

Reduced graphene oxide as a novel nanofiller for flexible polyurethane foams

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A new kind of carbon nanofiller can be used to achieve improved mechanical properties, such as apparent density, tensile strength, and elongation at break, of the modified materials.

Carbon nanocomposites are a recent development within the field of materials engineering.¹ Furthermore, the perfect mechanical strength, high thermal conductivity, and exceptional optical and electrical properties of graphene^{2–7} mean that it has attracted a substantial amount of attention in research fields such as electronics,^{8–11} catalysis sensors,¹² and composites.¹³ Polyurethane foam (PUF) matrices can be modified to obtain materials with unique properties. For instance, when graphene and PUF are combined in novel composites, the resultant material can have better mechanical properties than graphene, and greater flexibility and tensile strength than polyurethane. Unfortunately, the high cost of graphene has so far inhibited progress in research in obtaining such novel composites. In addition, there is a significant issue concerning the dispersion of the graphene nanofillers within the polymeric matrix.

One of the most promising ways to improve the dispersion and interphase binding between graphene and a polymeric matrix is chemical functionalization of graphene. This can be achieved by adding groups that contain oxygen (i.e., carbonyl, carboxyl, hydroxyl, and epoxy) to graphene, as well as the oxidation of graphene to graphene oxide.^{14, 15} Such modified graphene oxide can then be incorporated into the polymeric matrix via a covalent bond. In this way, graphene may act as both a cross-linking agent and a conventional reinforcing filler.^{16, 17} Scanning electron microscope images of graphene oxide and thermally reduced graphene oxide are shown in Figure 1. In the past, several different components have been used as nanofillers for PUFs. Aluminosilicate nanofillers have been used, for example, but these only improved the thermal stability of the composites. In addition, the foams that were obtained became more rigid and did not meet basic requirements. Other inorganic nanofillers have been used (e.g., nanosilicate or titanium oxide), but the properties of the resulting foams were also inappropriate.

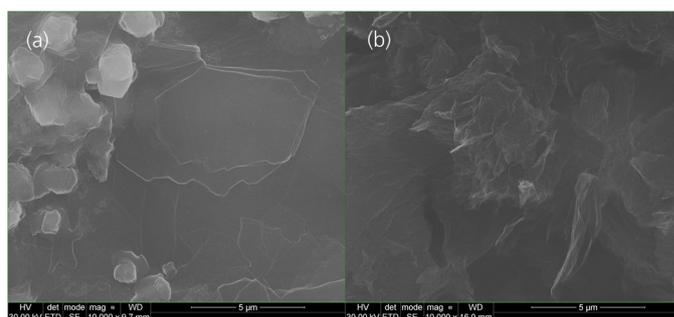


Figure 1. Scanning electron microscope images of (a) graphene oxide and (b) thermally reduced graphene oxide.

In this work,¹⁸ our primary aim was therefore to improve the mechanical properties—as well as the stiffness—of the foams. For this reason, we decided to use reduced graphene oxide (RGO) as the nanofiller material. To improve the dispersion of graphene within the polymeric matrix, we obtained the RGO from graphene oxide that was subjected to thermal reduction at 200°C. We produced this graphene oxide via a modified Hummers method, with the use of potassium permanganate and sulfuric acid. Our use of RGO was also advantageous for several other reasons. These reasons include the fact that RGO is a novel nanofiller material, there have been no previous studies of the interaction between RGO and a polymeric matrix, and that our work involves the use of two unique materials and presents an improvement in mechanical properties (e.g., tensile strength).

We obtained flexible nanocomposite foams on a laboratory scale with the use of the one-step method for a two-component (A and B) system, with an isocyanate/hydroxyl (NCO/OH) solution in a 1:0.9 ratio. We used a polyol mixture for component A, which consisted of two oligoethers (Rokopol M1170 and Rokopol F3000), catalysts, chemical blowing agents, surfactant, and 0.25–0.75wt% nanofillers. We prepared the foams by vigorous stirring with a mechanical stirrer for 30 minutes

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Table 1. Mechanical properties of flexible pure polyurethane foam (P_0) and polyurethane/reduced graphene oxide nanocomposite foams. The $P_{0.25}$, $P_{0.5}$, and $P_{0.75}$ foams contain 0.25, 0.5, and 0.75wt% reduced graphene oxide nanofiller, respectively. T_{sb} : Tensile strength. E_b : Elongation at break.

Properties	Flexible foams			
	P_0	$P_{0.25}$	$P_{0.5}$	$P_{0.75}$
Apparent density (kg/m ³)	114.4±3.3	119.4±3.8	121.0±3.4	122.0±3.4
T_{sb} (kPa)	85±4	95±6	110±4	91±3
E_b (%)	110±4	105±4	120±4	74±4
Cell size (μm)	103±14	174±15	233±26	365±44

Table 2. Dynamic mechanical analysis results for the flexible pure polyurethane foam and polyurethane/reduced graphene oxide nanocomposite foams. T_g : Glass transition temperature. E' : Storage modulus.

Properties	Flexible foams			
	P_0	$P_{0.25}$	$P_{0.5}$	$P_{0.75}$
T_g (°C)	-31	-28	-23	-22
E' (MPa)	-50°C	6.92	8.06	12.91
	-40°C	2.84	5.22	9.95
	-30°C	0.39	0.90	0.80
	-20°C	0.08	0.08	0.08

and subsequent sonication with the use of an ultrasonic homogenizer for 20 minutes. In the next step, we mixed the nanoparticulated polyol matrix with component B (4,4-methylene diphenyl diisocyanate) at a predetermined mass ratio for 10s at 1800rpm (using a dispersing turbine-type impeller of 2.5cm diameter at 25.8°C and 70% relative humidity). We then poured the resulting reaction mixture into an open metal mold (approximately 40 × 100 × 200mm). After demolding, we stored the PUF samples at room temperature for 48 hours.

We conducted a series of mechanical tests (with the use of a Zwick/Roell Z020) on our PUF composites. A comparison between the properties of a pure flexible foam and our polyurethane/RGO nanocomposite foams is presented in Table 1. These results demonstrate that the incorporation of thermally reduced graphene oxide into the structure of flexible PUFs results in improved mechanical parameters (e.g., apparent density, tensile strength, and elongation at break) for the modified materials.

We also used a TA Q800 instrument to perform a dynamic mechanical analysis on our foam samples. From the results of this analysis (see Table 2), we observed that the material stiffness increased with increasing content of the carbon nanofiller. This phenomenon is related to the reduced mobility of the polymeric chains. Our results also demonstrate that addition of even a small amount of RGO can cause increased thermal stability of the modified foam. In addition, we proved that after a

specific RGO content (0.5wt%) is exceeded, the physiochemical properties of the obtained foams start to deteriorate.

In summary, we have produced a set of polyurethane foams that include reduced graphene oxide as a novel nanofiller material. The results of our investigation into the characteristics of these flexible foams indicate that the incorporation of thermally reduced graphene oxide into flexible PUFs can enhance both the mechanical and thermal properties of the obtained materials. In our future work we plan to further modify our material systems and polymeric matrices. We will also study additional developments and modifications of graphene for nanocomposite purposes.

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