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Thin large-area graphene oxide film formation from multicomponent suspensions

K.A. Rayanova[1], S.I. Babenko[1], A.S. Bryleva[1],
K.V. Kanaev[1], O.A. Kudryavtsev[1], R.R. Nigmatullina[1],
A.D. Sudakova[1], I.A. Komarov[1,2]✉

[1] Moscow Polytechnic University, Moscow, Russia;

[2] GraphApta LLC, Andreevka, Russia

✉ master_kom@mail.ru

Abstract. In this study, we investigate the influence of additional organic components of the graphene oxide suspension on wetting properties of PET substrates. Insufficient wettability of polymer substrates is one of the important challenges for flexible electronic devices based on graphene derivatives. In our research we showed a possibility to enhance the wettability of graphene oxide suspensions by incorporating additional organic components. Based on solubility parameters we choose N-methylpyrrolidone, dimethylacetamide, and two types of lacquer paint thinners as additional components. In all instances, we observed a successful reduction in the contact angle.

We also analyzed the drying time of multicomponent dispersions. Depending on the component ratios and the type of dispersion, the drying time can vary significantly, ranging from 3 to over 40 times, that is important for choosing the optimal deposition method. The stability of dispersions containing N-methylpyrrolidone and dimethylacetamide was confirmed for more than two months, while dispersions with lacquer paint thinners remained stable for approximately 1.5 months.

We showed possibility of formation of large-area graphene oxide films on PET substrate with the use of multicomponent graphene oxide suspensions. In case of concentrations higher than 0.9 mg/ml we observed formation of uniform films that covers the whole substrate.

Keywords: contact angle, dispersion medium, graphene oxide, thin films, wetting, PET

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Формирование тонкой пленки оксида графена большой площади из многокомпонентных суспензий

К.А. Раянова[1], С.И. Бабенко[1], А.С. Брылева[1],
К.В. Канаев[1], О.А. Кудрявцев[1], Р.Р. Нигматуллина[1],
А.Д. Судакова[1], И.А. Комаров[1,2]✉

[1] Московский политехнический университет, Москва, Россия;

[2] Общество с ограниченной ответственностью «ГрафАпта», п. Андреевка, Россия

✉ master_kom@mail.ru

Аннотация. В данной работе мы исследуем влияние дополнительных органических компонентов суспензии оксида графена на смачивающие свойства ПЭТ-подложек. Недостаточная смачиваемость полимерных подложек является одной из важных проблем для гибких электронных устройств на основе производных графена. В нашем исследовании мы показали возможность повышения смачиваемости суспензий оксида графена путем введения дополнительных органических компонентов. На основании параметров растворимости мы выбрали в качестве дополнительных компонентов N-метилпирролидон, диметилацетамид и два типа разбавителей для лакокрасочных материалов. Во всех случаях мы наблюдали успешное уменьшение контактного угла смачивания. Мы также проанализировали время высыхания многокомпонентных дисперсий. В зависимости от соотношения компонентов и типа дисперсии время высыхания может значительно варьироваться — от 3 до более чем 40 раз, что важно для выбора оптимального метода осаждения. Стабильность дисперсий, содержащих N-метилпирролидон и диметилацетамид, была подтверждена более двух месяцев, тогда как дисперсии с разбавителями лакокрасочных материалов сохраняли стабильность около 1,5 месяцев. Показана возможность формирования пленок оксида графена большой площади на ПЭТ-подложке с использованием многокомпонентных суспензий оксида графена. При концентрациях выше 0,9 мг/мл наблюдалось образование равномерных пленок, покрывающих всю подложку.

Ключевые слова: угол смачивания, дисперсионная среда, оксид графена, тонкие пленки, смачивание, ПЭТ

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Introduction

One of the largest trends in the world in electronics is the development of flexible devices based on polymer substrates. However, this requires new materials which will be flexible and the conductivity of that won't be strictly dependent on the bending of substrate. Among flexible materials graphene [1] and its derivatives, graphene oxide and reduced graphene oxide [2] seem to be one of the most perspective for flexible electronics.

The first and one of the most important problems in the use of graphene derivatives for flexible electronics is formation of macrosize films on flexible substrates. In the case of graphene oxide and reduced graphene oxide wet deposition techniques including drop-casting [3], inkjet printing [4] etc. are usually used. Another two methods that allows to deposit large area GO films are spray [5] and spin [6] coating. One of the main advantages of this method is the high film uniformity of the deposited films and the possibility of deposition of a wide range of materials, including not only graphene derivatives but also organic semiconductors, perovskite layers, etc.

Successful film formation significantly depends on the properties of the suspensions deposited. We suggest that management of the graphene oxide and reduced graphene oxide suspension properties seem to be a promising way for the formation of large-area films by spin coating. Management of suspension properties can be done by two main parameters: particle concentration and dispersion media properties, including its composition. Moreover, the effect of dispersion on the quality of GO structure hasn't been studied properly. From the literature data [7–9] we can mention that for good dispersibility dispersion media in suspension should have Hildebrand parameter (δT) close or larger than of GO or rGO. Thus dimethylformamide, N-methylpyrrolidone, tetrahydrofuran, and ethylene glycol seem to be optimal candidates as additional components. We also suggest that from the point of view of size, the dye particle is very close to the graphene oxide flake, so such thinners can be used for graphene oxide dispersion. And a brand-new approach shown in this work is the use of thinners or dilutants for lacquer or enamel paints (ethylene glycol, butyl glycol, and methyl isobutyl ketone).

As a result of the use of additional components of dispersion media we showed possibility of the contact angle decrease compared to the initial aqueous suspension. We have also demonstrated that both the time of solution drying, and its concentration can affect the structural quality of GO. We showed that the use of thinner for lacquer paints is optimal for spin-coating and with the drying time close to the characteristic times of spin and spray coating. We also showed the possibility of formation of macrosized GO films and find concentration range when films are uniform and cover all the surface.

Materials and methods

The starting component for the preparation of multi-component graphene oxide suspensions was an aqueous suspension of graphene oxide with a concentration of 3.11 mg/mL, synthesized using a modified Hummers' method (LLC "MIP Graphene," Russia Federation). The additional components used were N-methylpyrrolidone (NMP, $\delta T = 23$ MPa$^{1/2}$, ECOS-1, Russia), dimethylacetamide (DMA, $\delta T = 22.50$ MPa$^{1/2}$, ECOS-1, Russia), and enamel paint thinner (LT, Tamiya Ink., Japan), and an enamel paint thinner with the addition of a retarder (LTr, Tamiya Ink., Japan). Lacquer thinner is a mixture of ethylene glycol ($\delta T = 33$ MPa$^{1/2}$), butyl glycol ($\delta T = 20.8$ MPa$^{1/2}$), and methyl isobutyl ketone ($\delta T = 17$ MPa$^{1/2}$). The specified additional components were mixed with the initial suspension in the ratios 1:9; 2:8; 3:7; 4:6; 5:5 (equivalent GO concentrations: 0.31 mg/ml;0.62 mg/ml; 0,93 mg/ml; 1.24 mg/ml; 1.56 mg/ml; 1.87 mg/ml). For film application, a PET film with a thickness of 125 μm was used without any prior surface treatment. To determine the contact angle, substrates measuring 15 × 15 mm were employed.

A custom-designed device based on a UM-301 microscope was used to study the contact angle. A mechanical pipette was used to apply droplets, with a droplet volume of 0.4 μL. The drying time was determined by the visual disappearance of the droplet in the objective of the contact angle meter and the leveling of the PET substrate surface. The measurement of time was conducted using a timeline in the digital camera control program, with the initial point being the moment the droplet landed on the substrate and the final point being the moment the liquid disappeared from the field of view of the objective.

For GO film formation, we used the EZ4 spin-coater (LEBO Science, PRC) with the following deposition profile: 500 rpm for 30 sec and 3000 rpm for 120 sec with a further 30 min heat treatment in the low-vacuum chamber VAC-24 (Stegler, PRC) at 110 °C.

Optical images were made with M837 Series Lab Trinocular Compound Microscope (OMAX Microscope, Republic of Korea) with magnifications from 40x to 400x. SEM images of the graphene oxide film surface and EDS data were collected on the Hitachi TM-3000 scanning electron microscope (Hitachi Ltd, Japan) with a 15 kV accelerating voltage and 1200× magnification. The thickness of the GO film was measured on NTEGRA PRIMA SPM (NT-MDT, Russian Federation) in semicontact mode with an NSG 30 cantilever: 320 kHz resonance frequency, 40 N/m force constant (Tipsnano OЬ, Estonia).

Raman spectra were obtained on an InVia Raman spectrometer (Renishaw, UK). FTIR spectroscopy data for films was collected on the Nicolet iS10 (Thermo Scientific, USA) in attenuated total reflectance mode.

Results and discussion

According to the contact angle measurements (Fig. 1) we observe a trend of increase in wetting angles with increasing GO concentration. The increase in the contact angle is associated with the peculiarities of the surface tension of the liquid containing nanoparticles near the triple line, which, in turn, changes due to the cohesive and adhesive interaction between water molecules and nanoparticles on the interfacial surfaces. That ultimately leads to an increase in the contact angle with an increasing concentration of nanoparticles reaching a peak at a certain concentration.

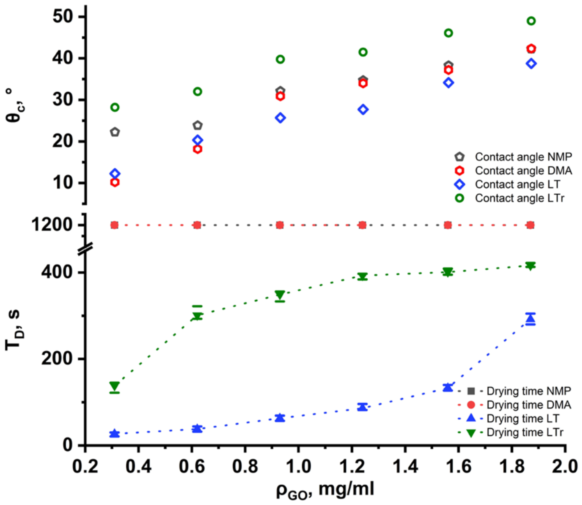

Fig. 1. Dependence of contact angle (θ_c) and drying time (TD) on the GO concentration (ρGO) and composition of multicomponent suspension

In addition, a decrease in the particle size in the dispersion, according to [10], leads to an increase in the contact angle, which is apparently observed in this article because, in the case of NMP and DMA, the average contact angle at high concentrations is 3–6 degrees greater than that in the case of LT. It is assumed that in the case of NMP and DMA, better dispersibility and a smaller particle size of GO were achieved. That is indirectly confirmed by the better stability of these dispersions when settling for a considerable time.

The obtained drop drying time values demonstrate, on the one hand, a significant drying time for dispersions containing NMP and DMA as additional components, amounting to more than 20 minutes (1200 s in Fig. 1 should be understood as “more than 1200 s”). Based on the drying time values, dispersions containing LT or LTr as an additional component should be considered most suitable for the tasks of film formation by spin-coating and aerosol deposition methods because, in these cases, drying times close to those for the above processes are ensured.

The stability of multicomponent dispersions was studied by visual observation of the presence of large GO agglomerates in the dispersion. When NMP and DMA are used as additional components, no agglomerate formation is observed for more than 60 days. In the case of using LT, agglomerates appear after approximately 40–45 days, while in the case of LTr, agglomeration occurs within several hours and is obviously associated with the presence of a retarder in the dispersion. This result also indirectly indicates the correctness of determining the optimal dispersion medium for graphene oxide based on data on the values of the Hildebrand parameter.

Thus, we showed the possibility of a contact angle decrease by adding the additional organic components to the initial graphene oxide water suspension. When comparing contact angle data spread and drying time, we can say that the most promising additional component is a thinner for lacquer paints. Moreover, in the case of LT addition, drying time is close to the typical time of spray and spin coating.

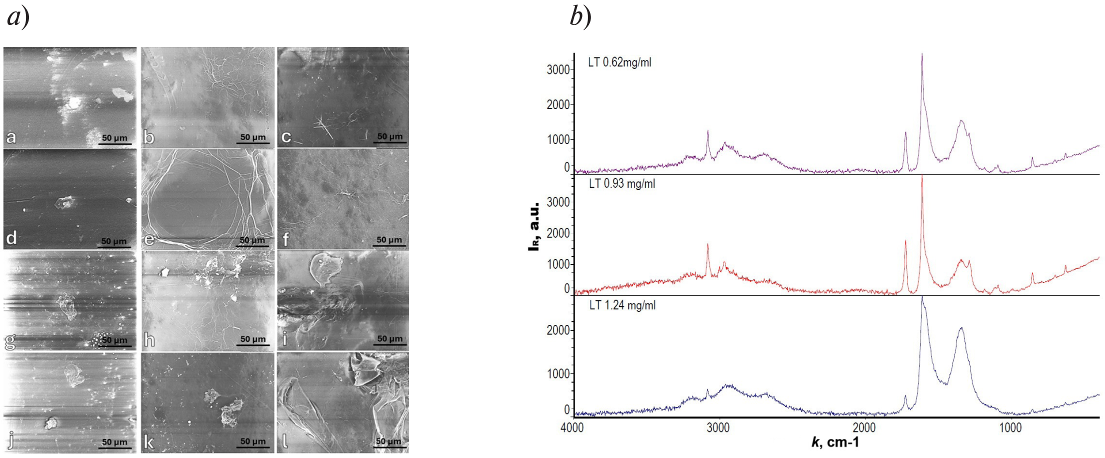

Fig. 2. SEM images of droplets of GO dispersions on a PET substrate (*a*) and Raman spectra of GO films deposited from multicomponent dispersion with LT (*k* is the wavenumber, I_R = relative Raman intensity) (*b*)

SEM images of a PET surface with deposited drops of multicomponent dispersions are shown in Fig. 2, *a*. We observed formation of island-type films in case of 0.33–0.62 mg/ml concentrations, and uniform films in other cases. Nevertheless, concentrations larger than ~ 1.5 mg/ml results in large-area films but with high roughness. These films can be used for chemical and biological sensors, as well as flexible electronic devices. In the case of higher concentrations, a continuous film is formed with less pronounced folding of the upper layer. Raman spectroscopy (Fig. 2, *b*) also confirms the SEM imaging data. Raman spectroscopy data show the presence of spectra typical of graphene oxide with characteristic peaks in the region of 1350, 1615, and 2950 cm^{-1}.

For large area film formation, we used spin-coating of the prepared multicomponent suspensions with parameters mentioned in "materials and methods" section. Optical images of the films after deposition from suspensions with different concentrations are on Fig. 3.

From Fig. 3 we see deposition of large area uniform GO films on area about 2 × 2 mm. We also observe presence of some "coffee ring" effect. We also used AFM for thickness measurements. AFM visualization (Fig. 4) tells us that thickness range is from about 10 nm in case of low concentration to ~250 nm in case of the highest concentrations. In the case of higher concentrations ~0.9–1.3 mg/ml), a continuous GO film is formed over an area of 50×50 μm and larger.

Based on the data obtained we can mention that using multicomponent GO suspensions we can successfully form large-area films on flexible substrates with the use of spin-coating method.

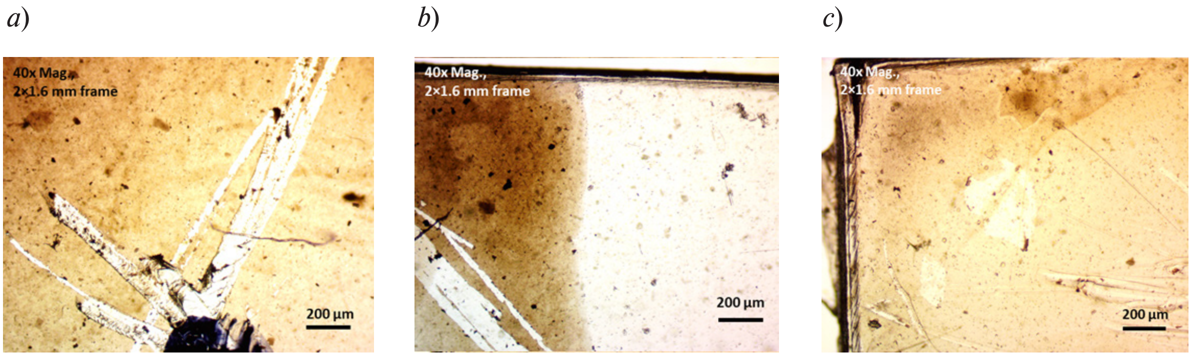

Fig. 3. Optical images of GO films spin-coated from multicomponent dispersions on a PET substrate 3:7 in LT (*a*); 4:6 in LT (*b*); 5:5 in LT (*c*)

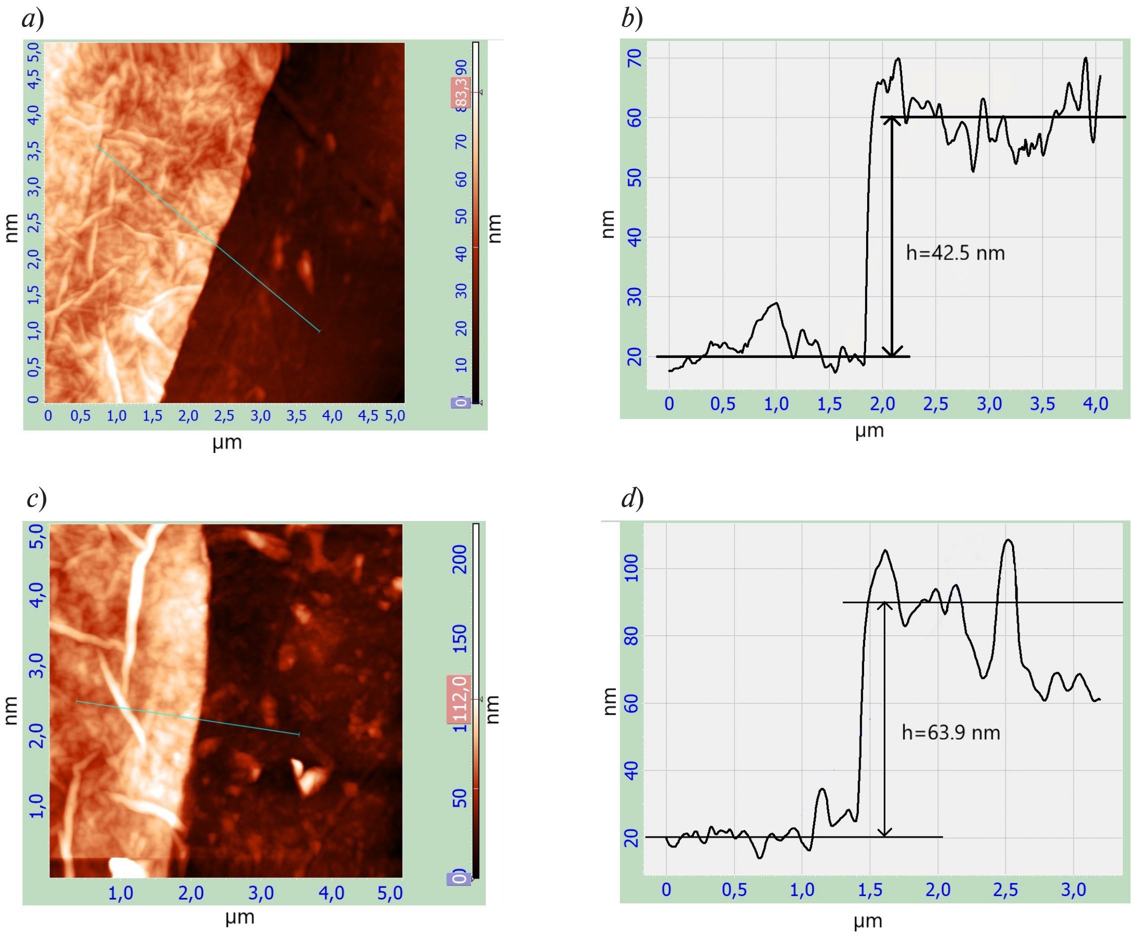

Fig. 4. AFM topography of the GO film deposited from 3:7 GO:LT (*a*) and cross-section (thickness of 42.51 nm (*b*)) and from 4:6 GO:LT (*c*) and cross-section (thickness of 63.90 nm (*d*))

Conclusion

The work successfully demonstrated the possibility of controlling the wetting characteristics of PET substrates by adding additional organic components to a commercially available aqueous GO suspension. From the point of view of manufacturability and the possibility of forming macro-sized films, the best of the considered options for additional components is a thinner for lacquer paints. However, N-methylpyrrolidone and dimethylacetamide can also be considered as additional components if there is a heating system for the substrate or the working chamber of the application system because in the case of using N-methylpyrrolidone and dimethylacetamide, the films are slightly less defective. Based on electron microscopy data, with a component ratio from 2:8 to 4:6, or ~0.6–1.3 mg/ml when calculated based on the concentration of graphene oxide, films of sizes sufficient for use in flexible electronics and sensor technology devices are formed. In addition, the article indirectly confirms the correctness of the concept of determining the optimal dispersion medium based on the Hildebrandt parameter.

GO dispersion with a 3:7 component ratio (GO concentration – 0.93 mg/ml) was successfully used for formation of large-area films on flexible substrates.

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THE AUTHORS

RAYANOVA KamillaA.
raanovakamilla@gmail.com

BABENKO Sofiya I.
sofi.bb@yandex.ru

BRYLEVA Anna S.
anniebryleva@yandex.ru

KANAEV Kirill V.
kir-kv2005@mail.ru

KUDRYAVTSEV Oleg A.
oleg6565657@gmail.com

NIGMATULLINA Razalina R.
razalina.n2004@gmail.com

SUDAKOVA Alexandra D.
asudakova12@gmail.com

KOMAROV Ivan A.
master_kom@mail.ru
ORCID: 0000-0002-6397-6671

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