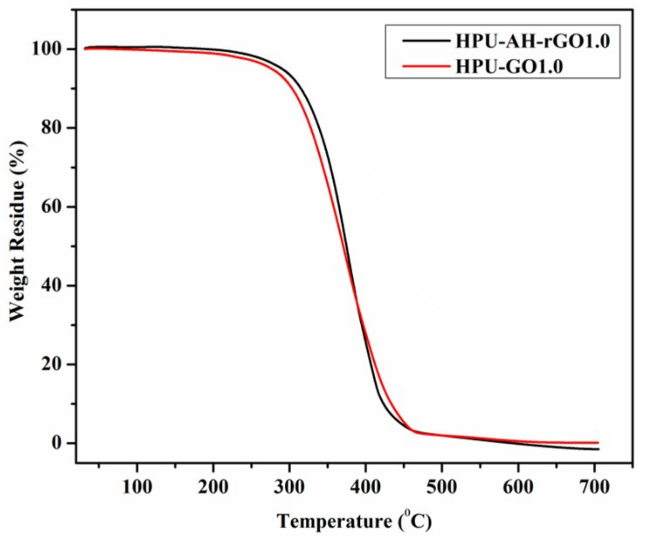

Figure S3 TG curves of HPU-AH-RGO1.0 and HPU-GO1.0

Shape memory study

The shape memory performance study of the HPU-GO nanocomposite was conducted with different external stimuli like thermal heating (60 (±5) °C) and microwave (300 W) and the results are tabulated in **Table S6**. The nanocomposite displayed longer shape recovery time than that of HPU-AH-rGO, under thermal heating (**Figure S4**) and microwave. Moreover, the shape recovery (%) of HPU-GO was low compared to HPU-AH-rGO. This result can be attributed to the GO acting as the nano-filler in the nanocomposite. The structure of GO contains some structural defects that perturb the graphitic domains. Due to these structural defects, GO behaves as a less conducting material than rGO, thereby causing fluctuation in distributing the restoring force within the polymer matrix to attain the original shape.

Table S6 Shape memory features of the HPU-AH-rGO1.0 and HPU-GO1.0

Stimulus		HPU-AH-rGO1.0	HPU-GO1.0
Thermal	Shape recovery time (s)	23	120
	Shape recovery (%)	96.8	96.1
MW	Shape recovery time (s)	97	220
	Shape recovery (%)	97.3	95.4

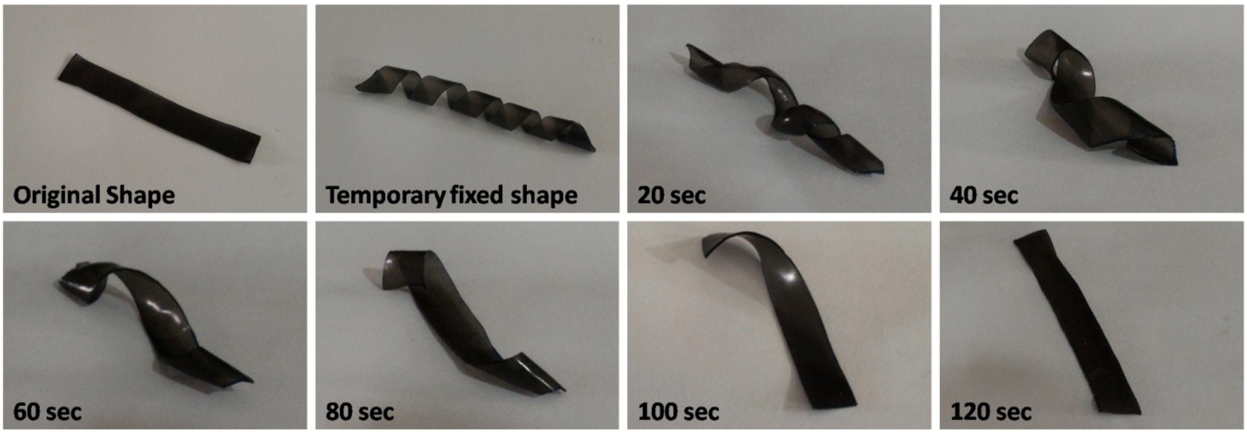

Figure S4 Shape memory behaviour of HPU-GO1.0 under thermal heating