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Evaluation of dispersibility of amine-modified graphene and ionic liquids based additive in lubricant

Bui Thi Le Thuy[1,*], Nguyen Thi Huyen Nga[2], Trinh Khac Vu[2], Ta Thi Toan[3], Do Thi Hai[4]

[1] *Key Research Group: Green Chemistry Process (HUMG-GCP), Department of Oil Refinery and Petrochemical Engineering, Hanoi University of Mining and Geology, 18- Vien Street, Dong Ngac Ward, Ha Noi, Viet Nam.*
[2] *Ly Tu Trong College Ho Chi Minh City: No. 390 Hoang Van Thu Street, Tan Son Nhat Ward, Ho Chi Minh City, Vietnam.*
[3] *Department of Prospecting and Exploration Geology, Faculty of Geosciences and Geoengineering/Economic Geology and Sustainable Development Research Team (EGSD), Hanoi University of Mining and Geology, Hanoi, Viet Nam.*
[4] *Department of basic Sciences, Ha noi University of Mining and Geology, 18 Vien, Duc Thang yard, Bac Tu Liem district, Ha Noi, Vietnam.*
** E-mail: thuykhai2001@gmail.com*

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ABSTRACT

To develop highly anti-friction additives, this study designed a synergistic dispersion system combining functionalized reduced graphene oxide (rGO) and an ionic liquids (IL). The experiments evaluated distinct components: octylamine-functionalized rGO (rGO-OcA at 0.004 wt%), an ionic liquid (IL at 2 wt%), and a resulting system comprising 0.2 wt% graphene dispersed within the IL base (2 wt% rGO-OcA + IL). The strategy aimed to leverage the long-chain alkylamines of rGO-OcA to establish initial compatibility with the lubricant, while utilizing the IL as a secondary stabilizing agent to prevent nano-additive agglomeration. Stability screening via relative concentration variations over 20 days demonstrated that while octylamine functionalization markedly enhanced baseline dispersibility compared to pristine GO, the rGO-OcA concentration still declined to 73.3%. Crucially, the hybrid system validated the hypothesis: the addition of highly soluble IL successfully arrested this decline, achieving superior long-term colloidal stability through enhanced IL-lubricant solubility and IL-graphene compatibility.

Introduction

Increasingly stringent regulations on energy safe and environmental protection have stimulated growing interest in the development of energy-efficient lubricants capable of improving fuel economy and reducing environmental pollution. In passenger vehicles, frictional losses are estimated to account for approximately 28% of the total fuel energy consumption. Moreover, friction and wear at mechanical interfaces lead to substantial economic losses, estimated at nearly 6% of the gross domestic product (GDP) in developed countries. Therefore, considerable efforts have been devoted to developing advanced lubricants with excellent anti-friction and anti-wear properties to enhance energy efficiency and extend engine lifetime [1–3].

Graphene oxide (GO), and reduced graphene oxide (rGO) have emerged as promising materials for a wide range of applications and exhibits outstanding anti-friction and anti-wear performance when used as an additive in liquid lubricants [3]. Functionalization of rGO

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is considered an effective strategy to improve its dispersion stability and tribological performance. Previous studies have demonstrated that rGO modified with amines, acids, ionic liquids, or alkyl groups can significantly enhance its dispersion behavior as well as its anti-friction and anti-wear properties [4–7]. These improvements are mainly attributed to the formation of a dense adsorbed film of functionalized rGO sheets on the contacting surfaces during sliding.

To further enhance lubrication performance, the combination of rGO with ionic liquids (ILs) has attracted considerable attention [8]. Ionic liquids not only exhibit intrinsic lubricating properties but also improve the dispersion of rGO in lubricant matrices, thereby enhancing the overall tribological performance. In our previous work, reduced graphene oxide functionalized with octyl amine (rGO-OcA) was prepared and its dispersion stability in ILs was systematically investigated [9].

While individual applications of rGO or ILs as lubricant additives have been documented, a systematic understanding of how the specific molecular architectures of ILs—particularly those derived from sustainable and renewable fatty acids—synergistically govern the long-term colloidal stability of amine-functionalized rGO remains poorly explored. To address this gap, this study systematically formulates hybrid additive systems by co-dispersing octylamine-functionalized reduced graphene oxide (rGO-OcA) with a comprehensive library of 20 distinct ionic liquids featuring varied cation core structures and aliphatic anion chain saturations. The novelty lies in revealing the dual-stabilization mechanism governed by the competitive π- π stacking/cation π -interactions from the IL cations and the steric hindrance from the fatty acid-derived anions, providing a strategic pathway for tuning nano-additive dispersibility in bio-based lubricants.

Experimental

Materials

Graphite (99,8%), H_2SO_4 (98%), $KMnO_4$ (99%), H_2O_2 (30%), HCl (36-38%), H_3PO_4 (85%), Octyl amine (97%) and $BaCl_2$ (99,7%), were purchased from Merck. Ethanol (99,9%) was obtained from Guangdong Guanghua Sci-Tech Co., Ltd. (China). The ionic liquids (ILs) used in this study were provided by the Laboratory of Refining and Petrochemistry, Hanoi University of Mining and Geology (Vietnam). The 20 fatty acid-based ionic liquids (ILs) were synthesized with a purity of >95% and pre-dried in desiccator prior to use. Lubricant was supplied by Ba Ria - Vung Tau Chemical Industry Joint Stock Company (Chemico) characterized by a density 0.88-0.9 g/cm^3 and funnel viscosity of 60-70 seconds

Preparation of rGO-OcA

Preparation of GO from graphite

The procedure follows the method of Bui *et al.* [10,11] and the details as follows. 2.5 g $NaNO_3$ and 5 g graphite were slowly added to 115 mL H_2SO_4 98% solution kept at 3-5 °C. The stirring with a magnetic stirrer was continued for 30 min and then 15 g $KMnO_4$ was gradually added while keeping temperature of the below 15 °C. The temperature of the reaction mixture was increased to 35°C and kept stirring for about 30 min; then, distilled water was gradually introduced to the reaction mixture to keep the temperature at around 45°C. Then temperature was increased to 95°C and the reaction mixture was stirred for extra 15 min at this temperature. Next, reduce the temperature of the system slowly to room temperature, add 50mL H_2O_2 solution to the mixture and stir for 20 minutes. The solid of final mixture was centrifuged with 8000 rpm in 6 min to get GO. Then, the GO were dispersed in HCl 0.1M solution, stirred for 15 min and centrifuged for purifying GO from impurities part. After drying at 70°C - 80°C, grinding with a ceramic mortar, the resulting product is GO.

Reduction and modification of GO by octyl amine [12]

Graphene oxide (GO, 500 mg) was dispersed in 100 mL of deionized water in a round-bottom flask and ultrasonicated at 40 kHz for 1 h. Separately, octyl amine (1.4 g) was dissolved in 80 mL of ethanol and subsequently added to the GO dispersion. The resulting mixture was refluxed for 24 h. During the reaction, the suspension gradually turned black with the formation of some black agglomerates, indicating partial reduction and functionalization of graphene oxide. The product was collected by vacuum filtration and washed several times with an ethanol–water mixture. Finally, the obtained material was dried at 60 °C for 48 h.

Evaluation of rGO-OcA dispersibility in lubricant

Mixture of additive containing rGO-OcA and ionic liquid triethylammonium oleate was prepared at a concentration of 0.2 wt%. These mixture was subsequently mixed with the lubricant at a concentration of 2 wt%. To evaluate the dispersibility of rGO-OcA within the lubricant, UV-Vis spectrophotometry was performed at various time intervals. The relative concentration of rGO-OcA was determined from the UV-Vis absorbance data using Equation (1). This

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procedure was systematically repeated for the 20 different ionic liquids listed in Table 1 to assess their respective dispersibility effects.

$$Relative\ con. = \frac{Absorption\ at\ certain\ time}{Absorption\ at\ initial\ time} * 100\% \quad (1)$$

Table 1. List of ionic liquids and samples in this research

Sample Code	Name / Description
[TEA][Oleate]	Triethyl ammonium oleate
[OcA][Oleate]	Octyl ammonium oleate
[Aliquat][Oleate]	Trialkyl methyl ammonium oleate (Alkyl: C_8H_{17} and $C_{10}H_{23}$)
[OMIM][Oleate]	Octyl methyl imidazolium oleate
[TEA][Stearate]	Triethyl ammonium stearate
[OcA][Stearate]	Octyl ammonium stearate
[Aliquat][Stearate]	Trialkyl methyl ammonium stearate (Alkyl: C_8H_{17} and $C_{10}H_{23}$)
[OMIM][Stearate]	Octyl methyl imidazolium stearate
[TEA][CO]	Triethyl ammonium carboxylate (Fatty acids separated from coconut oil)
[OcA][CO]	Octyl ammonium carboxylate (Fatty acids separated from coconut oil)
[Aliquat][CO]	Trialkyl methyl ammonium carboxylate (Fatty acids separated from coconut oil) (Alkyl: C_8H_{17} and $C_{10}H_{23}$)
[OMIM][CO]	Octyl methyl imidazolium carboxylate (Fatty acids separated from coconut oil)
[TEA][RSO]	Triethyl ammonium carboxylate (Fatty acids separated from rubber seed oil)
[OcA][RSO]	Octyl ammonium carboxylate (Fatty acids separated from rubber seed oil)
[Aliquat][RSO]	Trialkyl methyl ammonium carboxylate (Fatty acids separated from rubber seed oil) (Alkyl: C_8H_{17} and $C_{10}H_{23}$)
[OMIM][RSO]	Octyl methyl imidazolium carboxylate (Fatty acids separated from rubber seed oil)
[TEA][WO]	Triethyl ammonium carboxylate (Fatty acids separated from waste oil)
[OcA][WO]	Octyl ammonium carboxylate (Fatty acids separated from waste oil)
[Aliquat][WO]	Trialkyl methyl ammonium carboxylate (Fatty acids separated from waste oil) (Alkyl: C_8H_{17} and $C_{10}H_{23}$)
[OMIM][WO]	Octyl methyl imidazolium carboxylate (Fatty acids separated from waste oil)

Results and discussion

Characterization of GO and rGO-OcA

The FT-IR spectrum of graphene oxide (Figure 1) exhibits a prominent peak at 3358 cm^{-1}, which is characteristic of the stretching vibrations of O-H groups associated with carboxylic acids and alcohols. The bands located at 1714 cm^{-1}, 1616 cm^{-1}, 1217 cm^{-1}, and 1041 cm^{-1} correspond to the typical absorption of C=O, C=C, C-O-H, and C-O (alkoxy) groups, respectively. These findings confirm the successful preparation of GO with a high density of oxygen-containing functional groups within its structure. Upon modification of GO with octylamine, several new absorption peaks emerge, confirming the functionalization process.

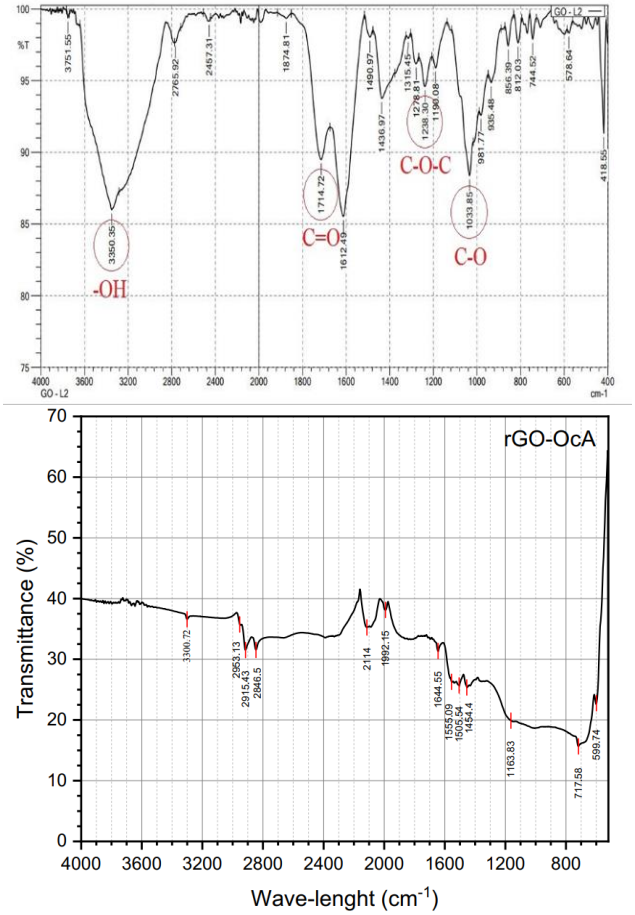

Figure 1. FT-IR of (a) GO and (b) rGO-OcA

A stretching vibration band appears at 3300 cm^{-1}, corresponding to the N-H bond in the substituted amide, while the peak in the 1600–1550 cm^{-1} range is attributed to the bending vibration of the same N-H bond. Furthermore, a broad shoulder stretching around 1500 cm^{-1} is assigned to the bending vibration of the N-

H bond in primary amines, indicating that a portion of the amine molecules was physically adsorbed onto the rGO surface. The stretching vibrations of the newly formed amide C=O and C-N bonds are observed at 1644 cm^{-1} and 1200 cm^{-1}, respectively. Finally, the absorption peaks at 2915 cm^{-1} and 2846 cm^{-1} originate from the stretching vibrations of sp^3 C-H bonds in -CH_3 and -CH_2 groups, complemented by the peak at 717.56 cm^{-1} that represents the bending vibration of long-chain -CH_2 units within the alkyl skeleton of the amine.

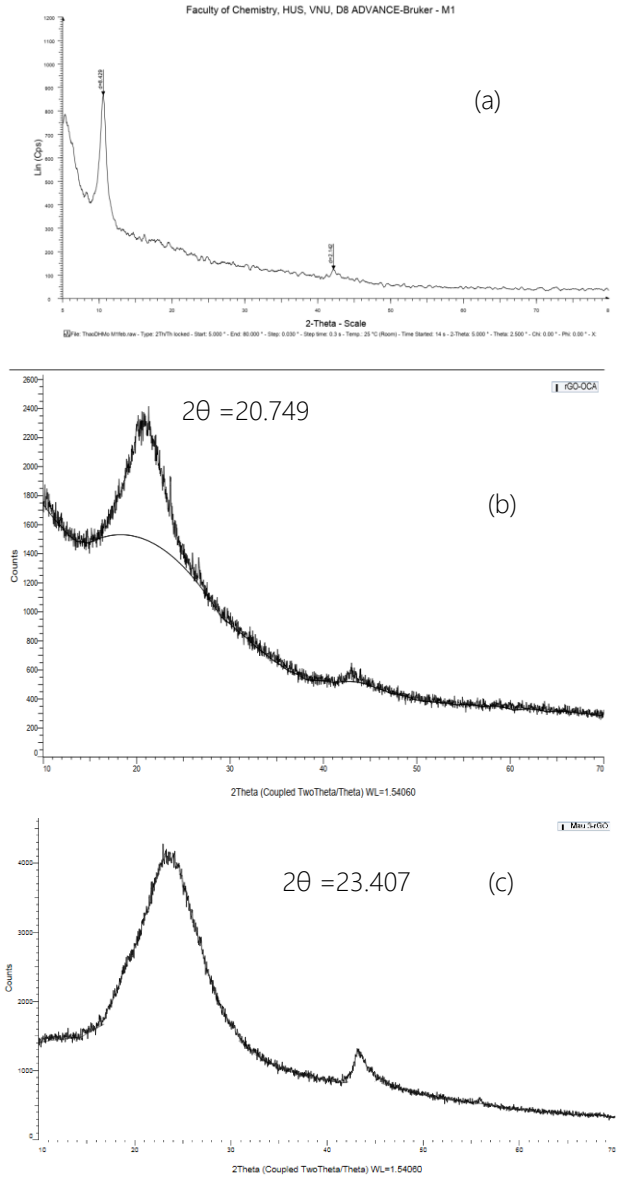

Figure 2. X-ray patterns of (a) GO, (b) rGO-DoA and (c) rGO

The X-ray diffraction (XRD) patterns of the GO, rGO-OcA and rGO obtained through reduction with ascorbic acid are displayed in Figure 2. Structural analysis reveals that the characteristic diffraction peak of GO at 2 theta = 10.58° (Figure 2a) completely disappears. Instead, new diffraction peaks emerge at 2 theta = 20.749°, which is closely aligned with the peak at 23.407 ° (Figure 2a) observed for the ascorbic acid-reduced rGO (Figure 2c). This transition demonstrates that the amines effectively acted as reducing agents to convert GO into rGO, concurrently leading to a reduction in the interlayer spacing of the carbon lattices. The fact that the 2 theta diffraction angles of rGO-OcA 20.749° is smaller than that of pristine rGO 23.407° demonstrates that the interlayer spacing of the carbon lattices in rGO-OcA is larger than that of unmodified rGO. This expansion is attributed to the chemical reaction between the amine molecules and the functional groups on the GO surface to form amide groups, which allowed the amine chains to intercalate between the graphene sheets during the formation of the modified rGO structures.

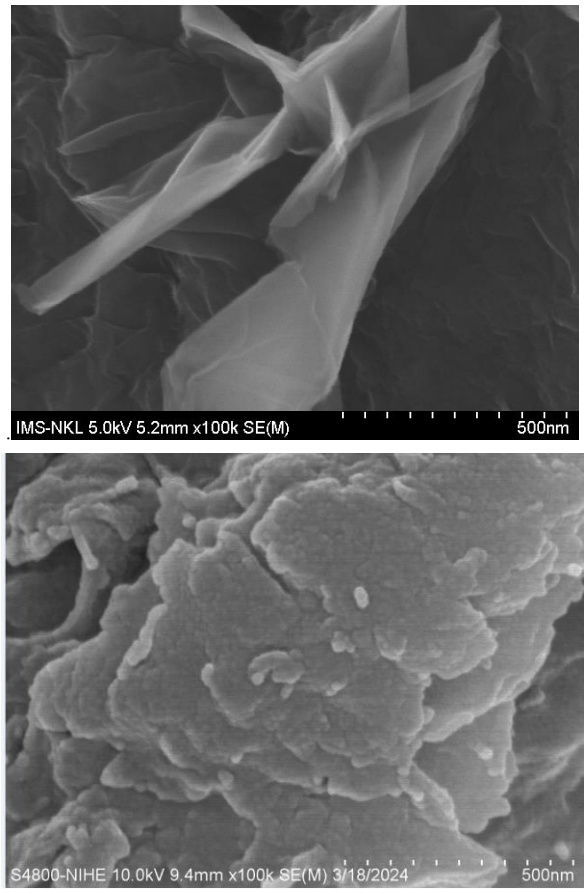

Figure 3. SEM patterns of (a) GO, (b) rGO-OcA

Scanning electron microscopy (SEM) images of the GO sample (Figure 3) show that the bulk graphite structure was successfully exfoliated into thinner layers, confirming the efficient oxidation of graphite into GO. Conversely, the SEM micrographs of rGO-OcA reveal that the carbon lattice layers tend to separate and shift further apart. This morphological alteration is attributed

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to the presence and coverage of amine groups on the surface of the graphene sheets, which induces a steric hindrance effect between the layers.

Dispersibility of GO and rGO-OcA in lubricant

In this section, the dispersibility of the additive mixture (consisting of rGO-OcA and the ionic liquid) within the lubricant base was evaluated. The additive mixture was mixed with the lubricant at a total concentration of 2 wt%, resulting in a final concentration of 0.004 wt% rGO-OcA and 2 wt% IL. For comparative purposes, two control samples were prepared by dispersing GO and rGO-OcA directly into the lubricant at the same concentration of 0.004 wt% without IL. The experimental results are summarized in Table 2.

Table 2. Relative concentration over time of GO, rGO-OcA in the lubricant without IL

Time (day)	Relative concentration of GO (%)	Relative concentration of rGO-OcA (%)
0	100	100
5	63.6	81.2
10	58.3	76.0
15	56.2	73.8
20	55.7	73.3

In the absence of IL, rGO-OcA exhibited superior dispersibility in the lubricant compared to GO. The reduction of GO to rGO by amine and modification with the grafting of amine functional groups, significantly enhanced its compatibility with the lubricant. Despite this improvement, the concentration of rGO-OcA still experienced a relatively rapid decline over time, with the relative concentration dropping to 73.3% after a 20-day period.

Dispersibility of rGO-OcA within lubricant in the presence of IL

Influence of IL cation structure on the dispersibility of rGO-OcA in lubricants

As illustrated in Figure 4, a gradual decrease in rGO-OcA relative concentration in lubricant+IL over time was observed across all experimental samples. Specifically, after 5 days, the relative concentration of rGO-OcA in lubricant + [OMIM] based ILs declined from 100% to approximately 93.0–95.4%. Similar trends were recorded for lubricant + other IL: [OcA] based IL (92.2–94.6%), [Aliquat] based IL (91.4–93.8%), and [TEA] based IL (90.6–93.0%).

After 20 days, the relative concentration of rGO-OcA in lubricant + IL further decreased but remained relatively stable compared to the control: [OMIM] based IL: 91.0–93.4%; [OcA] based IL: 90.2–92.6%; [Aliquat] based IL: 89.4–91.8%; [TEA] based IL: 88.6–91.0%. In comparison, the control sample (lubricant without ionic liquids) exhibited a significant drop in rGO-OcA concentration, falling to 81.6% after 5 days and only 73.7% after 20 days. These results indicate that the presence of ILs significantly enhances the relative concentration of rGO-OcA in the lubricant, effectively suppressing the sedimentation rate of the rGO-OcA over time. Furthermore, the results demonstrate that the functionalization of rGO with octylamine (forming rGO-OcA) enhances its dispersibility within the lubricant base, regardless of the presence of ionic liquids. In summary, the dispersion stability of rGO-OcA was most pronounced in [OMIM]-based ILs, followed by those based on [OcA], [Aliquat], and [TEA], respectively.

Dispersibility mechanism of rGO-OcA by ionic liquids (ILs)

The improved dispersion stability of rGO-OcA in the presence of ionic liquids (ILs) can be explained by several key intermolecular interaction mechanisms. Specifically, ammonium-based ILs containing [Aliquat], [OcA], and [TEA] cations can establish cation–\(\pi \) interactions with the delocalized electron cloud of the graphene sheets, thereby forming a protective barrier that suppresses re-agglomeration. Furthermore, the long alkyl chains present in ILs such as [OcA] (octyl) and [Aliquat] (trioctyl methyl ammonium) induce substantial steric hindrance between the rGO-OcA sheets. Due to their structural similarity, these extended hydrocarbon chains exhibit excellent compatibility with the octylamine (OcA) groups on the rGO surface, effectively "anchoring" the IL molecules onto the solid matrix and creating a buffer barrier that prevents close contact between the sheets. Conversely, [TEA] (tetraethylammonium), which features short ethyl chains (C_2H_5), exerts the weakest steric effect, consequently leading to the lowest sedimentation resistance among the studied groups. In short, the stabilizing efficiency of ILs for rGO-OcA suspensions is governed by a synergistic mechanism combining electronic (cation–π) interactions and spatial steric hindrance from the alkyl substituents.

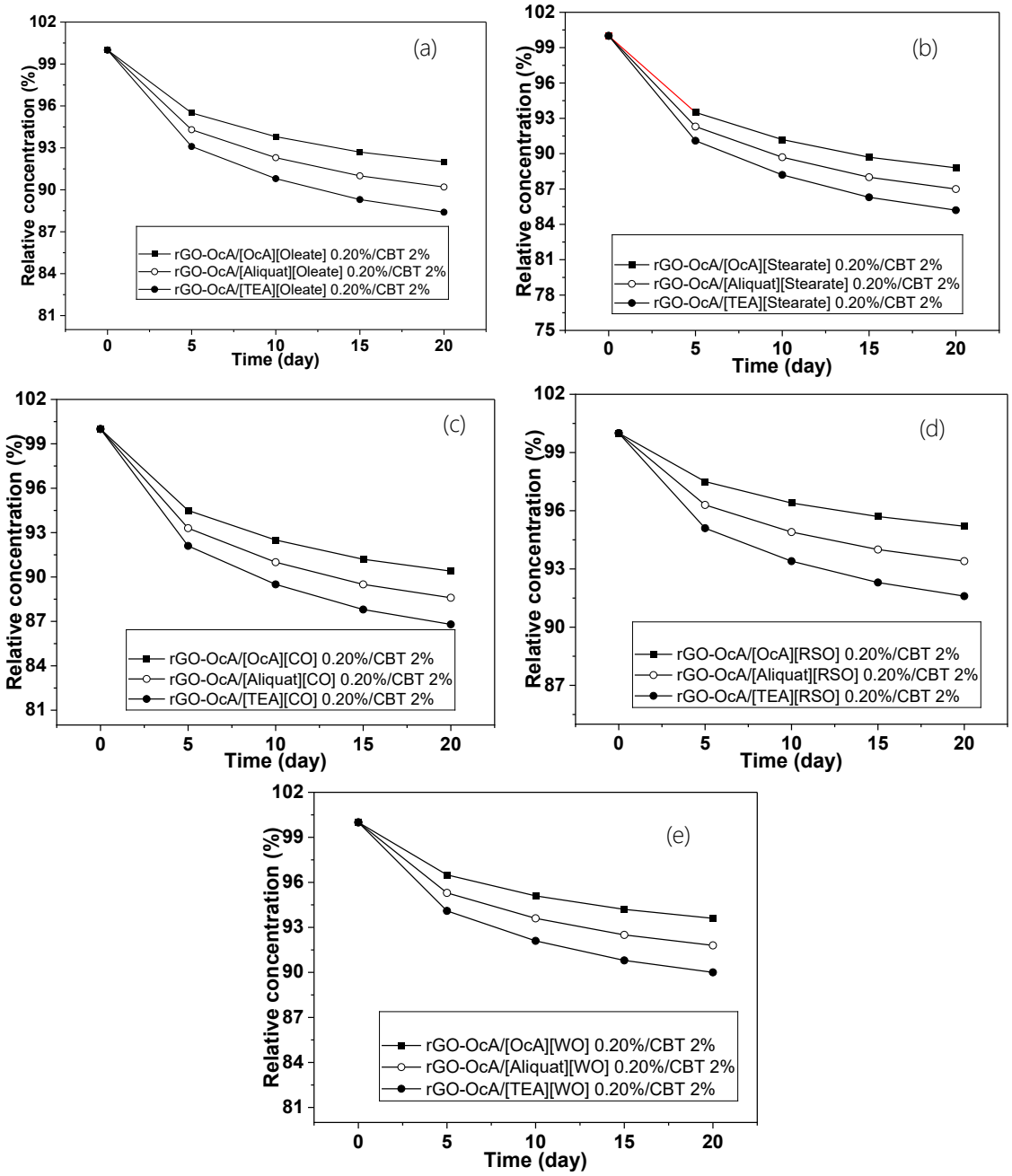

Figure 4. Influence of ionic liquid cation structure on the dispersion stability of rGO-OcA in lubricants and IL based on anion: (a) oleate; (b) stearate; (c) coconut oil fatty acids; (d) rubber seed oil fatty acids; (e) waste oil fatty acids. (rGO-OcA concentration in IL: 0.004 wt%; IL concentration in lubricant: 2 wt%).

Influence of IL Anion Structure on the dispersibility of rGO-OcA in Lubricants and IL

According to the results in Figure 5, a marginal decrease in rGO-OcA concentration over time was observed across all samples.

For instance, after 5 and 20 days, the relative concentration of rGO-OcA in lubricant + [RSO] based ILs declined from 100% to 93.0–95.4% and 91.0–93.4%, respectively. In lubricant + [WO] based ILs, the concentration decreased to 92.4–94.8% and 90.4–92.8%. For lubricant + [Oleate] based IL, the concentrations fell to 91.8–94.2% and 89.2–92.2%, while lubricant + [CO] based ILs showed a reduction to 91.2–93.6% and 89.2–91.6%. Finally, in lubricant + [Stearate] based ILs, the concentration remained at 90.6–93.0% and 88.6–91.0% after the respective intervals.

Based on these observations, rGO-OcA exhibits the highest stability in lubricant + [RSO] based ILs, followed by [WO], [Oleate], [CO], and [Stearate] in descending order: [RSO] > [WO] > [Oleate] > [CO] > [Stearate].

Since the ionic liquids (ILs) based on oleate, rubber seed oil (RSO), and waste oil (WO) possess a decreasing content of unsaturated fatty acids, the initial dispersibility of rGO-OcA within lubricant + ILs follows the order of anion: [Oleate] > [RSO] > [WO]. In contrast, coconut oil (CO) fatty acids consist primarily of saturated acids, which leads to a reduction in rGO-OcA dispersibility. Similarly, the dispersibility of rGO-OcA in lubricant + [Stearate] based ILs is the lowest due to its fully saturated nature.

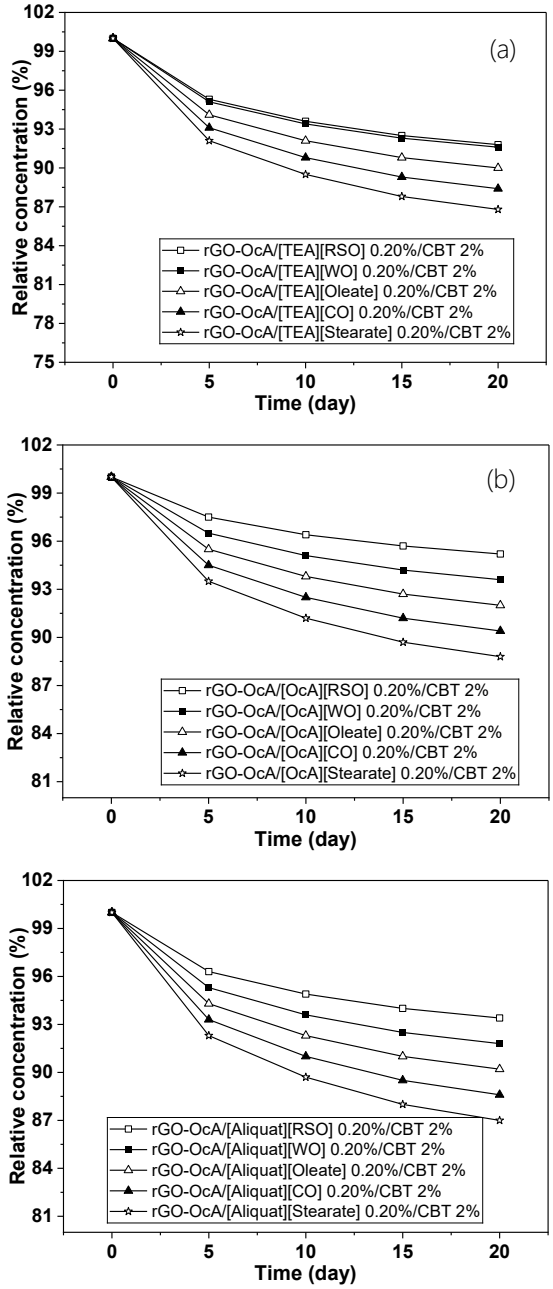

Figure 5. Influence of ionic liquid anion structure on the dispersion stability of rGO-OcA in lubricants and IL based on cation: (a) [TEA]; (b) [OcA]; (c) [Aliquat]. (rGO-OcA concentration in IL: 0.004 wt%; IL concentration in lubricant: 2 wt%).

Furthermore, when the rGO-OcA/IL mixture is dispersed into the lubricant at a 1:20 ratio, the chemical structure of the base lubricant significantly influences the overall stability of the system. The vegetable oil-based lubricant comprises a complex mixture of both saturated and unsaturated fatty acids, it exhibits a higher affinity and compatibility with ILs derived from fatty acid of vegetable oils (such as [RSO] and [WO]) compared to IL synthesized from fatty acids (like oleate or stearate).

Conclusion

The functionalization of GO with amine to form rGO-OcA significantly enhances its dispersibility compared to pristine GO. The reduction of GO to rGO, combined with the attachment of amine groups, substantially improves its compatibility with the lubricant. However, when rGO-OcA is dispersed in the lubricant without the assistance of ionic liquids (ILs), its concentration declines rapidly over time, with the relative concentration dropping from 96% to 73.7% after 20 days. The co-dispersion of rGO-OcA and ionic liquids into the lubricant leads to a remarkable increase in dispersibility, the [OMIM][RSO] system offering the highest stability among the investigated ILs. This synergistic effect can be attributed to the interaction between the polar amide functional groups on the rGO surface and the polar moieties of the ionic liquids. Furthermore, the long hydrocarbon chains of the amine groups ensure excellent compatibility with both the ionic liquids and the lubricant, effectively stabilizing the suspension.

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