Effect of Incorporation of Multiwalled Carbon Nanotubes on the Microstructure and Flow Behavior of Highly Concentrated Emulsions

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Supporting Information

ABSTRACT: Multiwalled carbon nanotubes (MWCNTs) were incorporated into highly concentrated water-in-oil emulsions with the ultimate aim of achieving a uniform and effective dispersion of MWCNTs within the emulsion matrix. The emulsion was formulated in such a way, wherein the internal phase consists of higher than 90 wt %. By keeping the same aqueous-to-oil phase ratio, the amount of MWCNTs in the oil phase was systematically adjusted to investigate their effects on the microstructure development and rheological behavior of the emulsion. The addition of MWCNTs led to a reduced droplet size and also resulted in a narrower distribution of the droplet size. The rheological behavior of nanotube-incorporated emulsions was characterized with varying MWCNT concentrations and also as a function of the emulsification time. The rheological characteristics of the nanotube-incorporated emulsions were identical to those of the neat emulsion and were primarily governed by the variation in the droplet size and droplet-size distribution. However, the yield strain and cross-over strain were independent of the mean droplet size and polydispersity of the emulsion. Emulsions that have smaller droplets exhibited higher storage modulus (G'), yield stress (τY), and apparent viscosity (η). For all refining times investigated, nanotube-incorporated emulsions have higher G', τY, and η values when compared to the neat emulsion, and these values further increased with the MWCNT concentration. This was primarily due to the decrease in the droplet size with MWCNT addition. Furthermore, our findings suggest that the incorporated MWCNTs did not induce any significant change in the rheological behavior of emulsions with identical droplet sizes, and it remained essentially unchanged with the concentration of MWCNTs. However, the nanotube-incorporated emulsions possessed solidlike behavior up to a higher applied stress when compared to a neat emulsion of identical droplet size.

1. INTRODUCTION

Emulsions containing dispersed phase volume fraction ($\phi$) higher than 0.74 are referred to as highly concentrated emulsions (HCEs). HCEs are extensively used in the food industry, paints, pharmaceuticals, cosmetics, and petroleum-based industries. In addition, HCEs are widely used as reaction media in chemical reactions1−3 and as templates for the preparation of low-density organic and inorganic substances.4−6 The preparation of stable HCEs with volume fractions exceeding the critical value is only possible by using extremely polydisperse systems and/or by the deformation of spherical droplets into polyhedrons.7 HCEs maintain their original structure at such high values of $\phi$ because of the polydispersity and the “compression” of spherical droplets within the system.8

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Relevant to this work, highly concentrated water-in-oil (w/o) emulsions find application in the mining industry as commercial explosives and are widely used in commercial blasting because of their superior characteristics such as water resistance, variable viscosity, low vulnerability to accidents, and higher detonation performance.\textsuperscript{5,6} The composition of an emulsion explosive comprises an oxygen-supplying dispersed phase and a continuous phase that contains an organic fuel.\textsuperscript{7} A supersaturated aqueous solution of oxidizing salts that makes up greater than 90 wt % of the emulsion forms the dispersed phase, whereas the continuous phase is a solution of the emulsifier in a blend of hydrocarbon oils. Several studies were reported on different aspects of w/o HCEs, such as the conditions of formation,\textsuperscript{8,9,11−15} preparation,\textsuperscript{14} and morphology.\textsuperscript{15} HCEs are characterized as viscoelastic liquids with complex flow behavior. A number of studies were reported on the influence of various governing factors on the rheological characteristics of HCEs, and emulsion explosives in particular.\textsuperscript{16−27}

Carbon nanotubes (CNTs) are an extremely valuable resource in nanotechnology, electronics, optics, and other areas of materials science. They are used as additives to enhance the thermal, mechanical, and electrical performances of various structural materials such as ceramics, metals, and polymers. CNTs are reported to be a unique nanomaterial towards the formation of both oil-in-water (o/w) and w/o Pickering emulsions.\textsuperscript{28−33} Wang et al. reported the first emulsion stabilized by CNTs, in which the single-walled CNTs (SWCNTs) were used to stabilize w/o emulsion system of toluene and water.\textsuperscript{28} Hobbie et al. demonstrated that the DNA-coated SWCNTs could stabilize the interface between two immiscible liquids.\textsuperscript{29} In addition, CNT-stabilized w/o and o/w emulsions exhibited a significant decrease in the rate of coalescence of droplets as compared to emulsions stabilized by various spherical particles.\textsuperscript{34,35} Thus, CNTs showed the potential to act as emulsion stabilizers.

Recently, CNTs and several other nanoparticles were incorporated into HCEs either as Pickering stabilizers or as co-stabilizers, and the role of various factors such as the particle size, hydrophobicity, and surfactant/particle ratio on the emulsion stability was studied.\textsuperscript{35−38} Multiwalled CNTs (MWCNTs) were also utilized as “cosurfactants” along with conventional surfactants to prepare w/o HCEs.\textsuperscript{38} Studies on poly high internal phase emulsion (polyHIPE) composite foams provided some useful insights regarding the formation of percolating networks in HCEs.\textsuperscript{39−43} Conductive polyHIPE composites having a low electrical percolation threshold were prepared by the polymerization of highly concentrated w/o emulsions incorporated with CNTs, where CNTs were either added in the aqueous phase or in the organic phase. Noh et al. had reported higher electrical conductivity of foams when CNTs were dispersed in the aqueous phase of HCEs.\textsuperscript{44} It was assumed that the dispersed CNTs in the aqueous phase could form an efficient two-dimensional network on the cell surface after the polymerized monolith becomes dry. By contrast, CNTs have to form a three-dimensional (3D) network structure inside the polymerized matrix of the foam if it is dispersed in the organic phase and hence requires a higher concentration of CNTs.\textsuperscript{45}

In the current study, MWCNTs were incorporated into the oil phase of highly concentrated w/o emulsions. If MWCNTs in sufficient quantity are uniformly and selectively dispersed in the continuous oil phase of the emulsion, a continuous 3D “networklike” structure of MWCNTs can be developed throughout the emulsion matrix. An efficient 3D network of MWCNTs within the emulsion can be utilized to vary its physical characteristics. Further, MWCNTs can impart additional properties through the 3D network formation, which could be utilized for the process enhancements and preparation of high-performance materials. To achieve this, MWCNTs should be selectively dispersed and localized in the oil phase of the emulsion. Because the continuous phase constitutes only less than 10 wt % of the total emulsion, the MWCNT network can be developed with a relatively low amount of nanotubes. The objective of the current investigation is to elucidate the influence of MWCNT incorporation on the microstructure, refining characteristics, and flow behavior of HCEs. A comparator w/o emulsion system with the internal phase volume fraction greater than 90 wt % was chosen for this study. Based on the emulsion composition and volume fraction of the phases, the rheological characteristics of these emulsion systems are identical to the precursor emulsion utilized in the preparation of “liquid explosives.” MWCNTs were incorporated into the oil phase of the HCE, and the influence of the incorporated MWCNTs on the microstructural development and rheological characteristics of HCEs has been investigated elaborately.

2. RESULTS AND DISCUSSION

2.1. Characterisation of MWCNTs. The morphology of MWCNTs, as observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses, is shown in Figure S1a−c provided in the Supporting Information. TEM analysis suggests that the average diameter of the MWCNTs is ∼10.2 ± 2 nm; MWCNTs exhibit a highly entangled and agglomerated structure. Figure S1d, provided in the Supporting Information, shows the Raman spectrum of MWCNTs, which exhibit a D-band at ∼1344 cm\textsuperscript{-1} and a G-band at ∼1581 cm\textsuperscript{-1}. The origin of the D-band is correlated with the defect concentration,\textsuperscript{46} and the G-band is assigned to the C=C stretching vibration in the graphene plane for ordered graphitic structures.\textsuperscript{46} MWCNTs exhibit the Raman intensity ratio, I\textsubscript{D}/I\textsubscript{G}, value of ∼1.22, which is used as a measure of nanotube perfection. X-ray photoelectron spectroscopy (XPS) measurement was performed to determine the elemental composition and functional groups present on the MWCNT surface. It was found that the amounts of carbon (C 1s) and oxygen (O 1s) present in the MWCNTs were 95.3 and 4.7 at. %, respectively. The XPS spectra of MWCNTs are shown in Figure S2.

2.2. Nanotube-Incorporated HCEs: Microstructure, Refining Characteristics, and Dispersion of MWCNTs.

2.2.1. Refining Behavior: Microstructure Development during Emulsification. As discussed in the section on emulsion preparation, the emulsification proceeds in two stages: “formation” and “refining.” The emulsion formed at the end of the “formation” step is a coarse emulsion with large droplets and high polydispersity. Subsequently, during the high-speed “refining” step, larger droplets of the coarse emulsion get refined further because of the high applied shear rate. As the “refining” stage of emulsification proceeds, the mean droplet size reduces and the distribution width becomes narrower. A thorough understanding of the refining behavior of HCEs is vital to prepare emulsions with the desired and essential characteristics. To evaluate the influence of MWCNTs on the refining behavior of HCEs, the emulsion...
samples were collected at varying refining times ($t_r = 0, 3, 6, \text{ and } 10$) during the “refining” stage. The refining time $t_r = 0$ indicates the coarse emulsion formed at the end of the “formation” step. For each sampling time, microscopic analysis was carried out for all emulsions with varied concentrations of MWCNTs to investigate their refining behavior. The neat emulsion had achieved the target viscosity within 10 min of refining, and hence all emulsion samples with different concentrations of MWCNTs were refined for 10 min. However, the nanotube-incorporated emulsions achieved a much higher viscosity within the 10 min of refining when compared to the neat emulsion, and the viscosity significantly increased with the increase in the MWCNT concentration.

Photographic images of nanotube-incorporated HCEs with varying concentrations of MWCNTs are shown in Figure S3. The emulsion color gradually changes to black with the increase in the concentration of MWCNTs. Confocal laser scanning micrographs of the neat and various nanotube-incorporated emulsions, at various stages of refining, are shown in Figure 1. These emulsions consist of multifaceted polyhedral droplets of a few micrometre size and are separated by a submicron-thin layer of the oil phase. Irrespective of the concentration of the MWCNTs, the droplet size of the emulsion decreased with an increase in $t_r$. As observed from Figure 1, “agglomerates” of MWCNTs were present in the emulsion matrix. Average agglomerate size of the remaining MWCNT agglomerates was estimated from the confocal microscopic analysis of emulsions of varying MWCNT concentrations. The number of MWCNT agglomerates and their average size increased with the concentration of MWCNTs (9.9 μm for 0.5NT emulsion, 11.3 μm for 1NT emulsion, 12.4 μm for 2NT emulsion, and 14.2 μm for 2NT emulsion).

Till date, the highest concentration CNT dispersions in organic solvents have reported a maximum concentration of nearly 2 mg mL$^{-1}$. However, in the present study, the concentration of MWCNTs in the oil blend ranges between 2.24 and 35.8 mg mL$^{-1}$, which is much higher than the previously reported highest concentration CNT dispersions in various organic solvents. Owing to the very high concentration of MWCNTs, achieving a homogenous dispersion of “debundled” MWCNTs in the oil blend is challenging. A fraction of MWCNTs remained as agglomerates in the oil blend–MWCNT dispersion after ultrasonication. Further, it was observed that even the extended ultrasonication could not provide any significant improvement in the dispersion state of MWCNTs in the oil blend. MWCNT agglomerates were more prominent in the dispersion that contains higher concentrations of MWCNTs.

For each sampling time, around 700–1000 droplets were considered, and the diameter data were processed to estimate the average droplet size and distribution. The droplet-size distribution and the corresponding probability distribution were then determined for each $t_r$ to investigate the microstructural development of emulsions. Figure S4 illustrates the droplet-size distribution of all emulsions with varying refining concentrations.
times. At all stages of refining, the droplet-size distributions can be well curve-fitted using the log-normal fitting. The curve-fitting data were extracted from the droplet-size distributions for the neat and nanotube-incorporated emulsions and were analyzed in detail. The width of the droplet-size distribution was found to decrease with the increase in $t_r$. Figure 2 depicts the superimposed droplet-size distribution curves for the neat and nanotube-incorporated emulsions at specific refining time intervals during the emulsification process. The superimposed droplet-size distribution curves at various stages of emulsification for each emulsion are shown in Figure S5. The analysis illustrates the variation in the droplet-size distribution with MWCNT concentration at various stages of emulsification and provides insights to understand the refining characteristics of the nanotube-incorporated emulsions. The strong influence of the concentration of MWCNTs in the evolution of the emulsion microstructure is clear from the refining characteristics. It is observed that the increase in the MWCNT concentration results in finer droplet size and a narrower droplet-size distribution.

The emulsion refinement data were analyzed further in detail to investigate the influence of the incorporated MWCNTs in the emulsion-refining characteristics. The Sauter mean diameters (mean volume–surface diameter, $d_{32}$) at different stages of refinement were calculated for the neat and nanotube-incorporated emulsions. The $d_{32}$ value for each refining time was determined as follows

$$d_{32} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}$$

where $n_i$ is the number of droplets with a diameter $d_i$. Figure 3 depicts the evolution of $d_{32}$ values of emulsions in terms of increasing $t_r$. In general, the droplet size decreased exponentially with increase in $t_r$ and asymptotically converged to saturating values with the further increase in $t_r$. This behavior is consistent with our previous study on the refining kinetics of HCEs as well as with the findings on other concentrated emulsions.

For the neat coarse emulsion, that is, the neat emulsion formed at the end of the “formation” step of emulsification ($t_r = 0$ min), the estimated $d_{32}$ value was 54.4 μm. Within 3 min of refining ($t_r = 3$ min), the $d_{32}$ value reduced rapidly to 23.6 μm. Subsequent to the initial abrupt refining, the droplet size further decreased gradually to 6.4 μm for $t_r = 10$ min. Nanotube-incorporated emulsions also exhibited an exponential reduction in $d_{32}$ values with the increase in the refining time. Moreover, $d_{32}$ values at various stages of refining for the nanotube-incorporated emulsions strongly depend on the concentration of the MWCNTs in the corresponding emulsion. For the 0.5NT emulsion, the coarse emulsion $d_{32}$ value reduced to 45.6 μm when compared to $d_{32} = 54.4$ μm corresponding to the neat coarse emulsion. With a further increase in the MWCNT concentration in the oil phase, there was a substantial decrease in the coarse emulsion $d_{32}$ value. The coarse emulsion $d_{32}$ value reduced to 13.9 μm with the addition of 4 wt % MWCNTs in the oil phase. At a specific refining time, the corresponding $d_{32}$ values for nanotube-incorporated emulsions decrease with the increase in the concentration of MWCNTs.
The $d_{32}$ evolution trend of different emulsions during the emulsion “refining” stage can be modelled using the following empirical model:

$$d_{32}(t) = d_i + d_f e^{-rt_i}$$

where $d_i$, $d_f$, and $r$ are the fitting parameters; $d_i$ is the saturating diameter, $r$ is the rupture rate, and $t_i$ is the refining time. The droplet diameter decreases exponentially with the increase in $t_i$ during refining, and $d_{32}$ asymptotically approaches a saturating value $d_f$. Further extended refinement does not produce any significant reduction in the droplet size. The saturating diameter strongly relies on the shearing rate and is inversely proportional to the shearing rate. Moreover, the rupture rate, $r$, depends on both the shearing rate and the coarse emulsion diameter. Coarse emulsions with large droplets exhibit high rupture rates, and the droplet break-up probability vanishes as the droplets converge to the saturating diameter. The experimental data were fitted using eq 2, and the values of $d_i$, $d_f$, and $r$ obtained for the neat and the nanotube-incorporated emulsions are presented in Table 1.

Table 1. Values of Fitting Parameters in Eq 2 Calculated for the Neat and Nanotube-Incorporated Emulsions

<table>
<thead>
<tr>
<th>Emulsion</th>
<th>$d_i$ (µm)</th>
<th>$d_f$ (µm)</th>
<th>$r$ (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat</td>
<td>4.85</td>
<td>49.34</td>
<td>0.0051</td>
</tr>
<tr>
<td>0.5NT</td>
<td>4.43</td>
<td>41.49</td>
<td>0.0058</td>
</tr>
<tr>
<td>1NT</td>
<td>4.36</td>
<td>17.60</td>
<td>0.0095</td>
</tr>
<tr>
<td>2NT</td>
<td>3.92</td>
<td>16.12</td>
<td>0.0100</td>
</tr>
<tr>
<td>4NT</td>
<td>3.56</td>
<td>10.35</td>
<td>0.0102</td>
</tr>
</tbody>
</table>

Figure 4a shows the variation of $d_i$ and $d_{32}$ values after the completion of 10 min of refining, with the MWCNT concentration in the oil phase of the corresponding emulsions. It clearly suggests that increasing MWCNT concentration leads to a decrease in the average droplet size. Similar reports have been documented in the case of Pickering emulsions, wherein the emulsion droplet size decreased with the increase in the concentration of silica particles, CNTs, and other hybrid nanoparticles. For the CNT-incorporated polyHIPE foams, the average cell size decreased with increase in the CNT content. Further, as observed from Figure 4a, the difference between $d_i$ and $d_{32}$ values becomes marginal with an increase in the concentration of MWCNTs. Hence, with increasing MWCNT concentration, the emulsion droplets approach the saturating diameter faster during emulsification. Figure 4b exhibits the variation in the rupture rate as a function of the concentration of MWCNTs in the emulsion. The rupture rate increases with the increase in the MWCNT loading. The $d_{32}$ value, after the completion of 10 min of refining, reduced from 6.7 to 5.1 µm with the addition of 0.5 wt % MWCNTs. For the emulsion with 4 wt % MWCNTs in the oil phase, $d_{32}$ value reduced by ~48% of that of the neat emulsion. This suggests that the rupture rate increases with the MWCNT concentration, and consequently, the mean droplet size decreases.

A rapid droplet refinement was exhibited by all emulsions during the early stage of the emulsion “refining,” irrespective of their MWCNT content. Further, with the extended shearing, the droplet size decreased slowly and asymptotically converged to a saturating value. The emulsification mechanism and the complex refining kinetics of HCEs are not well-understood. In general, the initial abrupt droplet refinement could be due to Rayleigh instability, in which the droplet undergoes rupturing when it attains the critical radius. Droplets undergo subsequent gradual rupturing, and the polydispersity decreases with further shearing. The stress needed to deform a droplet is higher for a smaller droplet, and hence, the rupture probability decreases with the reduction in the droplet size. In addition, various physical and formulation factors often affect the droplet size and the polydispersity of emulsions.

Fundamentals of droplet-rupturing mechanism were first derived by Taylor, and those analyses were based on a Newtonian continuous phase. Taylor’s theory was well-suited for dilute emulsions with a low surfactant concentration. Subsequently, researchers developed further much-needed extensions to Taylor’s theory to broaden its scope. The analysis has also been extended to HCEs by calculating the governing shear stress based on the effective emulsion viscosity instead of the continuous phase viscosity. The droplet breakup takes place when the capillary number is above a critical number, $Ca_{\text{crit}}$, which depends on the viscosity ratio and the type of flow. For HCEs, it is defined as $Ca_{\text{crit}} = \eta_{\text{eff}} \dot{\gamma} r / \Gamma$, where $\dot{\gamma}$ is the shear rate, $r$ is the radius of the droplet, and $\Gamma$ is the interfacial tension. The size of the droplet after the break up is given as $r \propto Ca_{\text{crit}} \Gamma / \eta_{\text{eff}}$. Thus, the average droplet size of HCEs primarily depends on the viscosity ratio (note, for HCEs, the viscosity ratio is defined as the ratio of the dispersed phase viscosity to the effective viscosity of the emulsion), interfacial tension, and the applied shearing stress during emulsification. It should be noted that these expressions were derived on the basis of simple shear flow experiments imposed on a single droplet without any interaction between the droplets. However, the actual situation
during the formation of HCEs is different, and the formation and refinement of HCEs could be significantly affected by the interdroplet interaction. Moreover, the flow during mechanical stirring may be a combined simple shear and elongational flow, instead of purely simple shear flow that was considered in the original analysis.

The microstructure of the nanotube-incorporated HCEs can be influenced by the concentration of MWCNTs and their degree of dispersion. The nanotube-incorporated emulsions exhibited a significantly higher viscosity when compared to the neat emulsion, and the viscosity of the emulsion increased significantly with increase in the MWCNT content. Thus, the trend of decreasing droplet size with the increase in the concentration of MWCNTs can be explained by the influence of the viscosity ratio on \( \Gamma_{\text{caut}} \). It has been reported that the effective viscosity of the HCE (\( \eta_{\text{d}} \)) is one of the major factors, which dictates the droplet refinement of the emulsion, and the shear thinning nature of the HCEs may enhance its monodispersity.

Viscosities of the oil phase of emulsions, as a function of the shear rate, were measured to estimate the variation in the viscosity of the continuous phase with respect to the concentration of the incorporated MWCNTs. Figure 5 illustrates the viscosity curves for the oil phases of all emulsions. The neat oil blend viscosity is in the order of \( \sim 0.08 \text{ Pa}\cdot\text{s} \) and exhibits largely Newtonian behavior. It can be seen that the viscosity of the oil blend–MWCNT dispersion (which constitutes the oil phase of the nanotube-incorporated emulsions) increases significantly with an increase in the MWCNT content. The oil blend–MWCNT dispersion showed a “solidlike” behavior at rest, followed by shear-thinning behavior at high shear rates. The viscosity of the oil blend–MWCNT dispersion that contains 0.5 wt % MWCNTs was 3 orders of magnitude greater when compared to the viscosity of oil phase of the neat emulsion at the shear rate of 1 \( \text{s}^{-1} \). It is likely that the viscosity of the oil phase plays a major role in the microstructure evolution of the nanotube-incorporated emulsions. It is known that the droplet size and the droplet formation frequency can be controlled by altering the viscosity of the continuous phase liquid.61 For a given shear rate, \( \gamma \), and continuous phase viscosity, \( \eta_c \), the shear stress applied on the droplet is \( \eta_c \gamma \). Thus, an increase in the oil phase viscosity results in a relatively higher shear force on the penetrating aqueous phase, and hence a there is a higher probability of droplet rupture. Therefore, the addition of MWCNTs in the oil phase results in an increase in the applied stress during refining, which in turn leads to a decrease in the droplet size. The rupture rate, being a function of the shearing rate, also increases with the increase in the concentration of MWCNTs.

Furthermore, the interfacial tension \( \Gamma \) is another important factor, which influences the droplet size. The estimation of the interfacial tension of HCEs and determining its change with an increasing concentration of MWCNTs are difficult. It is well-known that CNTs, depending on their surface functionality, can reside at the oil–water interface and act as Pickering stabilizers.28–32 MWCNTs used in the present study are pristine and are highly hydrophobic in nature, and they would prefer to stay in the oil phase of the emulsion. However, the XPS analysis suggests that the MWCNTs contain \( \sim 4.7 \text{ at. %} \) oxygen functionality. Therefore, there is a possibility that a minor fraction of dispersed MWCNTs may reside at the oil–water interface. If a fraction of the incorporated MWCNTs resides at the oil–water interface, it could act as a co-surfactant and lead to a reduction in the interfacial tension and diminish the coalescence rate in the emulsion.34,38 The reduction in the interfacial tension, if any, would also contribute to a reduction in the droplet size. Thus, the state of dispersion of nanotubes within the emulsion also plays a vital role in determining the final droplet size of the nanotube-incorporated HCEs.

2.2.2. State of Dispersion of MWCNTs in the Emulsion: Morphological Analysis Using Cryo-Field Emission Gun (FEG)-SEM. The cryo-FEG-SEM analysis was carried out to understand more directly the state of dispersion of MWCNTs in the emulsion. The emulsion samples were frozen using liquid nitrogen, and SEM images were captured with the fractured surfaces. The resulting cryo-FEG-SEM images of the neat and nanotube-incorporated emulsions at various magnifications are shown in Figure 6. Micrographs of the neat emulsion at different magnifications are shown in Figure 6a–d. The nonspherical droplets of the dispersed aqueous phase and the thin layer of the continuous oil phase between the polyhedral droplets, both are signatures of HCEs, can be clearly observed in the micrographs. The morphology of the 1NT emulsion (Figure 6e–h), 2NT emulsion (Figure 6i–I), and 4NT emulsion (Figure 6m–p) are depicted in the cryo-FEG SEM micrographs at different magnifications (Figure 6e–p). MWCNTs dispersed in the emulsion matrix can be seen on the fractured surfaces of the emulsion. However, the selective dispersion of MWCNTs in the continuous phase of the emulsion cannot be unequivocally concluded from the fractured surface morphology. Thus, cryo-FEG-SEM observation alone is not sufficient to fully understand the dispersion states of MWCNTs in the respective emulsions.

The majority of the incorporated MWCNTs are expected to remain in the oil phase of the emulsion and form a 3D networklike structure within the emulsion matrix. However, it is possible that a fraction of MWCNTs may reside at the interface or even move to the aqueous phase during the rigorous mixing. In addition, the maximum amount of MWCNTs that can be incorporated into the emulsion is limited. Stable emulsions were hardly obtained when the concentration of MWCNTs exceeded \( \sim 5 \text{ wt %} \) of the oil phase, or even if some emulsions were formed, they could not accommodate the same volume fraction of the aqueous phase. Hence, the aqueous-to-oil phase ratio will no longer remain the same if the concentration of MWCNTs exceeds \( \sim 5 \text{ wt %} \) of the oil phase. Alternately in HCEs, the thin film of the oil blend covers a large area between the dispersed aqueous
droplets, and hence the dispersed MWCNTs should be in sufficient amount to form an efficient 3D network throughout the oil phase of the emulsion. A homogenous dispersion of the individualized MWCNTs, which forms an efficient 3D network of MWCNTs throughout the oil phase, is necessary for modifying the emulsion properties.

2.3. Rheological Characteristics of Nanotube-Incorporated Emulsions. The rheological characteristics of HCEs, and emulsion explosives in particular, play a crucial role in the processing operations, packaging, and also when they are pumped through long pipelines during their use and transportation. Furthermore, rheological analysis can be used to probe the morphology and also to assess the stability of the emulsion. On the basis of the applied load, HCEs exhibit either “solidlike” or “liquidlike” rheological response. HCEs possess yield stress, and when subjected to small deformations that are lower than its yield stress, these emulsions demonstrate elastic, gel-like rheological response over a wide frequency range. When subjected to stresses exceeding its yield stress, HCEs demonstrate a shear rate-dependent viscosity and eventually start flowing like liquids with strong non-Newtonian behavior. The viscoelastic properties of HCEs have been shown to depend on the mean droplet size, droplet-size distribution, interfacial tension, and volume fractions of the phases.

Steady-state shear and dynamic oscillatory rheological tests were carried out to understand the manner in which the MWCNT incorporation and the resultant microstructure influence the rheological behavior of HCEs. Rheological properties of the nanotube-incorporated emulsions were characterized as a function of the emulsification time as well as the concentration of MWCNTs. Rheological tests were carried out on HCEs prepared with different mixing times to assess the role of droplet size in dictating the rheological behavior. Further, emulsion samples with an identical droplet size of \( d_{32} \approx 5 \mu m \) were chosen from HCEs with different MWCNT contents, and their rheological behavior was analyzed separately. This was intended to eliminate the effect of decreased droplet size, with the addition of MWCNTs, on the rheological behavior. Thus, the sole effect of the incorporated MWCNTs in dictating the rheological characteristics, if any, could be elucidated. The droplet-size distributions of the emulsion samples with an identical droplet size, along with their \( d_{32} \) and corresponding \( t_r \), are given in Figure 7.

![Figure 6. Cryo-FEG-SEM micrographs of the neat and nanotube-incorporated emulsions: (a–d) neat emulsion at different magnifications; nanotube-incorporated emulsions of varying concentration of MWCNTs at different magnifications: (e–h) 1NT; (i–l) 2NT; and (m–p) 4NT.](image)

![Figure 7. Droplet-size distributions of emulsions of varying MWCNT concentrations and identical droplet size of \( d_{32} \approx 5 \mu m \). The inset table shows details of the corresponding refining time \( (t_r) \) and \( d_{32} \) values for all emulsion samples.](image)

2.3.1. Oscillatory Tests: Amplitude Sweep Testing in Small and Large Deformation Regimes. The oscillatory amplitude sweep measurement results are illustrated in Figure 8, which depicts the variation of dynamic storage modulus \( (G') \) and loss modulus \( (G'') \) with shear strain \( (\gamma) \). The corresponding stress behavior data, which were extracted from the strain sweep tests that shows the variation in \( G' \) and \( G'' \) as a function of the increasing shear stress, are shown in Figure S6 provided in the Supporting Information. Amplitude sweep tests were performed in the strain range that covers both small and large amplitude deformation regimes to get a reasonable understanding of the linear viscoelastic (LVE) and non-LVE behavior of these emulsions. The results suggest that when subjected to low strain values, these emulsions exhibit LVE behavior, as indicated by the constant plateau values of both \( G' \) and \( G'' \) in the low deformation range. At higher deformation...
range, beyond the LVE regime, these emulsions exhibit a yield point and a cross-over point.

Figure 8a,b demonstrates the variation in $G'$ and $G''$ with increasing strain amplitude for the neat and nanotube-incorporated emulsion samples prepared with different $t_\text{r}$. For nanotube-incorporated emulsions, the amplitude sweep test results of only 1NT emulsion samples with different refining times are shown here because a similar trend with $t_\text{r}$ is demonstrated by all nanotube-incorporated emulsions. Evolutions of $G'$ and $G''$ of the nanotube-incorporated emulsions are quite similar to that of the neat emulsion, although $G'$ values increase significantly with the increase in the concentration of MWCNTs. The constant plateau values at low strain indicate that these emulsions exhibit a primarily solidlike elastic response in this strain range. At higher deformation amplitudes, $G'$ values decrease because of the collapse of the interdroplet structure. Eventually, the $G'/G''$ cross-over happens at the cross-over strain, indicating a solidlike to liquidlike transition, and the emulsions demonstrate a viscosity-dominant rheological response. The $G'$ and $G''$ curves do not fall constantly when the deformation is increased beyond the LVE range. The $G''$ curves show one peak, and the increasing $G''$ values in the partial range indicate the increasing portion of deformation energy, which is spent to change the internal structure before the final break down of the emulsion structure. Several studies have reported similar dependencies between the deformation amplitude and the shear modulus for HCEs. 21,22,25,66,67

Further, the amplitude results suggest that the yield strain and the cross-over strain is independent of the refining time (hence, independent of the droplet size and the polydispersity) of the emulsion. The yield strain and cross-over strain of the neat emulsion and nanotube-incorporated emulsions do not change significantly for samples prepared with different refining times. However, there is a considerable increase in $G'$ values with the refining time for all samples, irrespective of the concentration of MWCNTs.

There is a significant increase in the flow stress ($\tau_\text{f}$ shear stress at which $G' = G''$; for a deformation amplitude that exceeds $\tau_\text{f}$ viscous behavior dominates over elastic response) for both neat and nanotube-incorporated emulsions with the decrease in the droplet size (Figure S6a,b of the Supporting Information). The thin continuous oil phase layer between the dispersed droplets will get thinner with extended refining because of the reduction in the droplet size, and there will be a subsequent increase in the total interfacial area per unit volume. Eventually, a thicker and more elastic emulsion, which is capable of storing more interfacial energy per unit volume, will be formed. In addition, the surface area-to-volume ratio of the dispersed droplets increases with the reduction in the droplet size, which in turn leads to an improved interparticle interaction. Thus, the energy requirements for the emulsion to commence the flow increase with the decrease in the average droplet size. It explains the increase in $G'$ and $\tau_\text{f}$ with the increase in $t_\text{r}$.

Figure 8c presents the comparison of amplitude test results of emulsions with different MWCNT concentrations and identical droplet size ($d_{32} = 5 \pm 0.2 \mu m$). No significant changes in stress and strain behaviors are noticed over the range of studied MWCNT concentrations. However, there is a consistent and modest decrease in the $G'$ value with the increase in MWCNT loading. Presumably, this can be attributed to the increase in the average size of the remaining MWCNT agglomerates in the emulsion with the concentration of MWCNTs. As seen from the microscopic observations above, the number of agglomerates and their average size increase with the MWCNT addition, which in turn lead to a decrease in the $G'$ value of the emulsion. Further, there is a consistent increase in the flow stress, yield point, and cross-over strain of the emulsion with the increase in the
concentration of MWCNTs, implying the increase in the energy required to initiate the flow. The cross-over strain and flow stress values of the neat and nanotube-incorporated emulsions are listed in Table 2. An increase in the cross-over strain indicates the increased resistance of the emulsion to a strain-induced irreversible deformation. Thus, the flow of nanotube-incorporated emulsions seems to start at a slightly higher strain value when compared to the neat emulsion. The nanotube-incorporated emulsions possess solidlike behavior up to a higher applied stress, when compared to the neat emulsion, and the cross-over strain increases with the concentration of MWCNTs.

Figure 8d demonstrates the strain behavior of emulsions with different MWCNT contents and the same refining time, \( t_r = 10 \text{ min} \). Emulsions exhibit a consistent increase in \( G' \), \( \tau_{\text{c}} \), and cross-over strain with an increase in the MWCNT concentration (Figures 8d and S6d in the Supporting Information). A similar trend is observed at all measured refining times, and the observation is consistent with the observation in the microstructure analysis above. For a fixed \( t_r \), the emulsion droplet size decreases with the increase in the concentration of MWCNTs and makes the emulsion more elastic in nature. Thus, the important factor that led to the increase in rheological parameters of the nanotube-incorporated emulsions is the enhanced droplet refinement with the addition of MWCNTs.

### Table 2. Cross-over Strain, Flow Stress (\( \tau_{\text{c}} \)), and Storage Modulus (\( G' \)) Values for Emulsions with an Identical Droplet Size (\( d_{32} \approx 5 \mu m \)) and Varying Concentration of MWCNTs (\( G' \) Values were Estimated from the Plateau of the Angular Frequency (\( \omega \)) Dependence of \( G' \) Given in Figure 9)

<table>
<thead>
<tr>
<th>Emulsion</th>
<th>( t_r ) (min)</th>
<th>Cross-over strain (%)</th>
<th>Flow stress, ( \tau_{\text{c}} ) (Pa)</th>
<th>( G' ) (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat emulsion</td>
<td>15</td>
<td>52</td>
<td>532.8</td>
<td>2580</td>
</tr>
<tr>
<td>0.5NT</td>
<td>10</td>
<td>55</td>
<td>564.2</td>
<td>2430</td>
</tr>
<tr>
<td>1NT</td>
<td>8</td>
<td>59</td>
<td>580.0</td>
<td>2470</td>
</tr>
<tr>
<td>2NT</td>
<td>6</td>
<td>62</td>
<td>581.4</td>
<td>2390</td>
</tr>
<tr>
<td>4NT</td>
<td>3</td>
<td>69</td>
<td>583.5</td>
<td>2200</td>
</tr>
</tbody>
</table>

The frequency sweep test results of different samples that demonstrate the variation of \( G' \) and \( G'' \) with angular frequency (\( \omega \)) are illustrated in Figure 9. It is observed that \( G' \) is almost constant in a wide range of angular frequency covering several orders of magnitude for the neat and nanotube-incorporated emulsions, regardless of the droplet size and MWCNT concentration, as shown in Figure 9a–d. Often, this plateau value in the wide range of \( \omega \) is considered as the elastic modulus of the emulsion. Further, \( G' \) dominated over \( G'' \) in the measured frequency range for all samples, which indicates that the rheological response of these emulsions is mostly elastic during the frequency sweep tests. The dynamic behavior of different emulsions in terms of variation of complex viscosity (\( \eta^* \)) with \( \omega \) is shown in Figure S7 provided in the Supporting Information. The \( \eta^* \) data characterize the

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**Figure 9.** Frequency sweep results illustrating the behavior of storage modulus (\( G' \)) and loss modulus (\( G'' \)) with angular frequency (\( \omega \)) for different emulsion samples: (a) neat emulsions with different refining times (\( t_r \)); (b) 1NT emulsions with different \( t_r \); (c) emulsions with different MWCNT concentrations and an identical droplet size, \( d_{32} \approx 5 \mu m \); and (d) emulsions with different MWCNT concentrations and same \( t_r = 10 \text{ min} \) (frequency sweep tests performed by varying \( \omega \) from 0.05 to 200 rad s\(^{-1} \) at a constant strain of 0.5%; filled symbols denote \( G' \) and open symbols denote \( G'' \)).
Information and Figure 9d). However, there is a modest with identical droplet sizes (Figure S7d of the Supporting information) with changes in the MWCNT concentration for the samples

Steady-state rotary tests were performed to investigate the state yield behavior and apparent viscosity of emulsions. Steady-state rotary tests were performed to investigate the yield behavior of the emulsion against an applied stress. The viscosity with the addition of MWCNTs implies a higher total resistance of the emulsion against an applied stress. The increase in the number and average size of the remaining MWCNT agglomerates in the emulsion with the increase in the MWCNT concentration (Figure S7d of the Supporting Information). It indicates that the stability of emulsions could be affected because of the presence of MWCNTs in the continuous oil phase.

2.3.3. Rotary Shear Sweep Tests: Yield Behavior of HCEs. Steady-state rotary tests were performed to investigate the yield behavior and apparent viscosity of emulsions. Steady-state flow curves of different samples were procured in the upward shear rate-sweeping mode. The deformation behavior in terms of shear stress (τ) variation with respect to the shear rate (γ) is presented in Figure 10. The variation in viscosity (η) with γ is shown in Figure S8 provided in the Supporting Information. The flow curves show yield behavior (Figure 10), and the viscosity curves exhibit a reducing apparent viscosity (Figure S8 of the Supporting Information) with the increasing shear rates for all samples, irrespective of the concentration of MWCNTs. HCEs possess yield stress, and hence they do not undergo any irreversible deformation when the applied shear stress is below the yield value. However, at shear stresses that exceed the yield stress, HCEs exhibit shear-thinning behavior. As the shear stress increases and approaches the yield stress, droplets get deformed and the emulsion microstructure starts to break down. The collapse of the emulsion interdroplet structure results in a drop in the apparent viscosity, and subsequently, emulsions start to flow. Thus, the large decrease in viscosity with the increase in the shear rate suggests the fracturing of the stable emulsion structure.

The flow curve shifts to higher shear stress for an emulsion that is subjected to higher refining time and hence exhibits higher yield stress (Figure 10a,b). It is evident from the apparent viscosity curves that the emulsion with smaller droplets shows a higher viscosity, especially at low shear rates (Figure S8a,b of the Supporting Information). For all refining times, the emulsions being studied exhibit non-Newtonian shear-thinning flow behavior and possess a yield stress. These observations suggest that the yield stress and viscosity of the emulsions primarily depend on the droplet size and the polydispersity. For a given t_r, the yield stress and apparent viscosity of the emulsions increase with the MWCNT concentration (Figure S8d of the Supporting Information and Figure 10d). The reduction in the droplet size and the subsequent thinning of intervening liquid layers with the addition of MWCNTs affect the emulsion’s ability to flow, leading to an increase in their yield stress and apparent

Figure 10. Steady-state flow curves obtained through shear sweep tests for different emulsions, illustrating the variation in the shear stress (τ) with shear rate (γ): (a) neat emulsions with different refining times (t_r); (b) 1NT emulsions with different t_r; (c) emulsions of varying MWCNT concentrations and an identical droplet size, d_{90} ≈ 5 μm; (d) emulsions of varying MWCNT concentrations and same t_r = 10 min (shear sweep tests were performed by varying γ from 0.001 to 10 s⁻¹).

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viscosity. This reinforces the discussion in previous sections that the continuous oil phase layer between the aqueous droplets plays a crucial role in dictating the rheological behavior and consistency of HCEs.\textsuperscript{69} An increase in the yield stress and viscosity with an increase in the CNT content was reported in CNT-incorporated poly(styrene-co-divinylbenzene)-based HCEs.\textsuperscript{40} Similar observations were reported in the case of Pickering emulsions as well.\textsuperscript{70}

Further, it is noticed that the deformation behavior nearly remains the same as a function of the MWCNT concentration for emulsions with an identical droplet size for studied concentrations of MWCNTs, as shown in Figure S8c of the Supporting Information and Figure 10c. This suggests that the deformation behavior of HCEs is not much affected because of the presence of dispersed MWCNTs within the thin intervening oil phase. It should be noted that there was a considerable change in the apparent viscosity of the continuous oil phase with the addition of MWCNTs. However, this did not affect the overall viscosity of the HCEs. This is desirable because the pumping of nanotube-incorporated HCEs does not require much additional energy when compared to that of the neat emulsion. To summarize, the rheological behavior of nanotube-incorporated emulsions essentially remained the same for emulsions with an identical droplet size, regardless of their MWCNT concentrations. However, the decrease in the droplet size with the addition of MWCNTs plays a crucial role in modifying the rheological behavior of emulsions prepared with the same $t_{\text{imp}}$.

3. CONCLUSIONS

MWCNTs were incorporated into the highly concentrated w/o emulsions, which are identical to the precursor emulsion used in the production of liquid explosives. MWCNTs were initially dispersed in the oil phase of the emulsion to achieve an efficient 3D network of MWCNTs throughout the continuous phase of the emulsion, which can ultimately modify the emulsion characteristics. The refining characteristics and rheological properties of nanotube-incorporated emulsions have been investigated. This study shows a range of important features. The incorporation of MWCNTs led to a finer emulsion microstructure with a reduced droplet size and a narrowed droplet-size distribution. The decrease in the droplet size with the addition of MWCNTs is primarily because of the increase in the viscosity of the oil phase, which in turn results in an increased applied stress during the refining of the emulsion. The state of dispersion of nanotubes within the emulsion also plays a crucial role in determining the final microstructure of the nanotube-incorporated emulsions. The state of dispersion of MWCNTs in the emulsion was investigated through cryo-FEG-SEM analysis, and the majority of the incorporated MWCNTs were expected remain in the oil phase of the emulsion forming a 3D networklike structure at some percolation threshold. However, the selective dispersion of MWCNTs in the continuous phase was not unequivocally concluded from the fractured surface morphology.

The rheological characteristics of the nanotube-incorporated emulsions were identical to that of the neat emulsion. The influence of the refining time and the concentration of MWCNTs on the rheological properties were characterized separately. The rheological behavior of these emulsions was primarily governed by their droplet size and droplet-size distribution. However, the yield strain and cross-over strain values were independent of the droplet size and polydispersity of the emulsion. It was noticed that the storage modulus ($G'$), yield stress ($\tau_Y$), and apparent viscosity ($\eta$) values increased with the refining time. At higher refining times, the droplets get refined, and the smaller droplets are more tightly packed than the larger ones. The thickness of the continuous oil phase layer plays a crucial role in dictating the viscoelasticity and consistency of the emulsion. Investigations on the role of refining times indicated that, for any given refining time, nanotube-incorporated emulsions exhibited higher $G'$, $\tau_Y$, and $\eta$ values than the neat emulsion, and there was a consistent increase in their values with the increase in the MWCNT concentration. This can be attributed to the decrease in the droplet size with the addition of MWCNTs. The investigation on the influence of the MWCNT concentration on emulsions with identical droplet sizes suggested that the incorporation of MWCNTs did not induce any significant change in the rheological behavior of emulsions. However, the nanotube-incorporated emulsions possessed solidlike behavior up to a higher applied stress, when compared to the neat emulsion of identical droplet size, as indicated by the increase in the yield and cross-over strain values. Furthermore, the modest decrease in the $G'$ values indicates the reduction in the elasticity of emulsions because of the presence of MWCNT agglomerates in the emulsion matrix.

4. EXPERIMENTAL SECTION

4.1. Materials Used. Ammonium sulphate and ammonium chloride were obtained from Sigma-Aldrich. All constituents of the oil phase, that is, canola oil, paraffinic oil, and polystyrene-succinic anhydride (PIBSA)-diethanolamine derivative emulsifier were provided by Orica Australia Pty. Ltd. Thin, purified MWCNTs prepared by the catalytic carbon vapor deposition process were obtained from Nanocyl S.A., Belgium (grade: NC 3100; $D = 9.5$ nm, $L = 1.5$ $\mu$m, purity $> 95\%$ as per manufacturer). All emulsion samples were prepared using deionized water.

4.2. Preparation of Emulsions. 4.2.1. Dispersed Phase. An aqueous solution of inorganic salts forms the dispersed phase of the emulsion, and it constitutes $93.5\%$ of the total emulsion. Water constitutes $\sim 55\%$ of the dispersed phase, and the remaining material is ammonium sulphate and ammonium chloride salts and some trace additives. Trace additives of low concentration ($0.1\%$ each) are used to regulate the pH of the aqueous phase. The aqueous phase density is $\sim 1.2$ g/cm$^3$.

4.2.2. Continuous Phase. The mixture of the emulsifier in a blend of two industrial grade hydrocarbon oils, namely, canola oil and paraffinic oil forms the continuous phase. The emulsifier is an alkylamine derivative of PIBSA and is prepared through the reaction of 1:1 M ratio of PIBSA and diethanolamine. The molar mass of the PIBSA derivative surfactant ranges from 900 to 1300, and its hydrophile–lipophile balance value is low, between 2 and 4, and favors the formation of w/o emulsions. The hydrophilic moiety of the surfactant consist of ester, amide, and salt components, and the lipophilic moiety is derived from the PIBSA chain. The emulsifier is a mixture of the surfactant and diluent oil. The emulsifier makes up $36\%$ of the oil phase in all emulsions. The density of the oil phase (consisting of oils and the emulsifier) is 0.895 g/cm$^3$.

4.2.3. Preparation. The emulsion samples were prepared using Caframo BDC 1850, which is a high-torque mixer, along with a high-shear Jiffy impeller (Jiffy Mixer LM, 32 mm
Incorporated Emulsions gradually brought to ambient temperature after the phase throughout the emulsion temperature was kept above the fudge point of the aqueous phase. The sample in which MWCNTs constitute ∼0.5−4 wt % of the total emulsion. The aqueous phase-to-oil phase ratio in the emulsion ranges from 0.0325 to 0.26 wt % of the total emulsion; the corresponding concentration of MWCNTs in the study has been varied from 0.5 to 4 wt % of the oil phase of the nanotube-incorporated emulsions to maintain the phase of the nanotube-incorporated emulsions to maintain the aqueous phase in the oil phase of the nanotube-incorporated emulsions to maintain the aqueous phase-to-oil phase ratio. It should be noted that these emulsions are stabilized by a large amount of the surfactant, and hence these are not the Pickering emulsions. Details of the emulsion compositions and their sample codes are presented in Tables 3 and 4. The sample code nNT represents the emulsion sample in which MWCNTs constitute n wt % of the oil phase. Table 3 summarizes the concentration of MWCNTs in the oil phase and their corresponding fraction in the total emulsion for each emulsion sample. Table 4 depicts the oil-phase composition of the nNT emulsion.

The emulsification process is completed in two stages: a low-speed (700 rpm) “emulsion formation” stage and a high-shear (1400 rpm) “emulsion refining” stage. The detailed emulsion preparation procedure can be found elsewhere. The temperature was kept above the fudge point of the aqueous phase throughout the emulsification process and was then gradually brought to ambient temperature after the “refining” stage. The aqueous phase is a supersaturated solution and is at the supercooled condition at the ambient temperature, and hence the emulsion is thermodynamically unstable. Nevertheless, at least for several weeks, these HCEs are kinetically stable. All results presented in this study are based on the analysis performed on freshly prepared samples.

4.3. Characterization Techniques. 4.3.1. Characterization of MWCNTs. Raman spectroscopic analysis of MWCNTs was performed using an HR 800 micro-Raman spectrometer (HORIBA Jobin Yvon, France) with an incident laser excitation wavelength of 532 nm. TEM investigation was performed using a JEOL JEM-2100 F (Japan) field emission electron microscope for MWCNTs.

SEM analysis was performed using FEI-SEM (JSM-7600F, Japan) at 10 kV accelerating voltage. XPS was carried out using an AXIS Supra X-ray photoelectron spectrometer (Kratos Analytical, UK). Monochromatic Al Kα (1486.6 eV), 600 W X-ray source was used for XPS measurements. The energy resolution was ∼0.5 eV, and the XPS-imaging spatial resolution was ∼1 μm. Deconvolution of C 1s and O 1s XPS spectra was done by using XPSPeak 4.1 software.

4.3.2. Characterization of Emulsions. Confocal micrographs were captured using an Olympus IX 81 confocal laser scanning microscope. A thin layer of the emulsion was made between glass slides for the confocal microscopic analysis. The sample preparation for the confocal microscopic analysis can be found elsewhere. The emission droplet diameters were measured using ImageJ (National Institute of Health, USA) software.

The emulsion microstructure and the state of dispersion of MWCNTs in the emulsion were studied using the cryo-SEM facility, JSM-7600F, with a cryo-preparation system (PP3000T, Japan). The sample preparation for the cryo-SEM investigation can be found elsewhere. The rheological tests were performed at 25 °C using an Anton Paar Rheometer (model: Physica MCR302) with a sandblasted parallel-plate measuring system. The diameter of the sandblasted parallel-plate geometry was 40 mm, and the gap between plates was 1 mm. The dynamic behavior of emulsions was investigated through oscillatory rheological tests, and the steady-state flow curves were acquired through rotational shear sweep tests. The initial relaxation of emulsion samples was ensured during all measurements by operating the rheometer at constant initial values of the controlled parameter, that is, shear or strain. In rotary shear sweep tests, the shear rate ranged between 0.001 and 10 s⁻¹. In amplitude sweep tests, the % strain was varied from 0.01 to 200% at 1 Hz frequency. This strain range covers both small and large amplitude regimes and provided a reasonably good assessment of the LVE and non-LVE behaviors. Frequency sweep tests were conducted at a small strain amplitude of 0.5%, and the angular frequency was varied from 0.05 to 300 rad s⁻¹. The strain amplitude of 0.5% was within the LVE regime for all emulsion samples under study and was decided from the amplitude sweep tests.

4.3.3. Characterization of Emulsions. Confocal micrographs were captured using an Olympus IX 81 confocal laser scanning microscope. A thin layer of the emulsion was made between glass slides for the confocal microscopic analysis. The sample preparation for the cryo-SEM investigation can be found elsewhere. The rheological tests were performed at 25 °C using an Anton Paar Rheometer (model: Physica MCR302) with a sandblasted parallel-plate measuring system. The diameter of the sandblasted parallel-plate geometry was 40 mm, and the gap between plates was 1 mm. The dynamic behavior of emulsions was investigated through oscillatory rheological tests, and the steady-state flow curves were acquired through rotational shear sweep tests. The initial relaxation of emulsion samples was ensured during all measurements by operating the rheometer at constant initial values of the controlled parameter, that is, shear or strain. In rotary shear sweep tests, the shear rate ranged between 0.001 and 10 s⁻¹. In amplitude sweep tests, the % strain was varied from 0.01 to 200% at 1 Hz frequency. This strain range covers both small and large amplitude regimes and provided a reasonably good assessment of the LVE and non-LVE behaviors. Frequency sweep tests were conducted at a small strain amplitude of 0.5%, and the angular frequency was varied from 0.05 to 300 rad s⁻¹. The strain amplitude of 0.5% was within the LVE regime for all emulsion samples under study and was decided from the amplitude sweep tests.

**Table 3. Sample Codes and Their Compositions for Nanotube-Incorporated Emulsions**

<table>
<thead>
<tr>
<th>sample code</th>
<th>concentration of MWCNTs (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>neat emulsion</td>
<td>0 in oil phase, 0 in total emulsion</td>
</tr>
<tr>
<td>0.5NT</td>
<td>0.5 in oil phase, 0.0325 in total emulsion</td>
</tr>
<tr>
<td>1NT</td>
<td>1 in oil phase, 0.065 in total emulsion</td>
</tr>
<tr>
<td>2NT</td>
<td>2 in oil phase, 0.13 in total emulsion</td>
</tr>
<tr>
<td>4NT</td>
<td>4 in oil phase, 0.26 in total emulsion</td>
</tr>
</tbody>
</table>

**Table 4. Oil-Phase Composition for Different Nanotube-Incorporated Emulsions**

<table>
<thead>
<tr>
<th>sample code</th>
<th>oil phase composition of nanotube-incorporated emulsions</th>
</tr>
</thead>
<tbody>
<tr>
<td>nNT</td>
<td>64 − n, n, surfactant/diluent oil mixture (wt %)</td>
</tr>
</tbody>
</table>

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00579.

SEM and TEM micrographs and Raman spectrum of MWCNTs; XPS spectra of MWCNTs; photographs of nanotube-incorporated HCEs of varying MWCNT concentrations; evolution of the droplet-size distribution.
of the neat and nanotube-incorporated emulsions at different stages of emulsification; superimposed droplet-size distribution curves at various stages of emulsification for the neat and nanotube-incorporated emulsions of varied MWCNT concentrations; amplitude sweep test results illustrating the variation of the dynamic storage modulus ($G'$) and loss modulus ($G''$) with shear stress ($\gamma$); frequency sweep results illustrating the behavior of complex viscosity ($|\eta(*)|$) with angular frequency ($\omega$) for different emulsion samples; and steady-state flow curves obtained through shear sweep tests for different emulsions, illustrating the variation in the viscosity ($\eta$) with shear rate ($\dot{\gamma}$).

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**Notes**

The authors declare no competing financial interest.

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