Iraqi Journal of Physics, 2021 *Vol. 19, No. 50, PP. 43-50*
DOI: 10.30723/ijp.v19i50.669 *P-ISSN: 2070-4003*
E-ISSN: 2664-5548

Study the Effect of Graphene on the Contact Angle, Water Absorption and Thermal Stability (TGA, DSC) for Blend (Epoxy & Repcoat ZR)

Mena M. Husein[*], Seenaa I. Hussein[a]
Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq
[a]E-mail: seenaa.hussein@sc.uobaghdad.edu.iq
[*]Corresponding author: menamana111@gmail.com

Abstract

In this study, polymeric coating was developed by incorporating nano graphene in the polymer blend with applications to oil storage tanks. The oil storage tanks samples were brought from the oil Pipeline Company / Doura refinery in Baghdad. The coating polymer was formed with a blend (epoxy resin and repcoat ZR). The proportion of mixing the mixture was 3:1:1 epoxy resin 21.06 gm: repcoat ZR 10.53 gm: hardener 10.53 gm. The blend/graphene was prepared using in stui-polymerization method with different weight percentage 1, 3, 5, and 7 wt % added to blend. The resulting solution was put in a glass tube on a magnetic stirrer for one hour at a temperature of 40 $^{\circ}$C. The result of contact angle and water absorption the best ratio of 3wt % (73.46). The current work confirms that the thermal stability of the nanocomposites increases gradually with increasing the percentage of Gr compared to the blend without adding Gr nano and this is due to the thermal resistance of the Gr nano.

Article Info.

Keywords:
Graphene, repcoat ZR, Epoxy, contact angle, water absorption, TGA, DSC.

Article history:
Received: Mar. 25, 2021
Accepted: Jun. 24, 2021
Published: Sep. 01, 2021

1. Introduction

In Iraq, crude oil tanks are building and dispersed over numerous regions. Oil is broadly used in daily life; oil tanks play a critical part in its storage [1]. In the petroleum industry, damage or failure of the oil tanks, caused by corrosion, is one of the most common problems in the petroleum sector. It is considered as the biggest engineering and economical problem [2]. There are many reasons for crude oil tanks to be effected by corrosion. Firstly, tanks are exposed to very corrosive conditions, crude oil when full; moist atmosphere when empty; cyclic heating and cooling from atmospheric exposure. Secondly, often comes from having large surface and highly stressed areas, such as corners, edges, and welded seam areas. Thirdly, tank coating is a very complex job with many ramifications [3]. The epoxy coating consists of two parts which are mixed shortly before use. The main component of part A (Base) is an epoxy molecule group containing two so called epoxy-groups, while part B is a thinner (Hardener). When the two substances are mixed, a cross linked network is created, resulting in a hard substance that can be very strong [4]. Nanotechnology suggested many solutions to improve petroleum sector. It is used in the drilling process by using nanofluid (mixing of nanosized particles with the drilling mud) to improve the petroleum drilling process and thus increasing crude oil production. Also, nanomaterials are used as catalysts in petroleum refining reactors in petroleum downstream industry and as coating materials to the transportation pipelines and storage tanks in petroleum middle stream industry [5]. Chang et al. studied the dispersion of graphene on the polymer coating which led to improving the properties of the coating. The contact angle of water droplets on the surface of the sample containing the nanomaterial can be increased from -82 degrees (epoxy pure) to -127 degrees of composites epoxy with Gr [6]. Zaho et al. investigated the tribological and anti-corrosion properties of epoxy resin with nano graphene. They observed that fabric degradation happened when the content of graphene was higher than 0.5 wt % due to the agglomeration of nanoparticles [7]. Xing Wang et al. developed new high-performance composite coatings by incorporating nanoparticles in the polymer resins with applications to oil and gas pipelines. The graphene nanoplatelets under different concentrations were used to prepare the epoxy-based nanocomposites. The results suggested that the composite with 0.5~1.0 wt. % of the graphene nanofillers led to the largest improvement in both mechanical and electrochemical properties. Distribution of nanoparticles in the matrix was observed, with a scanning electron microscope, and surface roughness, using atomic force microscopy. Large agglomeration that was observed at the higher concentrations mainly resulted in the reduction of corrosion resistance and abrasion resistance [8].

The aim of the work preparation coating of Nano composites alight weight to protect oil tanks and study the effect of nano filler (Graphene (Gr) on the physical properties (contact angle &water absorption) and thermal stability (TGA & DSC).

2. Experimental work

2.1. Materials

Graphene: The color of grapheme nanopowder (from Graphene – a supermarket company, made in USA) is black and its purity equals 98.5 % with an average diameter of 59.22 nm.

Epoxy: Quickest 105 is a two-component resin and hardener. The epoxy was brought from a DCP company made in Jordan.

Repcoat ZR: is one component, the epoxy-based, zinc-rich primer, designed to supply active anti-corrosion coating for steel reinforcement, easy application, single component, excellent resistance to salt and chloride attacks. The report ZR was brought from DCP Company made in Jordan.

2.2. Simi killed steel ASTM A283 grade C

Semi-killed steel is generally deoxidized steel. A283 Grade C steel Applications: Used for general purpose structural applications of medium strength (60 ksi tensile) requirement. The information on mineral and chemical composition was obtained from the Oil Pipeline Company / Dora Refinery as shown in Table 1.

Table 1: Composition of Simi killed steel metal.

Carbon Max	Phosphorus Max	Manganese Max	Silicon plates over 11/2 thick	Silicon max plates ≤11/2thick	Copper min	Sulfur max
0.24 %	0.030 %	0.90 %	0.15- 0.40 %	0.40 %	0.20 %	0.030%

2.3. Atomic force microscopy analysis

The surface morphology of Graphene nanoparticles was observed with AFM micrographs as shown in Fig.1, the average diameter for Graphene was 59.22 nm.

2.4. Synthesis of polymeric blend, and blend / graphene nano composites

The coating polymer was made from a blend of epoxy resin and repcoat ZR using the cast method at room temperature. The ratio of the constituents (epoxyresin:repcoat ZR:hardener) of the mixture was 3:1:1 with weights of 21.06 gm 10.53 gm, and 10.53 gm. Samples were prepared from the blend and blend –Gr nanocomposites using the casting method. Gr powder of various weight percentages (0%, 1%, 3%, 5%, and 7%)

was used. The resulting solution was injected into a glass tube over a magnetic stirrer for 1 h. Finally, the nano composites were left at RT for 24 h. The prepared samples are shown in Fig. 2.

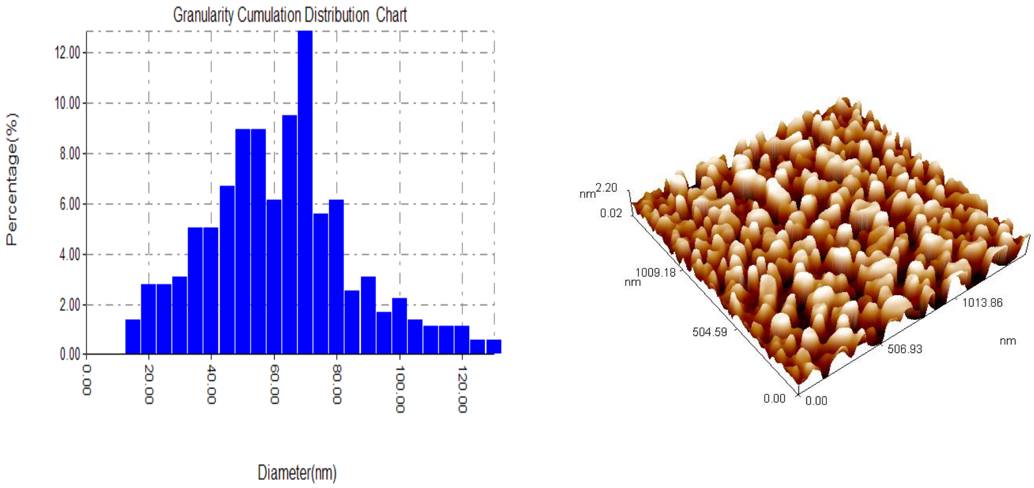


Figure 1: Scanning probe Microscope (Granularity Cumulation Distribution and 3D diagram) of Gr.

Figure 2: The samples blend / Graphene.

2.5. Oil tanks samples

Samples of oil tanks were brought from the Oil Pipelines Company of the Dora Refinery in Baghdad. The tanks samples were prepared using different mechanical operations including (cleaning, grinding, and cutting) and incorporate within the local workshop in Baghdad. These were cut into rectangular pieces of (5 x 8) cm dimension and the face of this sample was well polished as shown in Fig.3.

2.6. Contact angle

Contact angle is the angle at which a drop of liquid meets a solid surface. It quantifies the wettability of a substrate (surface). The contact angle of water was measured, (right and left) on a flat sample surface at an interim of 45-60 S. This test was carried out at the Ministry of Science and Technology / Environment and Water Research Department.

2.7. Water absorption

This test was carried out in a laboratory where a quantity of rainwater was collected, and when a pH test was conducted, it was found that it was equal to 7. The samples were immersed in rain water inside cylindrical plastic.

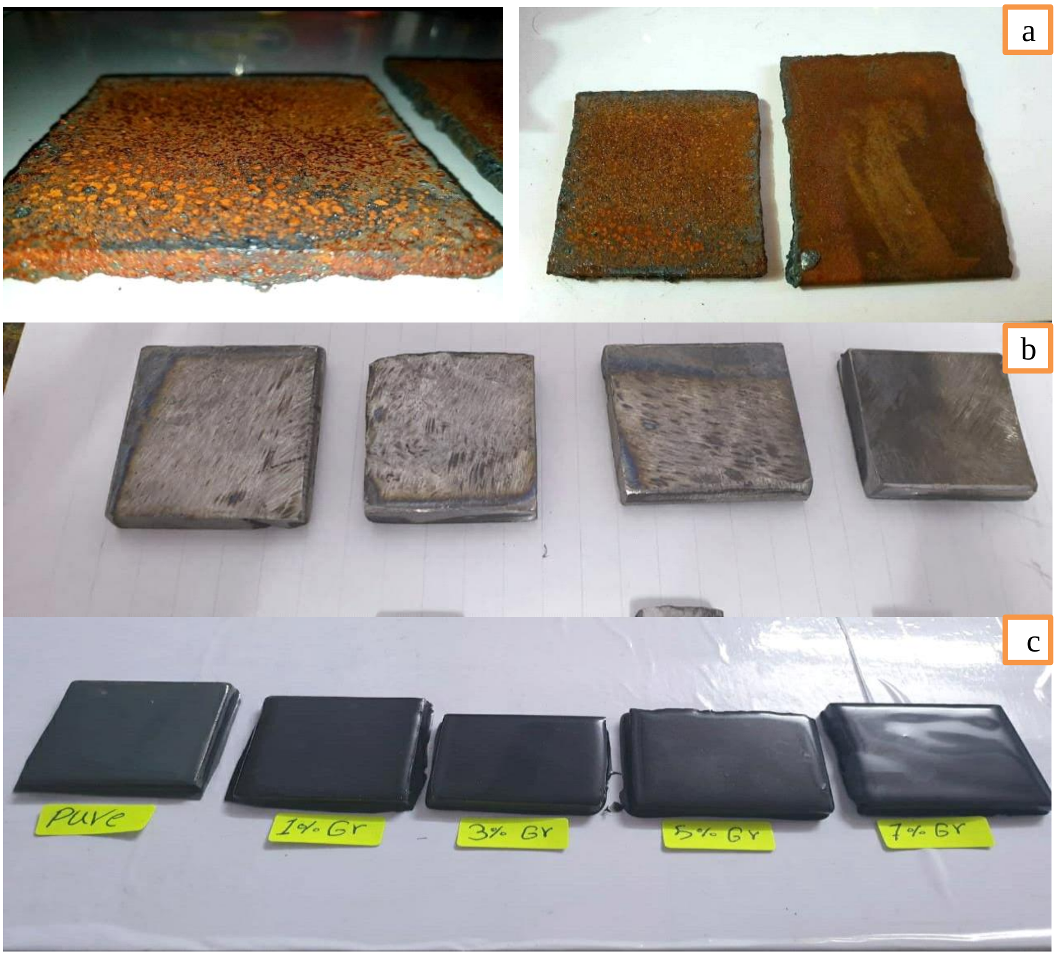


Figure 3: The samples: a- before cutting and cleaning, b- after cutting and cleaning, and c- after coating with blend and nano composites.

2.8. Thermal gravimetric analysis (TGA) and Differential Scanning Calorimetric (DSC)

The TGA and DSC measurements were carried out in a temperature range of 0-1200 $^{\circ}$C and at a heating speed of 10 $^{\circ}$C/min. TGA is a technique in which the mass of the sample is monitored against temp. DSC is a technique in which the difference in temperature between the sample and a reference material is monitored against temp.

3. Results and discussion

3.1. Contact angle and water absorption

The wetting conduct of the nanocomposites concerning water was analyzed. The effect of the filler concentration on the wetting surface was studied. It was found that the blend is hydrophilic where the angle was less than 90° and when including the rate of graphene to the blend, the angle values expanded. The most elevated value was 73.46° at Gr 3wt % as shown in Figs.4 and 5 with the surface within the frame of a compact fluid bead. This could be attributed to the existence of the residual groups containing oxygen on the structures of Gr, consequently on the surface of the coating. On the other hand, the chemical composition and/or surface roughness can affect the wetting ability of a coated surface [9]. It was clearly observed that the highest contact angle value was obtained after coating with thin Gr. This result indicates that the chemical composition of the surface as well as its roughness changed and that the water capillary penetration (porosity) was affected. This could be explained as due to the low hydrophilicity and the barrier effect of Gr nano-fillers in the blend, which lead to a decrease of the penetration of the coated surface and significantly improved the protection of the coating against wear rate. Table 2 shows the contact angle (θ) (right and left) for the blend polymer and nanocomposites.

Table 2: Water contact angle of nanocomposites.

Samples	Left	Right	Average contact angle
Blend	46.09	51.83	48.96
1% Gr	57.41	59.17	58.29
3%Gr	74.33	72.60	73.46
5%Gr	63.44	64.55	63.99
7%Gr	63.44	62.24	62.84

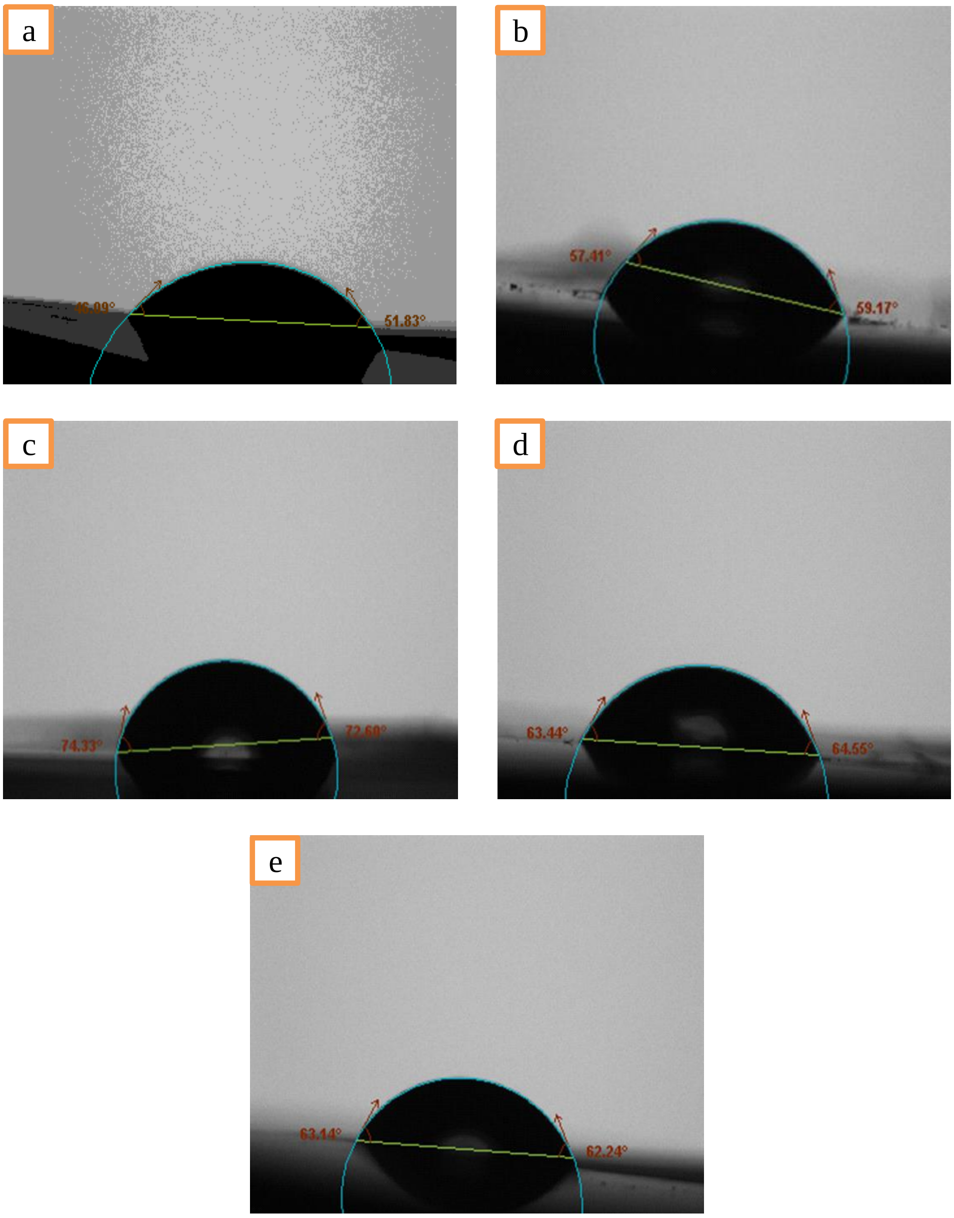


Figure 4: Contact angle for: (a) blend (Eboxy resin and Repcoat ZR), (b)1%wt Gr, (c)3%wt Gr, (d)5%wt Gr, and (e)7%wt Gr.

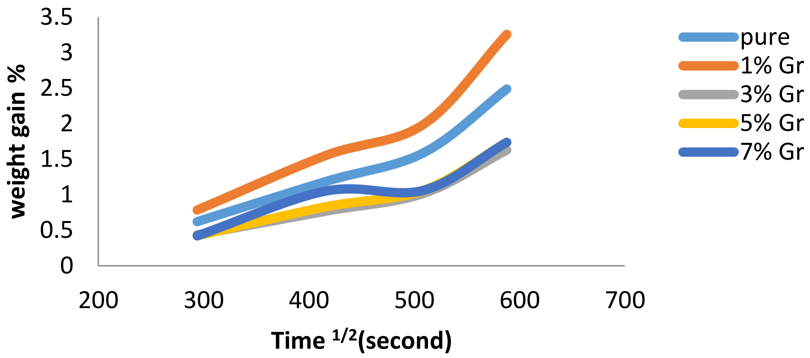


Figure 5: Weight gain as a function of time for blend (Eboxy resin and Repcoat ZR)/Gr.

3.2. Thermal stability (TGA & DSC)

Thermo gravimetric analysis (TGA) was applied to evaluate the thermal stability of the blend (epoxy & Repcoat ZR) with the added Gr. The TGA curves of the neat blend and its composites with different Gr content are shown in Table 3 and Fig.6. One could see that all the TGA curves displayed a one-step degradation mechanism, suggesting that the existence of Gr did not significantly alter the degradation mechanism of the matrix polymers. For the blended epoxy, the initial decomposition occurred at 300 ˚C, for all samples blend and nanocomposites. The second decomposition occurred at 520 ˚C for blend epoxy and 530°C for a blend with Gr. The results indicate that the composites would become highly cross linked with increasing the content of Gr. Thermal weight loss of the composites decreased with increasing the Gr content. At the temperature of 1000 ˚C, the total weight loss of blend was 98.43%, and it was 7% at 97.01% for nanocomposites (blend with Gr). This result agrees with that of Bo Qi et al. [10]. Fig.7 shows the DSC curves for the blend (epoxy & ZR rebcoat) and nanocomposites. One peak from the DSC curve represents the glass temperature (Tg). The nanocomposites showed a decrease of Tg with increasing filler content. The fillers are distributed randomly within the entire volume of the polymer blend. Glass transition temperature (T_g) of blend and its nanocomposites are shown in Table 3. T_g of blend is approximately 116.14 ˚C. The Tg of neat epoxy was found to decrease slightly when Gr was added to the resin, there was 18 ˚C decrease in the T_g with the addition of 7 wt. % Gr. The decrease in Tg softens the polymer backbone while the pinholes are formed in the polymer chains, thereby increasing the movement of ions freely through the material [11]. As a result, the optimized ratio of epoxy and curing agent in curing reaction was impacted. This is expected to reduce the polymer cross-link density and so increase polymer chain mobility. The micrographs of the scanning electron microscope (SEM) (Fig. 8) show the Gr nanoparticles and their distribution in the blend matrix and the homogeneity between the blend and graphene. This agrees with the results of Wang et al. [8].

Table 3: Weight loss, Tg, and Td for blend and nanocomposites.

Samples	Weight loss (1)	Weight loss (2)	Total weight loss	Tg (Glass Transition Temp.) ˚C	Td (decomposition temp.) ˚C
Pure	11.91% at 300 ˚C	68.59% at 520 ˚C	98.43% at 1000 ˚C	116.14	411.5
1% Gr	-	73.73% at 520 ˚C	97.21% at 1000 ˚C	115.9	431.90
7% Gr	6.06% 270 ˚C	64.03% at 530 ˚C	97.01% at 1000 ˚C	98.36	440.22

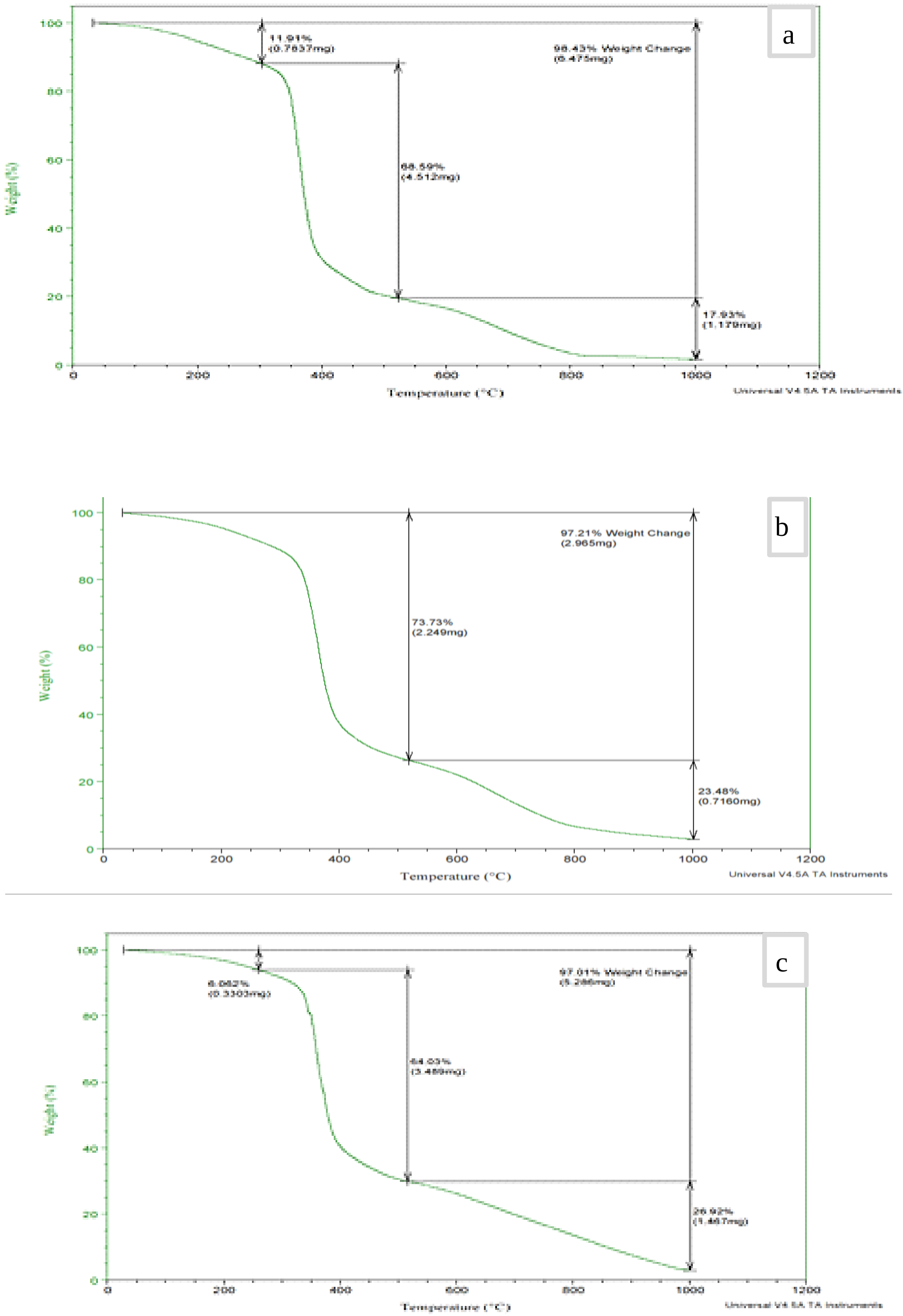


Figure 6: Weight loss as a function of temperature: a. blend, b. 1%Gr, and c.7%Gr.

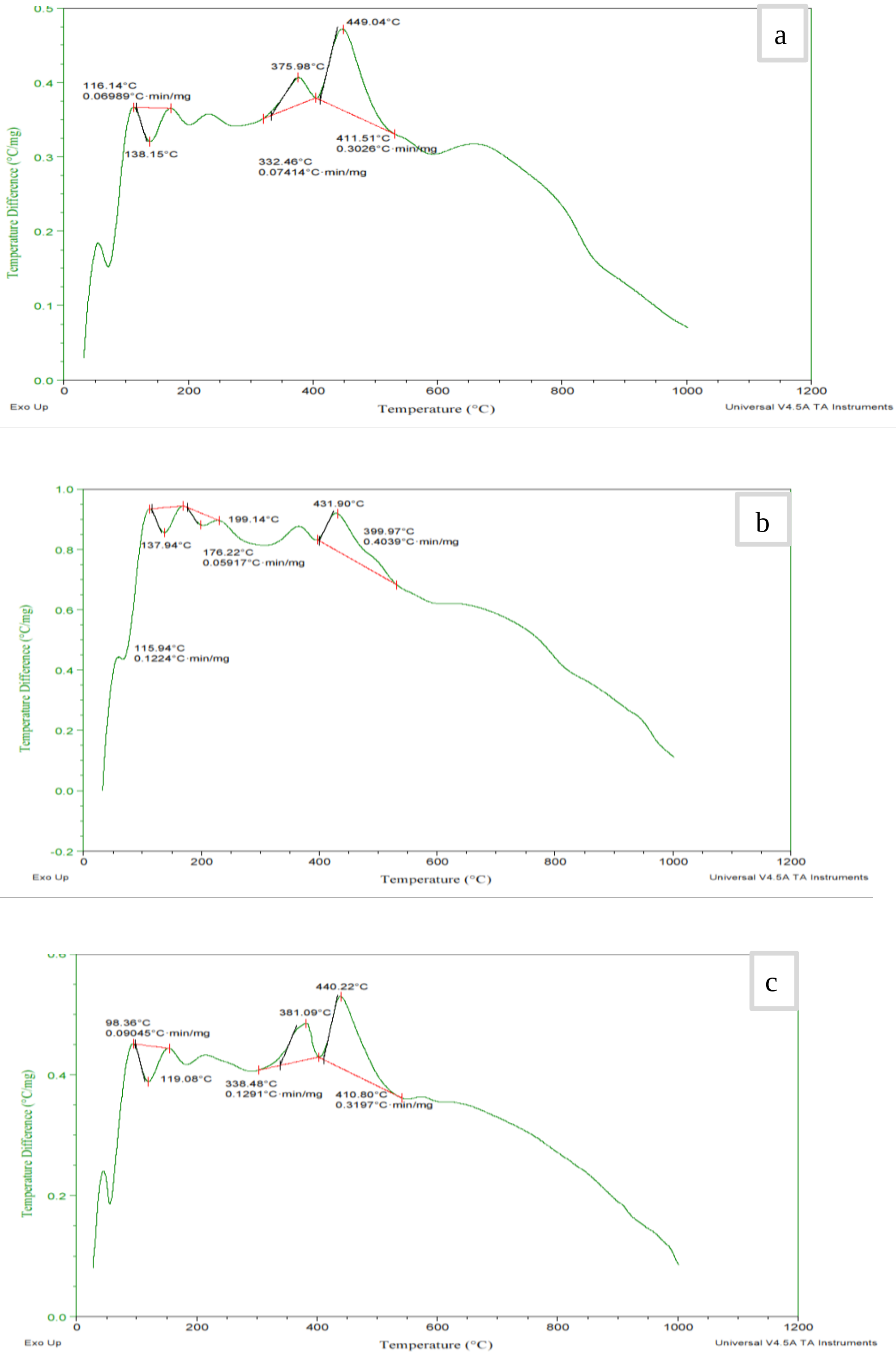
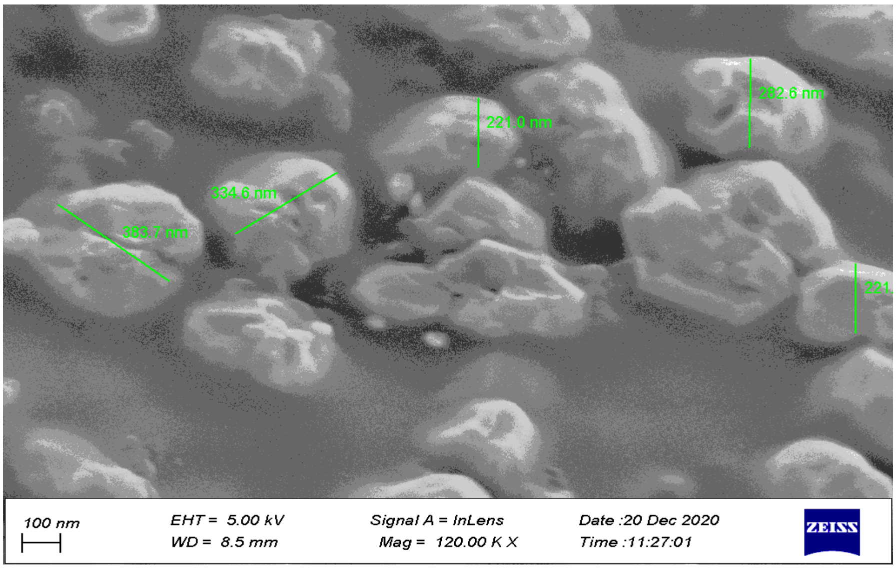
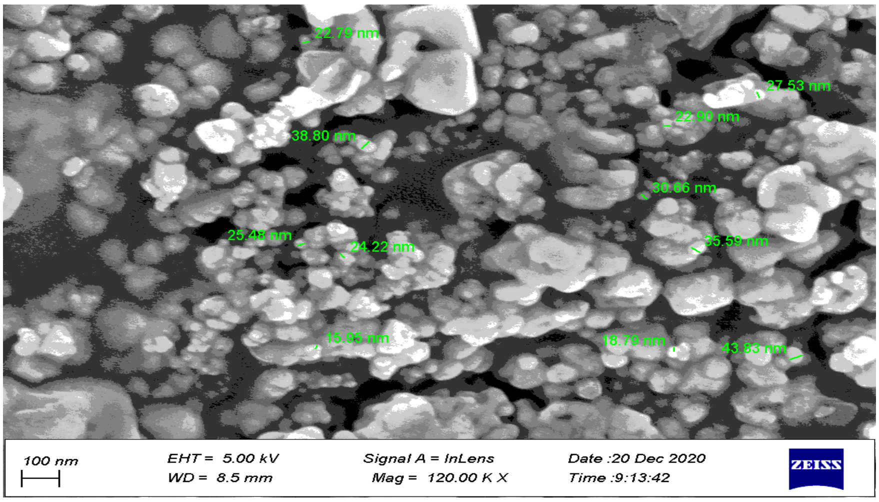


Figure 7: DSC for blend and nanocomposites: a. blend, b.1%Gr, and c. 7% Gr.



(a)



(b)

Figure 8: SEM micrograph of: a.blend (epoxy& Repcoat ZR) and b. blend with graphene nanocomposites.

4. Conclusions

The contact angle and water absorption of blend polymer coating increased with increasing the weight percentage of Gr at 3wt% i.e., the resulting nanocomposite becomes a non-wetting surface. Thermal stability of the nanocomposites increased gradually with increasing the percentage of Gr compared to the blend without adding Gr nano.

Acknowledgments

The authors would like to thank Chief Engineer in the Oil Pipelines Company, Pipe Maintenance Department / Al-Dora Refinery, Jamal Abdel Mohsen Abbas, to help me obtain the metal of the oil tanks.

Conflict of interest

Authors declare that they have no conflict of interest.

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دراسة تأثير الكرافين على زاوية التماس, امتصاصية الماء والاستقرار الحراري لخليط (الأيبوكسي و الريب كوت)

مينا محمد حسن, سيناء ابراهيم حسين
قسم الفيزياء, كلية العلوم، جامعة بغداد، بغداد، العراق

الخلاصة

في هذه الدراسة تم تطوير طلاء بوليمري من خلال دمج المادة النانوية (الكرافين) في مزيج البوليمر وتطبيقه على الخزانات النفطية. حيت تم احضار نموذج عينات الخزان النفطي من شركة خطوط انابيب النفط/ مصفى الدورة في بغداد. الطلاء البوليمري مكون من خليط) راتنجات الايبوكسي و الريب كوت (باستخدام طريقة الصب بدرجة حرارة المختبر. وتترك العينة حتى تجف لمدة 24 ساعة بدرجة حرارة المختبر. حيث كانت نسبة خلط الخليط (3:1:1راتنجات الايبوكسي 21.06 غرام), (ريب كوت الغني بالزنك 10.53 غرام), (المصلب 10.53 غرام. (تم تحضير المزيج مع الكرافين النانوي بطريقة البلمرة باستخدام نسب مختلفة تم اضافة 1 ,3 ,5 ,7 %الى المزيج, ثم وضع المحلول في وعاء زجاجي على محرك مغناطيسي عند درجة حرارة 40 درجة مئوية لمدة ساعة واحدة. كانت النتيجة ان زاوية التماس وامتصاصية الماء افضل نسبة 3% وقيمتها (73.46) وهذه الدراسة تؤكد ان الاستقرار الحراري للمركبات النانوية يزداد تدريجيا مع زيادة نسبة الكرافين مقارنة بالخليط الخالي من الكرافين وهذا السبب يعود الى المقاومة الحرارية العالية التي يمتلكها الكرافين النانوي.