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ARTICLE

Reactive emulsion mixing as a novel pathway toward water borne reduced graphene oxide/polymer composites

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A new, simple and versatile technique for synthesis of water-borne poly (methyl methacrylate/butyl acrylate)/reduced graphene oxide (rGO) composites is presented. The technique is based on emulsion mixing process, during which a water dispersible polyurethane crosslinker containing free isocyanate functionalities on both chain ends is added. The crosslinker bonds covalently the polymer and the rGO, in one complex hybrid structure. The bonding was established through spontaneous NCO reaction with OH functionalities presented on the rGO platelets surface and through OH functionalities presented on the polymer nanoparticles surface (introduced by addition of functional monomer 2-hydroxyl ethyl methacrylate during polymer synthesis). As a result highly stable composites were obtained, in which the rGO platelets were strongly bonded within the polymer matrix. This good bonding resulted in highly improved mechanical properties of the composites; thus for composite containing 1 wt% rGO, Young's modulus of elasticity increased about 14-fold, the storage modulus increased up to 100% and the modulus of elasticity increased about one order of magnitude with respect to the neat polymer. The composites exhibit electrical conductive properties, which open possibilities for their application as electrically conductive coatings in electromagnetic interference (EMI) shielding application or as flexible electronics.

Introduction

Water-borne polymers are products with a great application possibility and huge commercial value.¹ By introduction of graphene into these types of materials a wide variety of novel and interesting composite materials could be synthesized, which expands the existing applications and open new ones.

One of the most investigated techniques for synthesis of water borne graphene/polymer composite is the emulsion mixing technique.²⁻¹¹ The main advantage of this technique is the simplicity; the composites are prepared by simple mixing of two components, polymer and graphene, both in stable aqueous dispersions. Besides, emulsion mixing is a quite versatile technique and up to now diverse composites have already been synthesized with: polystyrene,^{2,4} polystyrene-butadiene rubber,⁵ poly(styrene-co-acrylonitrile),⁷ poly (methyl methacrylate),^{9,10} polyurethanes^{3,8} etc. The emulsion mixing technique offers the possibility of higher control of the polymer properties (composition, particle size and distribution, gel content and molecular weight and distribution), since their syntheses is performed prior to mixing, without influence of the presence of rGO sheets. In comparison with solution or melt blending, this

technique has the potential to produce composites with better dispersed graphene platelets, which already has been shown by preparation of polycarbonates/graphene nanoplatelets composites, in which the percolation thresholds of around 0.14 and 0.38 vol% for emulsion mixing and solution blending, respectively, were obtained.⁶

The main drawback of this technique is that the prepared composites are simple physical mixtures, with no or with weak interaction between the polymer and graphene, which highly influences the mechanical properties of the composites and their stability. The attempts to overcome this disadvantage were focused on *in situ* polymerization techniques, such as emulsion,¹²⁻¹⁵ miniemulsion,^{16,17} microemulsion,¹⁸ or Pickering emulsion¹⁹⁻²² polymerization, where the polymerization is usually carried out in the presence of graphene platelets. Mainly stronger interactions were formed during *in situ* reaction, thus the formation of hydrogen bonds,¹⁶ polar-polar interactions,¹⁵ or even covalent bond formation^{12,17} have been reported. However, the *in situ* techniques are more complicated to perform, the heterogeneous colloidal system of water borne polymers and composites additionally make it more complex

and it is almost impossible to control the polymer properties and the rGO aggregations. Furthermore, established covalent bonds between the polymers and the platelets could decrease or suppress the electrical conductivity.

In the present work, in order to use all the presented advantages of the emulsion mixing technique and to overcome its main drawback and introduce more stable interactions between the polymer chains and graphene platelets, a novel method of reactive emulsion mixing was developed. This novel method implies the addition of bi functional cross-linkers to the hybrid dispersions, aimed to establish covalent bondings with the functional groups in both, the polymer chains and the graphene platelets. For that aim, the polymer nanoparticles were functionalized with OH groups by introducing the functional monomer 2-hydroxyethyl methacrylate (HEMA) in the formulation of methyl methacrylate/butyl acrylate (MMA/BA) during the synthesis by semicontinuous seeded emulsion polymerization. As graphene material, reduced graphene oxide (rGO) was used, which between other oxygen functionalities, contains the hydroxyls groups attached to its surface. Both components were covalently connected by a water dispersible polyisocyanate crosslinker, containing free NCO on both chains. As a result, by simple physical mixing of the composites constituents, their crosslinked into stable composites was achieved, without decreasing the conductivity and with improved mechanical properties. Namely, the covalent bonds established between the NCO from the crosslinker and the existing OH groups from rGO did not introduce additional sp^3 hybridized C atoms formation in the rGO structure. Thus, with the proposed method, a new route for synthesis of water-borne graphene polymer composites was developed, in which the advantages of the both well known techniques are combined.

Experimental

Materials

The following materials were used without further purification in order to prepare emulsion polymers: technical grade monomers - methyl methacrylate (MMA, Quimidroga), butylacrylate (BA, Quimidroga) and 2-hydroxyethyl methacrylate (HEMA, Fluka); as a surfactant - sodium dodecyl sulfate (SDS, Aldrich); as initiators - 4,4'-Azobis(4-cyanovaleric acid) (V-501, Aldrich) dispersed in 1 N solution of sodium hydroxide (Aldrich) for seed preparation and potassium persulfate (KPS; Fluka analytical) for polymerization. A water-dispersible polyisocyanate, Bayhydur XP 2547, based on hexamethylene diisocyanate, (HDI, Bayer MaterialScience LLC) was used as a cross-linking agent. Oxygen-free grade nitrogen was used for purging the polymerization reactor. Tetrahydrofuran (THF, Scharlau) and acetone (Scharlau) were used as solvents.

Graphene oxide (GO) aqueous dispersion was acquired from Graphene Supermarket (concentration 4 g/L, 60% monolayer, 400 nm average platelets diameter). Polyvinyl pyrrolidone (PVP, Aldrich) was used as a stabilizer of the rGO platelets in

aqueous dispersions during the reduction of GO by hydrazine monohydrate (Aldrich).

Procedures

GO reduction. The reduction of GO was performed by hydrazine in the presence of PVP ($10.000 \text{ g mol}^{-1}$) at 90°C over 3 h-periods at a ratio hydrazine/GO of 5:1. In order to remove the side products of the reduction reaction and the excess of PVP from the dispersions they were dialyzed until neutral pH was reached, using a dialysis membrane Spectral/Por (Spectrumlabs) with MWCO: 12-14,000 Daltons.

Synthesis of polymer latexes. Semi-continuous seeded emulsion polymerization was used to synthesized poly(MMA/BA/HEMA) at a ratio 49.5/49.5/1. First, 10 wt% solids content (s.c.) seed was prepared by batch emulsion polymerization with V-501 as a free radical initiator in a 1 L-jacketed glass reactor at 75°C under a nitrogen atmosphere for 180 minutes. Agitation was provided by a stainless steel impeller at 250 rpm. In the second step, an initial charge containing the seed latex, the total amount of initiator KPS and part of the water were added to the reactor and let to reach 70°C . The pre-emulsion containing the rest of the water and the surfactant (SDS) was feed until 45 wt% s.c. was reached, for 240 minutes, after which it was left to react for another 60 minutes. The formulation used is presented in Table 1. Complete conversion was achieved. Particle size was 278 nm and gel content 31%.

Table 1. Formulation for synthesis of 45% SC latex by seeded semi-continuous emulsion polymerization

Compound	Batch reaction	Semi-continuous reaction	
	10 wt% s.c. seed charge (g)	Initial charge (g)	40 wt% s.c. latex stream (g)
Seed latex	-	160.0	
MMA	39.6	-	263.34
BA	39.6	-	263.34
HEMA	0.8	-	5.32
V-501	0.8	-	-
KPS	-	3.04	-
SDS	0.8	-	5.32
NaOH	1.9995	-	-
H ₂ O	719.4	78.34	325.5

Emulsion mixing. 4 g of polymer latex were slowly added (dropwise for 10 minutes) to the rGO dispersions (the amount of which was calculated in order to get from 0.25 to 1 % of rGO in relation to polymer), which previously was mixed with the cross-linking agent HDI. The HDI amount was approximated to have an NCO:OH ratio in the hybrid dispersion of 2:1; 1:1; and 0.5:1 (considering that the content of free NCO in the HDI structure was 25%).

Film formation. Composite films were formed by water evaporation under controlled conditions (25°C and 80% humidity) in a Temperature and Humidity Chamber (Espec,

SH-641). Different quantities of hybrid latex, in order to obtain a 0.5 mm thick composite film, were casted into a 5.5x2.5 mm silicone moulds and allowed to form a film for 24 hours.

Characterization

Dynamic light scattering (Zetasizer Nano Z, Malvern Instruments) was used to measure polymer particle average diameters. In order to prepare the sample, one drop of latex was diluted in deionized water. The particle diameters reported are the z-average of 2 measurements, each of them analyzed in 11 runs of 30 s each. Monomer conversion was determined gravimetrically. The electrical conductivity was measured by a four point probe (Miller Inc.m model FP500), the measurements were performed in several points of the film on top and bottom interfaces of the composite film. The presented conductivities are the average of 5 measurements.

FT-IR spectra were recorded on an ALPHA coupled to a Golden Gate single reflection attenuation total reflection (ATR) unit.

The morphology of the composite films was studied by scanning electron microscopy (SEM) (Hitachi S-4800) at an accelerating voltage of 5 kV. Samples were scanned as prepared without sputtering metal on their surface.

Tensile measurements. The free-standing films with thickness of ca. 0.5 mm were prepared by depositing the latexes in silicone moulds which were allowed to dry for seven days. Tensile specimens (15 mm x 3.5 mm x 0.5 mm) were cut from the dry films. The size of the samples was checked before starting the measurements. Stress-strain measurements were carried out with a commercial instrument TA.HD plus texture analyzer (Stable Micro Systems Ltd., Godalming, UK) with a constant strain velocity of 1.5 mm/s. As the initial length between jaws was 15 mm, the nominal strain rate in the experiments was 0.1 Hz. From each sample three replicate experiments were performed.

Dynamic mechanical analyses (DMA) were carried out on a DMA Q800 instrument from TA Instruments. Rectangular samples, with approximate dimensions of 10 mm x 3.5 mm x 0.5 mm were cut from dry films and analyzed in a tension mode at a frequency of 1 Hz and 10 μ m deformation amplitude with a gage length of 5 mm. All samples were scanned from a temperature sweep of -40 to 120 $^{\circ}$ C at a constant heating rate of 4 $^{\circ}$ C per min.

Results and discussions

Reactive emulsion mixing procedure used in this study to prepare water-borne polymer/rGO composites is presented schematically in the Fig.1. Water dispersible polyisocyanate, having free NCO groups on both sides of the polymer chains, was added in the composite blends containing 45 wt% s.c. MMA/BA/HEMA latex and PVP stabilized rGO platelets in aqueous dispersion. The rGO was prepared from stable GO aqueous dispersions by hydrazine reduction in the presence of PVP, resulting in mostly one layer platelets with average lateral dimensions of 300 nm dispersed in water (the procedure and the

rGO characteristics are presented elsewhere).²³ NCOs reacted spontaneously at room temperature with OH from the polymer chains and with OH presented on the rGO platelets, forming a highly crosslinked composite particles in the aqueous dispersions. The composite films were prepared by water evaporation in controlled atmosphere ($T=25^{\circ}\text{C}$ and humidity of 80%).

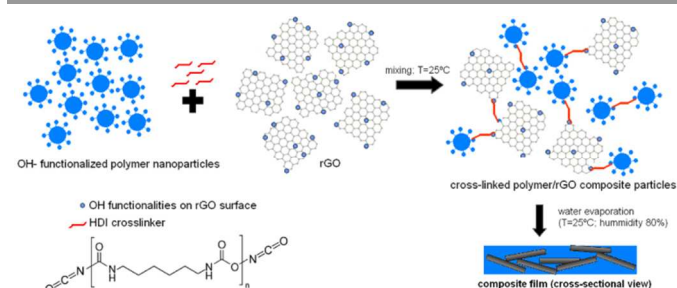


Fig.1. Reactive emulsion mixing procedure

In the Fig.2 the FTIR spectra of the composite films with 1wt% rGO and different amounts of HDI crosslinker are presented and compared with FTIR spectra of the polymer film and the crosslinker. Although many characteristic peaks overlapped, in the region 1500-1700 cm^{-1} new vibrations appeared, whose assignment is presented in the Fig.2, and indicates incorporation of rGO in the composites (presence of C=O and C=C from rGO) and formation of urethane amide i.e. realization of NCO-OH crosslinking reaction.

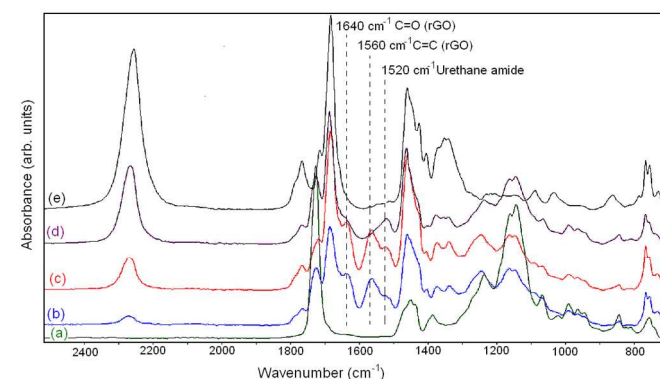


Fig.2. FTIR spectra of (a) poly(MMA/BA/HEMA); (b) polymer/rGO composite films, containing 1% rGO and NCO:OH = 2:1; (c) polymer/rGO composite films, containing 1% rGO and NCO:OH = 1:1; (d) polymer/rGO composite films, containing 1% rGO and NCO:OH=0.5:1; (e) HDI crosslinker.

In order to check if the system is crosslinked, the solubility test of the composites in THF and acetone was performed. Small pieces (50 mg) of the composite materials were placed in the solvents (Fig.3a). After 24 h at room temperature (Fig.3b), the composites swelled significantly in both solvents. No signs of composite degradation were noticed and neither rGO nor polymer left the composites, indicating high composites stabilities at room temperature. Further, the solvents with the composites were heated to 70 $^{\circ}$ C in a period of 24h (Fig.3c). It is clear that rGO platelets were held in the integrated structure,

although some polymeric part was dissolved in the acetone. The high swelling capacity of the composites and their stability in the solvents indicate that rGO is bonded strongly in a crosslink structure. For comparison, in Fig.3d the composite blends fabricated without crosslinker in the same solvents after 24h at room temperature are presented. These composites did not swell, but degraded even at room temperature, showing rGO powder dispersed in the solvents.

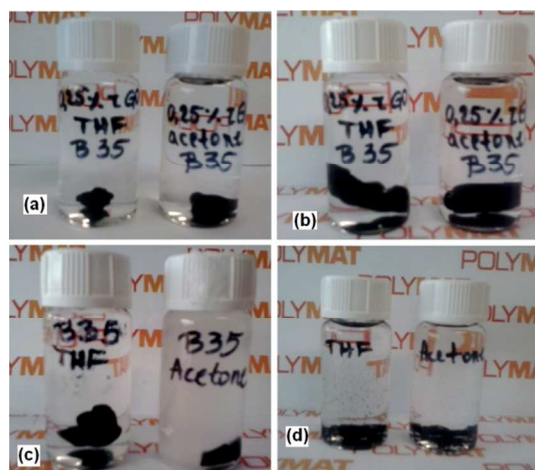


Fig.3. Solubility test of composite materials, performed in THF and acetone: just placed in the solvents (a); after 24 h at room temperature (b); after additional 24 h at 70°C (c); and composite blends fabricated without crosslinker (d).

In Table 2 the degrees of equilibrium swelling of the composites in THF are presented and indicate the degree of crosslinking in the composites obtained with different rGO or crosslinker content.

Table 2. Properties of reactive composite blends: equilibrium swelling in THF, electrical conductivity and glass transition temperature

rGO content (%)	NCO: OH ratio	Electrical conductivity ($S m^{-1}$)	Swelling	T_g ($^{\circ}C$)
1	2:1	0.0324	7.00	20.4
1	1:1	0.1361	10.18	20.6
1	0.5:1	0.0670	10.71	21.2
0.5	2:1	0.0098	12.04	15.2
0.5	1:1	0.0012	11.82	17.3
0.5	0.5:1	0.0007	13.81	18.3
0.25	2:1	/	14.21	18.7
0.25	1:1	/	15.56	
0.25	0.5:1	/	16.21	
0.125	2:1	/	14.21	17.2
0.125	1:1	/	17.64	
0.125	0.5:1	/	20.20	
0	/	/	24.00	12.1

The equilibrium swelling of the polymer P(MMA/BA) is 24.49. As it could be seen from Table 2 all prepared rGO composites showed lower swelling capability, indicating higher crosslinked structure (as the crosslinking increases, the number of cross-

links is higher and the distance between them lower, thus the possibility to augment the volume during swelling is lower). The rGO positively influences the crosslinking, thus for the higher rGO content, the swelling is lower. This is more pronounced for higher HDI content, signifying that rGO is included in crosslinking reactions and resulted in covalently bonded rGO within polymer matrix.

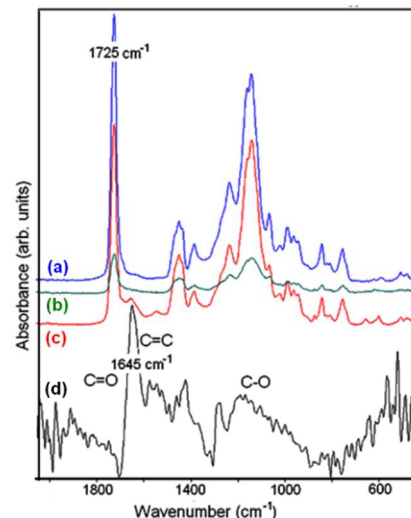


Fig.4. FTIR spectra of (a) poly(MMA/BA/HEMA) film; (b) the soluble part of the composites; (c) insoluble part of the composites; and (d) the rGO.

In order to confirm the establishing of the covalent bonds, ATR FTIR spectra from poly(MMA/BA/HEMA) film (Fig. 4a), the acetone soluble part of the composites (Fig. 4b), acetone insoluble part of the composites (Fig. 4c) and the rGO (Fig. 4d) were compared. Fig.4b clearly indicates that the soluble part is polymeric and no presence of rGO was identified. Fig.4c (insoluble part) shows the presence of C=O from both, the polymer (at around $1725 cm^{-1}$) and the rGO (at around $1645 cm^{-1}$). Bearing in mind that the spectra were collected from dry materials after 24 h extraction in acetone at boiling point, one can conclude that the rGO presented in insoluble part (actually, the whole rGO amount) is bonded strongly with the polymer in the cross linked structure.

In Fig.5 and in Table 2 the electrical conductivities of the composites are presented.

Fig.5 demonstrates the percolation behavior of the composites and that the percolation threshold falls within the range of 0.25-0.5 wt% rGO. The low percolation thresholds are a characteristic feature of the technique of blending of polymer latexes with graphene.⁶ In our previous work it was demonstrated that by covalent bonding of rGO nanoplatelets within polyMMA/BA matrix, produced by *in situ* emulsion polymerization, the electrical conductivity was decreased substantially.²⁴ The present results demonstrate that in the proposed method of reactive emulsion mixing no additional sp^3 hybridized C atoms were formed within rGO structure, thus the conductivity was not suppressed by covalent bonding of the nanosheets within the matrix.

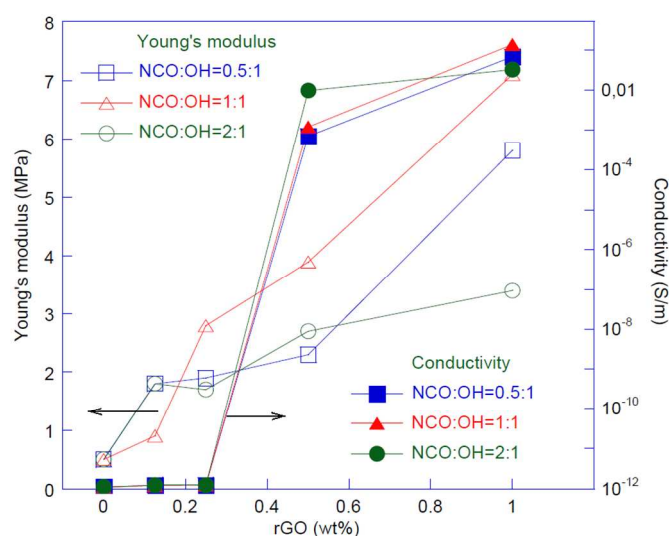


Fig.5. Electrical conductivity and Young's modulus of the poly(MMA/BA/HEMA)/rGO composites as a function of the rGO content for different HDI crosslinker amounts

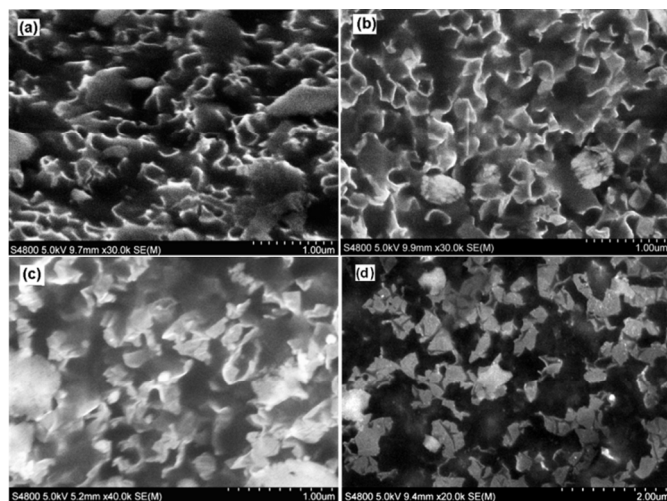


Fig.6. Morphology of the composite films, containing 1 wt% rGO. Fracture surface view of (a) NCO:OH = 2:1; (b) NCO:OH = 1:1; (c) NCO:OH = 0.5; and (d) top surface view of NCO:OH = 1:1

The morphology of the composite films was followed by SEM imaging. In Fig.6 the morphology of the composites loaded with 1 wt% rGO (maximum amount through this study) for different HDI crosslinker amounts is presented, showing white rGO flakes distributed in the dark polymer matrix. The photos were obtained from the neat composite surface, not covered with metal conductive layer. Obviously the conductive network is formed within the polymer matrix. The added amount of HDI influences a lot the composite morphology and obviously the electrically conductive properties. Higher amount of crosslinker promotes partial encapsulation of polymer particles by the rGO sheets, by bending the rGO sheets around the particles, creating more organized structure and highly oriented rGO platelets in direction perpendicular to the fracture surface (Figures 6a and 6b). The occurrence of rGO nanoplatelets orientation in hybrid

mini-emulsion systems is a well explained event.²³ It is worth noting that the composites containing 1 wt% of rGO and medium amount of HDI (NCO:OH= 1:1) showed the maximum electrical conductivity achieved in this study (0.1361 S m⁻¹, Table 2) and a highly homogeneous distribution of rGO (Fig.6e), thus a kind of optimum combination of rGO and HDI amounts. When higher HDI amount was added (at the same rGO loading of 1wt%) very probably part of it remained free and was incorporated into the composite matrix, decreasing the conductivity and influencing the morphology (Fig.6a). By decreasing the HDI content (Fig.6c) the rGO platelets are randomly oriented in the matrix, less bended and more aggregated. Very probably the amount of crosslinker used (NCO:OH=0.5;1) was not enough to bond with the individual rGO sheets, which promoted aggregation between the not bonded. Consequently, the electrical conductivity of these composites dropped significantly (Table 2). One could conclude that it is of extreme importance to control the amount of added HDI crosslinker in relation to rGO loading in order to optimize their distribution and electrical conductivity.

In the Fig.6d a SEM image of the top view of the composite film (1 wt% rGO and NCO:OH=1) is presented and confirms the organized structure and orientation of the rGO in the polymer matrix parallel to the top view direction. This means that the composites are highly anisotropic in nature, and their properties will greatly depend on the measurements direction during characterizations.

Fig.5 presents the dependence of Young's modulus and conductivity of nanocomposites on rGO concentration and NCO:OH ratio. The Young's modulus or modulus of elasticity was obtained experimentally from tensile stress-strain curve, in the early (low strain) portion of the curve, where the nanocomposites obey Hooke's law to a reasonable approximation,²⁴ so that stress is proportional to strain. As it can be seen from Fig.5, Young's modulus increased with the addition of rGO in relation to neat polymer, and increased further with rGO content, independently on the HDI amount, due to the higher stiffness coming from the rGO presence in the nanocomposites. The maximum value (7.1 MPa) for the Young's modulus was achieved with the highest concentration (1wt%) of rGO at NCO:OH=1:1, which confirms that this combination of rGO and HDI amounts is the optimal one. This amount is 14 times higher than the Young's modulus of the neat polymer. The measurements were performed by applying the force in direction parallel to the rGO sheets. The high modulus in these cases corroborate to very good polymer/rGO interaction at the interface, since no slicing between layers of both phases occurred, which from the other hand ensures very good stress transfer in the composites.

A contradictory result was obtained for the lowest HDI and highest rGO contents, for which combination, opposite to the expected, very high modulus was obtained. Very probably this inconsistency comes from nature of this composite film, which according to Fig.6c showing randomly distributed rGO platelets in the polymer matrix, should present isotropic properties. If so, efficient stress distribution in all directions could be expected,

resulting in a response higher than expected. This effect has been noticed previously for platelet like high aspect fillers.²⁵ The Young's modulus obtained for this composite abruptly increased and presented deflection from the general trend (curve d in Fig.5).

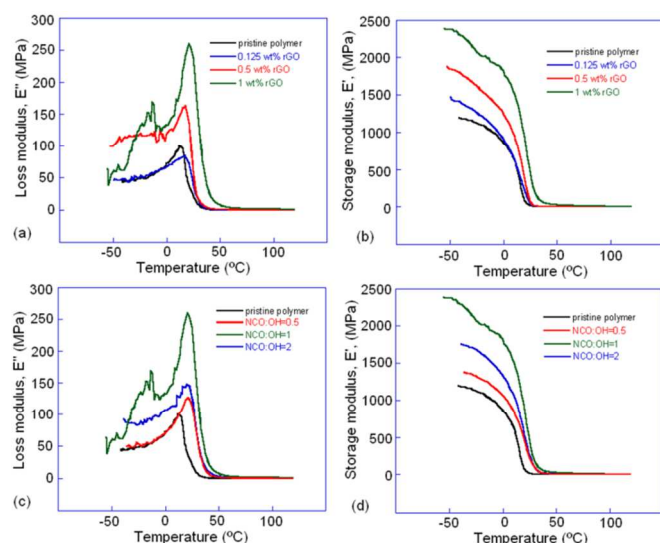


Fig.7. Viscoelastic properties as a function of temperature of nanocomposites: (a) loss modulus at various rGO loadings, NCO:OH=1; (b) storage modulus at various rGO loadings, NCO:OH=1; (c) loss modulus at various NCO:OH ratios, for rGO content of 1 %wt; and (d) storage modulus at various NCO:OH ratios, for rGO content of 1 %wt.

The viscoelastic properties of the nanocomposites were studied by DMA. Fig.7 presents comparison between the storage (E') and the loss modulus (E'') of the pristine polymer and nanocomposite. The glass transition temperature (T_g) of the composites and the neat polymers, determined from the loss modulus maximums (Fig.7a and c) are presented in Table 2. In general, the presence of rGO induced increasing of T_g values from 12.1 °C of the polymer into the range 17-20°C in the composites, depending of the rGO loading, which positively influenced the T_g values. The rGO platelets act as stiff cross-points, which delay segmental oscillations of the polymer matrix, so more thermal energy is needed to excite relaxational motions. Fig.7a shows that the areas under the peak are increased with the rGO presence, more pronounced for higher loadings (1%wt. rGO), perhaps due to the increasing segmental motions at T_g in the nanocomposites respect to the neat polymer. It is obvious that the addition of rGO into the polymer matrix provides enhancement in the mechanical behaviour. Fig.7b shows that the storage modulus gradually increased with the rGO loading, resulting in an increment of 100% for 1 wt% rGO content in the composite. This means that the presence of rGO has transferred more stiffness to the polymer matrix and altered the strength and the rigidity, and verified the reinforcing effect.

In Figures 7c and d the influence of variations of HDI crosslinker content on the nanocomposites loss modulus (E'') and storage modulus (E'), respectively, in respect to the neat polymer are presented. No significant difference between T_g

was noticed, because in all of them the rGO content is high (1%wt). The HDI crosslinker's content influences the mechanical properties in the similar manner as the other properties (electrical conductivity and morphology) since obvious trend, but pointing out the ratio of NCO:OH of 1 as an optimal for 1% rGO loading in the polymer matrix. The lower crosslinker amount is not sufficient for efficient crosslinking of rGO sheets, thus the aggregation is increased, the aspect ratio is decreased and less reinforcement is induced. In the case of higher crosslinker amount, the non reacted part is distributed in the polymer matrix, influencing negatively the properties. Clear reinforcement effect of covalently bonded rGO platelets in the polymer matrix is obtained, additionally confirmed in Fig.8, where the complex modulus or modulus of elasticity E^* and $\tan\delta$ are presented.

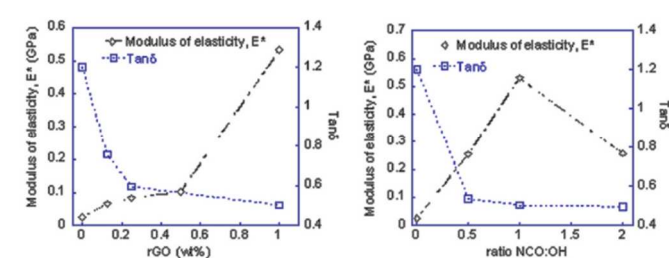


Fig.8 Modulus of elasticity, E^* and $\tan\delta$ as a function of (a) rGO content and (b) HDI crosslinker amount.

Fig.8 shows augmentation of the modulus of elasticity up to one order of magnitude for 1 wt% rGO. $\tan\delta$, on the other hand, decreases with increasing of rGO concentration confirming that stiffer nanocomposites were obtained. For NCO:OH=1 the highest E^* was obtained (Fig.8), which is in line with the previous discussions of highly crosslinked system, in which rGO platelets are homogeneous distributed.

Conclusions

New pathway for synthesis of water borne rGO/polymer composites is presented, based on the simple emulsion mixing technique. Combining colloidal stable dispersions of rGO and polymer nanoparticles in the presence of water dispersible polyisocyanate crosslinker, resulted in highly crosslinked composites, in which the polymer chains and rGO nanoplatelets are covalently bonded. The composite films have shown very good stability in solvents at room temperature, keeping a completely integrated structure. At increased temperature, small amounts of polymer were dissolved in the solvents, very probably low molecular weight polymer chains that were not incorporated in the crosslinked structure. However, rGO platelets even at increased temperature were kept in the structure, opposite to the simple composite blends prepared without crosslinker, where rGO easily left the composite and dispersed in the solvents even at room temperature.

The composites, despite covalent bonding of the rGO sheets in the composite matrix have shown electrical conductivity properties, percolation behavior, with threshold between 0.25 and 0.5 wt% content of rGO. The reinforcing effect of the rGO presence was demonstrated by the increase of Young's modulus of elasticity of about 14 fold, the increase of storage modulus up to 100% and the increase of complex modulus of elasticity about one order of magnitude for composite containing 1 wt% rGO in respect to the neat polymer. This confirms an excellent stress transfer between the phases, very probably resulting from the very good interfacial bonding.

By changing the amount of the added crosslinker, it was determined that this parameter is of extreme importance in order to obtain maximum of the technique. The determined optimal crosslinker amount (in this case, NCO:OH=1) decreased aggregation and ensures homogeneous distribution of rGO platelets in the matrix, and subsequently improved properties in comparison to the composites with same rGO content at different crosslinkers amounts.

The presented technique, besides simplicity is quite versatile and could be used to improve the interactions between different components in preparation of composites. Additionally, the aggregation of the filler could be decreased and its distribution in the polymer matrix improved, thus the reactive emulsion mixing technique offers similar output as *in situ* polymerization techniques, alongside with possibility to control polymer properties prior to mixing.

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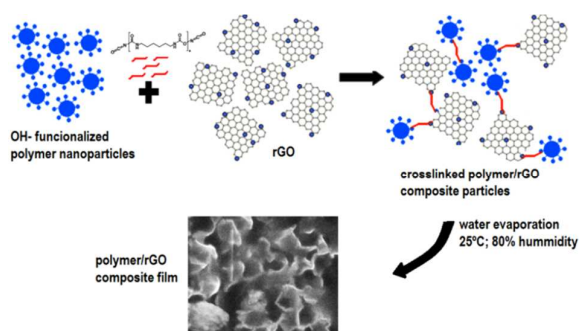
References

- 1 J. M. Asua, editor. *Polymer Reaction Engineering*, Oxford: Blackwell Publishing; 2007
- 2 E. Tkalya, M. Ghislandi, A. Alekseev, C. Koning, J. Loos, *J. Mat. Chem.*, 2010, **20**, 3035.
- 3 Raghu, Y. Lee, H. Jeong, C. Shin, *Macromol. Chem. Phys.*, 2008, **209**, 2487.
- 4 Y. Syurik, M. Ghislandi, E. Tkalya, G. Paterson, D. McGrouther, O. Ageev, J. Loos, *Macromol. Chem. Phys.*, 2012, **213**, 1251.
- 5 J. Kim, S. Hong, D. Park, S. Shim, *Macromol. Res.*, 2010, **18**, 558.
- 6 M. Yoonessi, J. Gaier, *ACS Nano*, 2010, **4**, 7211.
- 7 R. Wissert, P. Steurer, S. Schopp, R. Thomann, R. Mlhaupt, *Macromol. Mat. Eng.*, 2010, **295**, 1107.
- 8 N. Yousefi, M. Gudarzi, Q. Zheng, S. Aboutalebi, F. Sharif, J. Kim, *J. Mat. Chem.*, 2012, **22**, 12709.
- 9 V. Pham, T. Dang, S. Hur, E. Kim, J. Chung, *ACS Appl. Mater. Interf.*, 2012, **4**, 2630.
- 10 J. Yang, X. Yan, M. Wu, F. Chen, Z. Fei, M. Zhong, *J. Nanopart. Res.*, 2012, **14**, 717.
- 11 M.M. Gudarzi, F. Sharif, *J. Colloid Interface Sci.*, 2012, **366**, 44–50
- 12 H. Hu, X. Wang, J. Wang, L. Wan, F. Liu, H. Zheng, R. Chen, C. Xu, *Chem. Phys. Lett.*, 2010, **484**, 247.
- 13 G. Zheming, Z. Ling, L. Chunzhong, *J. Macromol. Sci. B*, 2009, **48**, 226.
- 14 S. Das, A. Wajid, J. Shelburne, Y. Liao, M. ACS *Appl. Mater. Interf.*, 2011, **3**, 1844.
- 15 T. Kuilla, S. Bhadra, D. Yao, N. Kim, S. Bose, J. Lee, *Progress in Polymer Science*, 2010, **35**, 1350.
- 16 H. Etmimi, R. Sanderson, *Macromolecules*, 2011, **44**, 8504.
- 17 Y. Tan, L. Fang, J. Xiao, Y. Song, Q. Zheng, *Polym. Chem.*, 2013, **4**, 2939
- 18 A. Patole, S. Patole, H. Kang, J. Yoo, T. Kim, J. Ahn, *Journal of Colloid and Interface Science*, 2010, **350**, 530.
- 19 M. Gudarzi, F. Sharif, *Soft Matter*, 2011, **7**, 3432.
- 20 X. Song, Y. Yang, J. Liu, H. Zhao, *Langmuir*, 2011, **27**, 1186.
- 21 P. Xie, X. Ge, B. Fang, Z. Li, Y. Liang, C. Yang, *Colloid Polym. Sci.*, 2013, **291**, 1631-1639.
- 22 S.H.C. Man, S.C. Thickett, M.R. Whittaker, P.B. Zetterlund, *J. Polym. Sci. A: Polym. Chem.*, 2013, **51**, 47–58.
- 23 A. Arzac, G. P. Leal, R. Fajgar, R. Tomovska, *Part Part Syst Charact*, 2014, DOI: 10.1002/ppsc.201300286
- 24 T. H. Courtney, *Mechanical Behavior of Materials*, McGraw-Hill, New York, 1990.
- 25 J. R. Potts, D. R. Dreyer, C. W. Bielawski, R. S. Ruoff, *Polymer* 2011, **52** 5–25.

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Conductive crosslinked polymer/reduced graphene oxide (rGO) composites with highly improved mechanical properties were synthesized by novel reactive emulsion mixing technique.