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On the wetting of polyethylene terephthalate substrates with multicomponent graphene oxide dispersions

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Abstract. In this work, we investigate wetting properties of polymer polyethylene terephthalate (PET) substrates with graphene oxide multicomponent dispersions. Overcoming poor wettability polymer substrates like PET, promising for flexible electronics applications, with commercially available water graphene oxide suspensions is proposed to solve by adding organic components. We used dimethylacetamide (DMA) and thinner for lacquer paints (LT) to successfully show the decrease of wetting angle. Moreover, we showed stability of multicomponent dispersion with DMA within more than 6 months and LT within more than several weeks and also found out that drying time of droplets of mixed dispersions with different additives may vary more than 15 times that is important for choice of the preferred deposition method.

Keywords: Graphene oxide, mixed dispersions, organic solutions, DMA, PET substrate

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Материалы конференции

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О смачивании подложек полиэтилентерефталата многокомпонентными дисперсиями оксида графена

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Аннотация. В данной работе исследуется смачивание полимерных подложек из полиэтилентерефталата (ПЭТ) многокомпонентными дисперсиями оксида графена. Для обеспечения улучшения смачиваемости полимерных подложек, таких как ПЭТ, являющихся перспективным для применения в гибкой электронике, с помощью коммерчески доступных водных суспензий оксида графена предлагается пойти путем добавления органических растворителей. Мы использовали диметилацетамид (ДМА) и разбавитель для эмалевых красок (ЛТ). Было успешно продемонстрировано уменьшение угла смачивания. Кроме того, показано, что стабильность многокомпонентной дисперсии с ДМА составляет более 6 месяцев и с ЛТ – более нескольких недель. Также установлено, что время высыхания каплей смешанных дисперсий с разными добавками может различаться более чем в 15 раз, что важно для выбора предпочтительного метода нанесения.

Ключевые слова: Оксид графена, смешанные дисперсии, органические растворы, ДМА, ПЭТ подложки

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Introduction

Carbon nanomaterials, especially graphene derivatives that include graphene oxide (GO) and reduced graphene oxide (rGO) are very promising materials for different applications in flexible electronics [1], chemical and biological sensors [2], energy storage systems [3], drug delivery platforms [4] etc. One of the main requirements for flexible devices is large-area uniform conductive and dielectric nanomaterials-based layers. Highly uniform films can be formed on polymer substrates via different methods such as Langmuir–Blodgett technique [5], dip-coating [6], spin-coating [7], spray coating [8] or roll-to-roll technology [9] and many others, but only the latter three are compatible with at least small batch production. On the other hand, most of commercially available GO forms are water suspension with poor wettability of polymer substrates. This limitation can be overcome by mechanical or plasma pre-treatment, but in case of need of nanometer thick films those cannot be applied. On the other hand, wettability can be improved by the dispersion's properties themselves.

In the current study, we tried to introduce additional organic components to the water-based GO suspension to improve its wettability characteristics. Additional components in the dispersion media should at least provide good dispersibility of GO. According to the data obtained from [10], GO can form long-time stable dispersions in such organic solvents (besides water) as dimethylformamide (DMF), N-methylpyrrolidone (NMP) and tetrahydrofuran (THF), and less stable in ethylene glycol, acetone and toluene. On the other hand, it is known that dimethylacetamide (DMA) is a good dispersion media for carboxylized carbon nanotubes [11].

Thus, we tried to form a multicomponent mixed dispersion media that contains water-based GO suspension, DMA and thinner for lacquer paints (LT) that is a mixture of ethyleneglycol, butylglycol, methylisobutylketone at different GO concentrations. We investigated wettability of these multicomponent GO dispersions with respect to PET substrates. We also study morphology and Raman spectra of the dried up droplets of multicomponent dispersions.

Materials and Methods

Dispersions were prepared from commercially available GO water suspension (4,7 mg/ml) produced by improved Hummer's method (LLC MIP Graphene, Russian Federation). Additional components: ultrapure DMA (EKOS-1, Russian Federation), thinner for lacquer and enamel paints (Tamiya Inc., Japan) were mixed with initial suspension with 50 : 50 ratio. We made five concentrations for each additive: 0.01; 0.025; 0.05; 0.1 and 0.25 mg/ml.

As a substrate for film deposition, we used high opacity PET film without additional surface treatment. Substrates with 5×10 mm dimensions were cleaned with 2-propanol and water and dried in the 2 bar airflow.

For wetting angle investigations, we used home-made device with 3.5× lens, digital camera for optical photos of dispersion droplets with further image processing using ImageJ software. Dispersions were deposited on substrates by drop-casting (drop volume was 0.25 μl)

Optical images of morphology and Raman spectra were obtained by InVia Raman spectrometer (Renishaw, UK). SEM images were obtained with Hitachi TM-3000 (Hitachi Ltd, Japan).

Results and Discussion

For wettability investigation of multicomponent dispersions, we used ImageJ software that can calculate wetting angle from photos (Fig. 1). Submitted data for each concentration and additional component was averaged over eight samples. Dependence of wetting angle on the additional organic component of the dispersion, GO concentration and drying time is shown in Fig. 2,*a*. Initial GO water suspension wetting angle is 41.6°. From the obtained data, one can



see that dispersion with LT as additional component has two shoulders with approximate linear dependence of wetting angle (under and above 0.05 mg/ml concentration). Drying time on the concentration dependence can be approximated with linear function. This result, on the one hand, means that we reached basic goal to reduce wetting angle. In case of LT as an additional component we clearly see the decrease of wetting angle by 2–8 times to the initial GO water suspension. The effect of the relatively strong dependence of wetting angle of dispersion with LT as additional component may be related to different surface charges of these particles and their Hamaker constants, which characterize the particle–water dispersion interaction same as observed in this article [12].

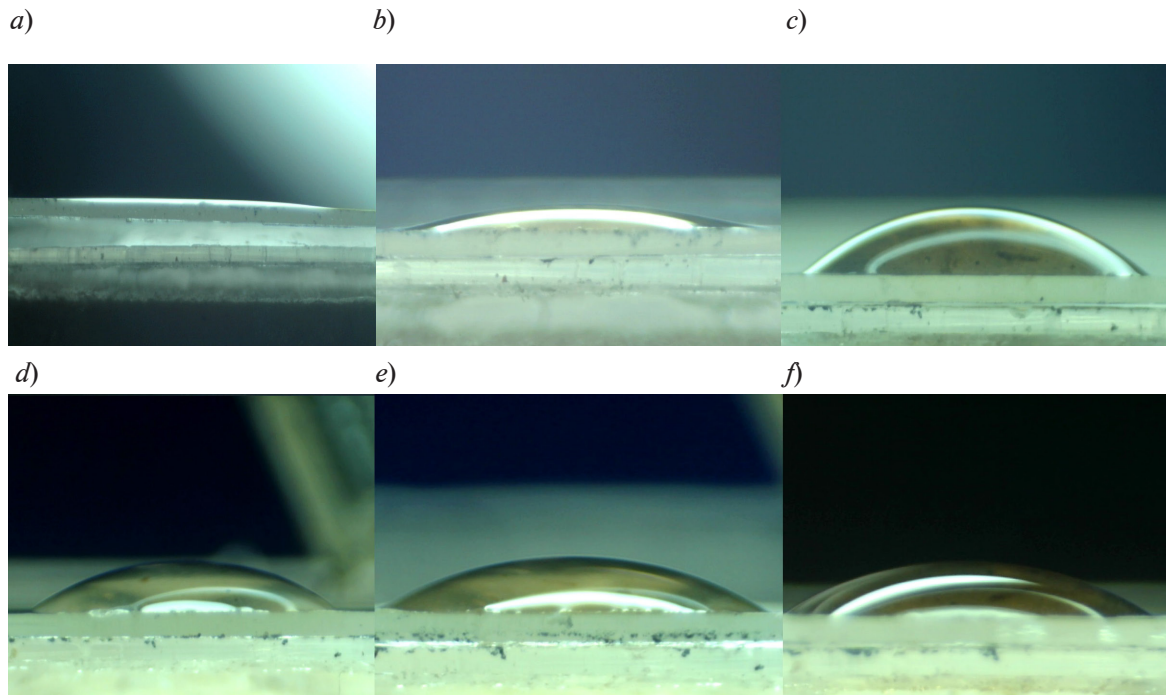


Fig. 1. Photos of GO dispersions droplets on PET substrate: 0.01 mg/ml in LT (a); 0.05 mg/ml in LT (b); 0.25 mg/ml in LT (c); 0.01 mg/ml in DMA (d); 0.05 mg/ml in DMA (e); 0.25 mg/ml in DMA (f)

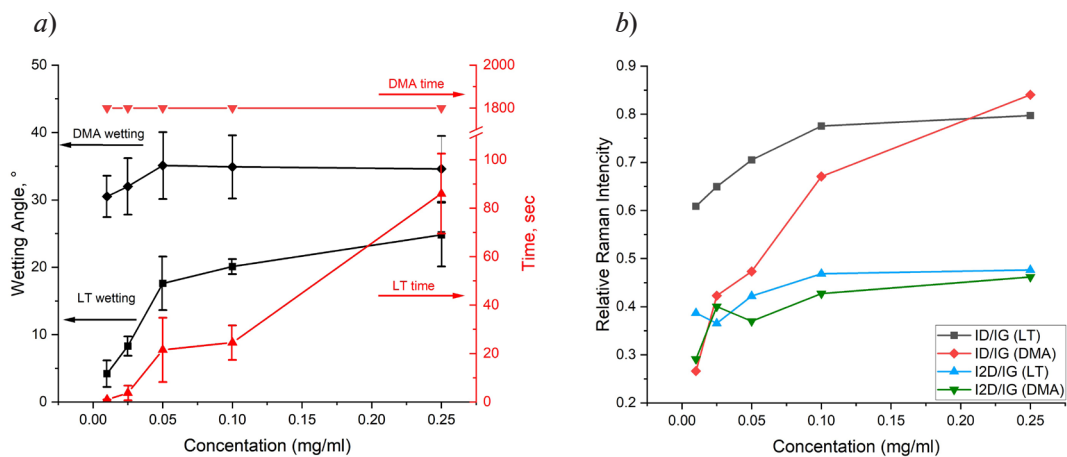


Fig. 2. Dependence of wetting angle and drying time on the type of the additional component and GO concentration (a); dependence of main Raman bands ratios of deposited films on the GO concentration (b)

On the other hand, pronounced dependence of wetting angle may be used to efficiently control wetting properties. High volatility (low drying time) of LT-based dispersion is due to the basic purpose of the LT as a thinner for lacquer or enamel paints for airbrush applications. We can see that the use of the LT as a second component makes this dispersion perspective for spray coating of thin GO films.

Dispersion with DMA on the contrary did not show strong dependence of the wetting angle or time on the GO concentration. This mixture also showed decrease in wetting angle, but the decrease is much lower than in case of LT and only 1.18 – 1.38 times lower than initial wetting angle. We suppose this effect is due to the high evaporation time of both pure water and DMA. In fact the evaporation time of GO water suspension mixture with DMA is more than 1800 seconds is more than 20 times bigger than in case of LT addition.

Drying time in range of tenth of minutes means that DMA-containing dispersion will be better for spin-coating deposition due to the characteristic time of spin-coating process (few minutes). But spin-coating unit should have option of camera heating. In conclusion of this block we can claim that in general addition of organic components to the commercially available graphene oxide suspension leads to the reduction of the wetting angle and in case of lacquer thinner – to reduction of drying time.

We also study morphology (Fig. 3) and Raman spectra (insets to Fig. 3) of thin films formed from the multicomponent dispersion droplets. By analyzing morphology and Raman we can in some approximation predict future film properties in case of spin-coating or aerosol deposition.

As it was mentioned before, in case of deposition from LT with concentration 0,01 mg/ml we observed few separate multilayered graphene oxide flakes without any interconnections between it on the $200 \times 150 \mu\text{m}$ area. Same situation with film deposited from 0,01 mg/ml DMA dispersion. In case of deposition from 0.05 mg/ml multicomponent dispersions we observed formation of thin film with larger than $100 \mu\text{m}$ lateral dimensions in case of LT as additional component and more than $50 \mu\text{m}$ in case of DMA. In our prediction this concentration will be useful for large area formation by aerosol deposition. Such films may be useful for flexible display formation or photonics applications. In case of largest concentration – 0.25 mg/ml we observed formation of large area films with more than 0.5 mm lateral dimensions in both LT and DMA cases. This

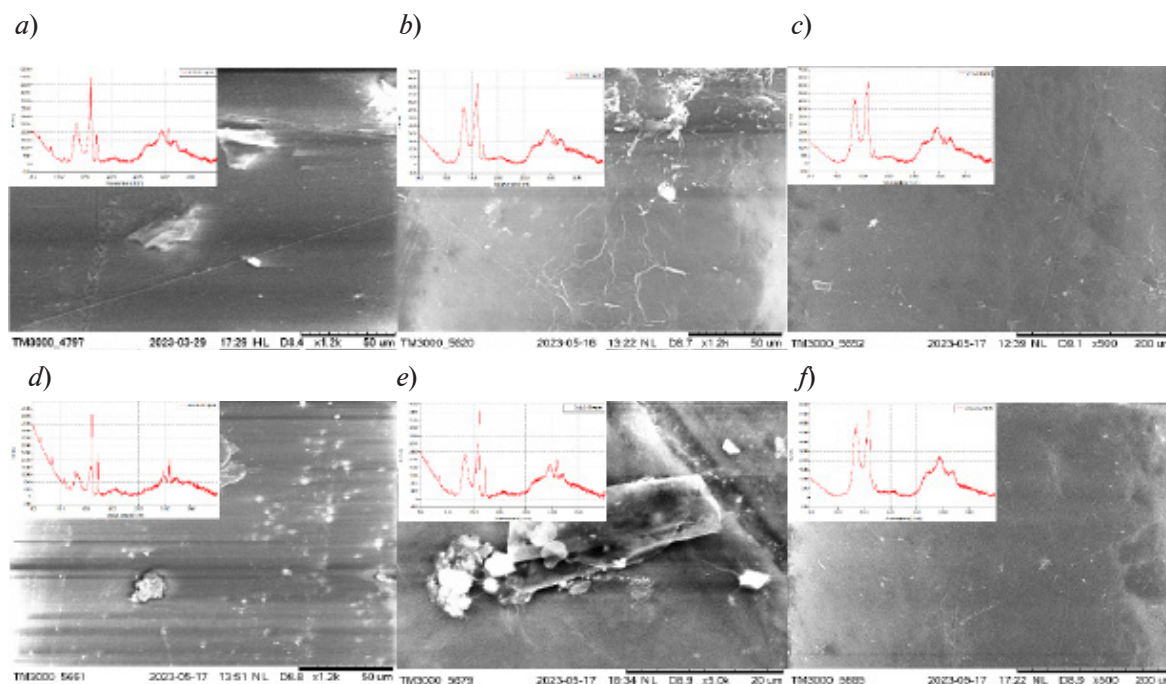


Fig. 3. SEM images of GO dispersions droplets on PET substrate (attributed Raman spectra are on inserts): 0.01 mg/ml in LT (a); 0.05 mg/ml in LT (b); 0.25 mg/ml in LT (c); 0.01 mg/ml in DMA (d); 0.05 mg/ml in DMA (e); 0.25 mg/ml in DMA (f)



concentration may be used for thicker film formation by aerosol deposition and by spin-coating for such applications as flexible electronics and sensors.

As it can be observed from Raman data general view of spectra matches well with known spectra of GO [13]. On the all samples we observed three main peaks: G ($\sim 1580\text{ cm}^{-1}$) that represents the in-plane stretching vibrations of the sp^2 bonded carbon atoms, D ($\sim 1350\text{ cm}^{-1}$) is the peak which highlights defects in the sample, so the more intensive this band is, the higher the level of disorder within the sample and 2D ($\sim 2950\text{ cm}^{-1}$) that indicates the number of layers present in the sample. The 2D-band originates from a double resonance enhanced two-phonon lateral vibrational process.

On spectra obtained from 0.01 mg/ml and 0.05 mg/ml concentrations we can see presence of Raman peaks at 860 cm^{-1} , 1097 cm^{-1} , 1728 cm^{-1} , 3083 cm^{-1} that can be attributed to PET with good congruence to the literature [14]. Thus in case of low concentrations film thickness is relatively low (few nanometers) due to the presence of PET peaks.

Analysis of morphology images and intensity of main Raman bands of GO (I_D is the intensity of D band, I_G is the intensity of G band and I_{2D} is the intensity of 2D band) shows that concentration of GO under the 0.05 mg/ml leads to the island-type film formation. Difference is that in case of LT we observe islands as mixture of many small flakes, whereas in case of DMA islands are relatively large individual multilayered GO flakes. Over the 0,05 mg/ml concentration films are uniform. Raman spectra and band ratio are classic for thin GO films [15].

Stability of the multicomponent dispersions was investigated by visual observations. Stability criteria was presence of macrosized agglomerates. In case of LT agglomerates were observed after two months of holding in test tube rack. On the contrary, dispersions with DMA showed absence of agglomerates within more than 6 months even in case of 0.25 mg/ml concentration.

Conclusion

In this work, we showed the possibility to decrease and control wetting angle on GO suspension/PET interface by adding organic components to the commercially available GO water-based suspension. We found out that addition of the thinner for lacquer and enamel paints leads to the formation of highly volatile dispersion that can form relatively large area (up to 0.5 mm) thin film that will be perspective for deposition by spray coating due to the fast drying time. According to formation of relatively thin film, thinner for lacquer or enamel paint may be useful for flexible displays and photonics applications. In case of DMA as the second component drying time is about 20 times larger that may be useful for spin-coating deposition but in case of additional heating. DMA as additional component may be used in flexible electronics applications and sensors. Also multicomponent dispersions have good time stability from few weeks to few months that is important for mass production applications.

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