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Organic Chemistry

Synthesis of UV Curable rGO/PDMS Nanocomposites

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ABSTRACT. Liquid UV curable PDMS was produced with rGO for SLA printer. Lab homogenizator was used for good dispersion of filler into polymer. Nanocomposites were produced with different content of 0.5-0.8 wt% filler for further characterization of electrical, electromagnetic, thermal and mechanical properties. Materials structure and composition were identified by FT-IR, NMR, TEM, Raman, X-ray and DSC analyses in order to determine the filler dispersion, exfoliation, defects and thermal characteristics. *© 2018 Bull. Georg. Natl. Acad. Sci.*

Key words: synthesis, nanocomposite, 3D printer

Stereolithography (SLA) employs a single beam laser to polymerize or crosslink a photopolymer resin. By drawing on the liquid photopolymer resin with a light beam, thin layers of polymer are stacked layer by layer [1]. Elastomers based on polydimethysiloxanes (PDMS) are important materials due to the properties, such as chemical inertness, flexibility, optical transparence. Also they have a very low surface tension (20.4 mN/m) and glass transition temperatures (146 K) [2]. It is possible to print support material that holds the PDMS pre-polymer in place until it can be treated by UV light using a photoactive cross-linking agent [3].

PDMS needs crosslinking to satisfy operating requirements. The traditional thermal treatment of PDMS takes much time and energy. Because of this UV treated PDMSs were synthesized by different methods. Also reduced graphene oxide (rGO) used as filler in nanocomposites was obtained.

Materials structure and composition in all stages of the projects were characterized by FT-IR, NMR, TEM, Raman, X-ray and DSC analyses in order to determine the filler dispersion, exfoliation, defects and thermal characteristics.

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Materials and Experimental Methods

Materials. We used aminopropyl terminated polydimethylsiloxane (Mw ~ 25 000; 30 000) in liquid form supplied by *Gelest*. 2-Isocyanatoethyl methacrylate (MOI), 2-ethylhexyl acrylate, Diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide supplied from *Sigma Aldrich*.

Synthesis of polymers, rGO and nanocomposites was conducted in Sichuan University and SITP. Nanocomposites were obtained by physical mixing method in homogenizator at speed 200 rpm during 4 h.

Syntheses of polymers, rGO and nanocomposites were conducted. Liquid polymer nanocomposites with content (0.5, 0.6, and 0.8 %) rGO were produced in amounts of 30 g and previously treated by UV for 2-3 h.

Table 1.Nanocomposites for SLA printer

Polymer	Monomer	Dopant %
A-31	20	rGO – 0.5%
A-31	30	rGO – 0.5%
A-32	20	rGO – 0.5%
A-32	30	rGO – 0.5%

Methods. Modern instrumental methods are used in research process:X-ray diffraction analysis of the synthesized nanopowders and polymeric materials were carried out on DRON-3M with diffraction molecules. CuKα radiation (λ = 1.54178 Å); used copper antioxidant x-ray apparatus BSV – 28. Data were recorded in 2θ range of 5°-70° at the scan rate of 40/min at room temperature. The time constant was 1 second.

The particle size analysis is performed using a nanometer (Dynasizer-Analysette-12, FRITSCH). Measuring range is from 1 nm to 6000 nm. Measurement concentrations are done between 0.0003 up to 40 Vol. Direct sample application without cuvettes. Intelligent evaluation with high-performance Padé-Laplace algorithm, measurement of the real particle size distribution, user-friendly operation, simple simulation of measuring data. ISO 13321/21 CFR part 11 are used.

FTIR spectra were obtained on a Nicolet Nexus (Thermo Nicolet Corp., Madison, WI) 470 machine with an mercury-cadmium-telluride detector type B (MCTB). ^{1}H-NMR spectra were recorded on a Bruker (Rheinstetter, Germany) ARX400 NMR spectrometer at a 400-MHz operating frequency with $CDCl_3$ as the solvent and an internal standard.

DMTA - Dynamic Mechanical Thermal Analysis

Equipment. AR-G2 Rheometer& DMTA; temperature range from -80°C to 20°C; regime of oscillation: Load = 1N; frequency = 1 Hz are identified.

Experiments. At first A-31/A-32 and MOI were mixed with 1:1 molar ratio at ambient temperature and stirred for 1 h. The reaction goes without catalyst. End of the reaction is identified by FT-IR when peak at 2271 cm^{-1} of the –N=C=O disappeared. The second step is addition of photoinitiator is dissolved in monomer, then polymer treatment by Ar for removal oxygen and UV for 2-3 h.

Liquid polymer nanocmoposites are prepared with different content (0.5, 0.6, 0.8 %) rGO and optimized the process. For this purpose, 0.5% rGO was added to polymers and homogenized at speed 200 rpm for 4 h. Then nanocomposite was placed to Teflon form and treated by UV.

We used natural powder graphite to prepare a GO colloidal solution (20 $mg \cdot mL^{-1}$) using modified Hummers' method (20). In brief, a blend of natural graphite powder (2 g) and $NaNO_3$ (1.5 g) were placed in cold (0°C) concentrated H_2SO_4 (69 mL), and then $KMnO_4$ (9 g) was gradually and slowly added by stirring. The mixture was placed in to ice water for 12 hours and then heated up to 35°C for 1 hour. The deionized water (200 mL) was added when the mixture was cooled to room temperature and then heat to 60°C for 18 hours. H_2O_2 was added drop wise until the solution became bright yellow, and then the solution was first washed by centrifugation with 10% hydrochloric acid solution for 3 times and then washed with deionized water to neutral to obtain the GO colloidal solution. Reduction of GO solution was carried out in microwave.

Results and Discussion

In this work UV curable PDMS synthesis method was investigated. Synthesized polymers are vitreous liquids. Structure and composition of reaction products were established according to FT-IR and NMR (Fig. 1). In the 1H-NMR spectra of polymers we observed signals characteristic for methyl protons of ≡Si-CH3 with chemical shifts ofδ≈0.12 ppm and 0.55 ppm. Also we observed triplet signals characteristic for – urea fragment with chemical shift of δ≈6.1 ppm.

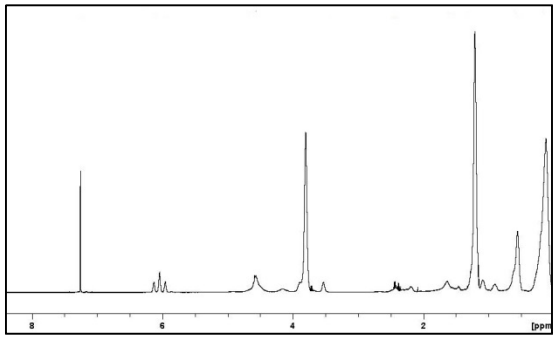

Fig 1.1H-NMR spectrum of UV curable PDMS.

The obtained rGO were characterized by XRD, Raman, SEM(Fig 2,3). In XRD we observed peak at 200 which belongs to rGO and SEM shows that obtained rGO layers have thickness ≈20-40.

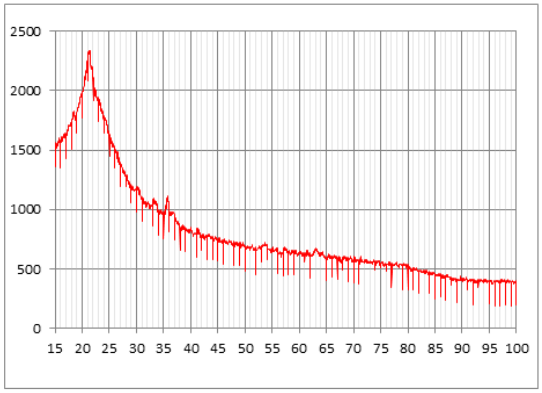

Fig 2. XRD of rGO.

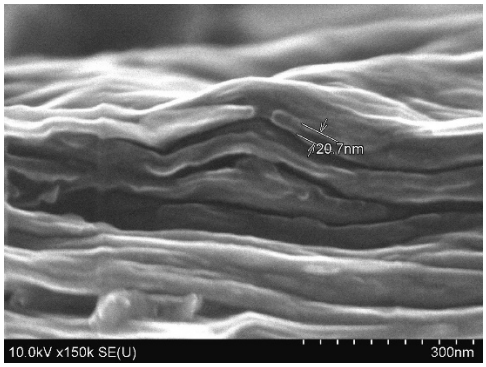

Fig 3. SEM of rGO.

Laser nanosizer was used for determination of nanoparticles. rGO suspension was treated before determination in ultrasound bath, then one drop was placed on the lens.

Table 2. Measurement of nanoparticles Dn 10%: 40.78 Dn 50%: 51.39 Dn 90%: 81.59 Mean Size (Number): 56.98 nm

Peak	Mode	Mean	StdDev	Intesity
1	51.39 nm	51.08 nm	17.27 %	89.89 %
2	93.73 nm	93.46 nm	9.37 %	10.11 %

Pure PDMS, PDMS with 05.% and 0.8 % content filler were investigated by DMTA analysis. Fig 4 shows that by increasing of filler relaxation time is increasing too.

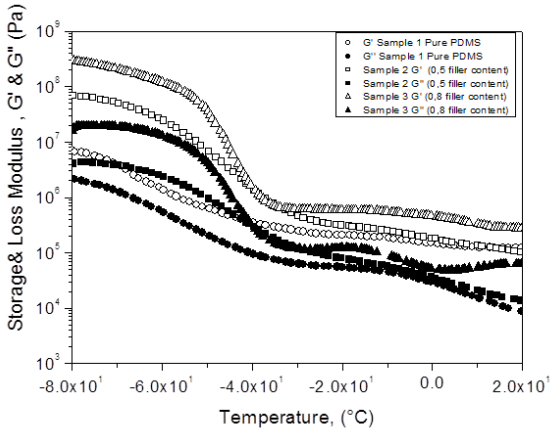

Fig 4. Storage modulus and loss modulus as a function of temperature.

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Conclusions

Liquid UV curable PDMS was produced with rGO for SLA printer. Lab homogenizator was used for good dispersion of filler into polymer. 2 formulations were produced with different content of 0.5-0.8 wt% filler for further characterization of electrical, electromagnetic, thermal and mechanical properties. Nanocomposites mechanical properties improve by increasing of filler content.

ორგანული ქიმია

უი სხივებით გაკერვადი აღდგენილი გარფენისოქსიდი/პოლიდიმეთილსილოქსანის ნანოკომპოზიტის სინთეზი

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**ბულგარეთის სამეცნიერო აკადემია, მიკრო და ნანო მექანიკის ექსპერიმენტალური ლაბორატორია, მექანიკის ინსტიტუტი, სოფია, ბულგარეთი

(წარმოდგენილია აკადემიის წევრის შ. სამსონიას მიერ)

სამგანზომილებიანი (3D) ბეჭდვა ხშირად მიიჩნევა დამატებითი წარმოების სინონიმად. ცნობილია 3D პრინტერების რამდენიმე სახეობა, სადაც ჩვეულებრივ გამოყენებულია პოლიმერები. სტერეოლითოგრაფიის აპარატში გამოყენებულია ლაზერის ერთი სხივი პოლიმერიზაციისთვის ან ფოტოპოლიმერის გასაკერად. სინათლის სხივების მოქმედებით თხევად ფოტოპოლიმერზე იქმნება მასალა ფენა-ფენა. პოლიდიმეთილსილოქსანის ელასტომერი (PDMS) არის ნივთიერებების მნიშვნელოვანი კლასი მათი თვისებების გამო, როგორიცაა ქიმიური ინერტულობა, მოქნილობა, ოპტიკური გამჭვირვალობა, ასევე მათ გააჩნიათ ძალიან დაბალი ზედაპირის დაძაბულობა (20,4 მნ/მ) და გამინების ტემპერატურა (146 K). შესაძლებელია PDMS-ის ჯაჭვზე ფოტოაქტიური ჯგუფების დამაგრება და ახალი უი სხივებით გაკერვადი პოლიმერების მიღება. სამუშაოს ფარგლებში დასითეზებულია უი სხივებით გაკერვადი პოლიდიმეთილსილოქსანი, რომელშიც შემავსებლად დამატებულია აღდგენილი გრაფენის ოქსიდი სხვადასხვა კონცენტრაციით (მას. %). პოლიმერში შემავსებლის კარგად გადანაწილების მიზნით, გამოყენებულია ლაბორატორული ჰომოგენიზატორი. საწყისი მასალების და მიღებული ნანოკომპოზიტების სტრუქტურა და შედგენილობა შესწავლილია ბმრ, იწ და რამან სპექტროსკოპული მეთოდებით, ელექტრონული მასკანირებელი მიკროსკოპით, რენტგენით და დინამიკურ-მექანიკური ანალიზატორით. დადგენილია, რომ შემავსებლის კონცენტრაციის გაზრდით უმჯობესდება მასალის მექანიკური თვისებები.

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