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STUDY ON THE EMULSION STABILITY OF TRIPROPYLENE GLYCOL DIACRYLATE IN WATER

Oil-in-water emulsion is thermodynamically unstable system that undergoes destabilization with time. The tripropylene glycol diacrylate (TPGDA) monomer which can potentially to increase the crosslink density of polymer blends is unstable in water due to its low water solubility properties. However, the stability of TPGDA emulsion could be improved by adding an adequate amount of surfactant. This study addresses the effect of different Tween 20 (surfactant) concentration on emulsion stability of TPGDA. Model emulsion ranging between 0.1 wt% to 3 wt% of Tween 20 and a control were prepared using heavy duty homogenizer. The emulsion was characterised by FTIR, microstructure analysis, phase separation observation and creaming index during storage time. Emulsion containing 0.4 wt% Tween 20 showed the longest stability at 24 hours and a creaming index of 0%, which is enough for an ideal emulsion. The FTIR spectra displayed the interaction of TPGDA and Tw-20, proving that the emulsion is fully mixed and stabilized. The results are further supported by optical microscopy, which observed no droplet aggregation and flocculation in the TPGDA emulsion with the presence of 0.4 wt% of Tw-20 surfactant. This information about Tw-20 is beneficial, making it a promising surfactant for enhancing the emulsion stability of the TPGDA emulsion.

Keywords: emulsion; Tripropylene glycol diacrylate; stability; Tween 20; waste tire dust

1. Introduction

Traditionally, emulsions are classified as oil-in-water (O/W) emulsions when the water content is above 45% of the total weight. The stability of an emulsion can be defined as its ability to maintain its properties; that is, the capability of the phase emulsion to remain mixed together [1]. When the oil component is added to water (or vice versa), their emulsion is a thermodynamically unstable system, so they immediately divide into separate oil and water layers [2]. This is due to the incompatible contact between oil and water molecules and different densities between oil and aqueous phases. To increase kinetic stability of the emulsion, stabilizers such as surfactants (emulsifiers), weighting agents, ripening inhibitors, and texture modifiers (thickeners and gelling agents) are often used [3].

Tripropylene glycol diacrylate (TPGDA) is a difunctional reactive diluent with a branched alkyl polyether backbone. Polymerization occurs when TPGDA is exposed to sources of free radicals. It is widely employed as a primary diluent in the formulation of ultraviolet light (UV) and electron beam (EB) for plastics, inks, and adhesives as well as curable coatings for various kinds of material such as woods, metals and polymers [4]. It is also a commonly used material, mostly for its balance of dielectric and structural properties [5]. TPGDA further exhibits good jetting performance and great thermal stability [6]. In a previous study, TPGDA was used as a crosslinking agent, proving that it is efficient for promoting crosslinking with an increase of about 45% in gel fraction of tribological properties of ultra-high molecular weight polyethylene (UPE) compared to pure UPE [7]. Therefore, it was proposed that TPGDA should be grafted onto waste tire dust (WTD) for industrial structures [8]. The incorporation of TPGDA grafted WTD in the formulation may help increase the compatibility of polymer composites while reutilizing waste accumulated in the environment.

It is known that with the right amount, TPGDA can potentially to increase the crosslink density of polymer blends. But due to low water solubility of the TPGDA monomer, increasing its stability was suggested as a solution that help improve the polymer blend's compatibility for industrial structures. To enhance emulsion stability of the TPGDA monomer, Tween-20

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(Tw-20) was selected as the surfactant. Tw-20 is a polysorbate surfactant that consists of fatty acid ester moiety and a long polyoxyethylene chain of polyethylene-glycolated sorbital. It has very low critical micellar concentrations (CMC = 0.06 mM), and the hydrophile-lipophile balance (HLB) value is 16.7. It is widely used in pharmaceutical, daily chemical, food, textiles, and other industries [9,10] as emulsifiers, dispersant, solubilizers, and stabilizers. Recently, many researchers have applied Tw-20 as a surfactant to stabilize O/W emulsions [11,12]. This indicates the potential of Tw-20 as a stable emulsion preparation for the TPGDA monomer.

To the best of our knowledge, only a few studies are present regarding utilizing Tw-20 as a surfactant to form and stabilize TPGDA emulsions for industrial applications. Therefore, the TPGDA emulsion stabilized by the Tw-20 surfactant was prepared in this study, and its stability characterizations were optimized to develop a stable emulsion system before further treatment of TPGDA grafted WTD compatibilized polymer blend was developed.

2. Methodology

2.1. Materials

A commercial grade of tripropylene glycol diacrylate and Tween-20 supplied by Sigma-Aldrich were used as a monomer and surfactant in the emulsion preparation, respectively. All solvents were reagent grade and used as received without further purification. Ultra-pure water (organic free) was used for all sample preparations and was supplied by Sartorius Arium water purification system.

2.2. Emulsion preparation

An emulsion solution was prepared by mixing 1 wt% TPGDA in ultra-pure water with different concentration of Tw-20 solution (0.1 wt% to 3 wt%) at room temperature. The oil in water (O/W) emulsion was subjected to stirring using a heavy-duty homogenizer (Scilogex D500, United States) until the mixture became opaque, milky white, and visibly homogenous. The mixtures were prepared at 10,000 rpm for 15 minutes with emulsor screen for liquid/liquid preparation.

2.3. Phase observation

The stability of TPGDA emulsions with different concentration Tw-20 was evaluated by performing a storage experiment. All emulsions were transferred into clear glass vials (20 mL) and sealed properly to avoid evaporation from occurring. The emulsions were stored at room temperature. The phase separation of all emulsions was determined, and visually monitored by taking photographic images for 24 hours.

2.4. Creaming Index

The creaming index of the emulsions was measured at 0 h, 1 h, 3 h, 5 h, 8 h and 24 h by a visual observation method [23]. Capped, glass vials were filled with 20 mL of emulsion and the total height was measured in millimetres using a precise ruler. During this storage experiment, the vials for determination of the creaming index were not shaken and kept with extra precaution not to disrupt the cream layer. The height of the upper cream layer was measured at a different hour, allowing to calculate the creaming index. The total emulsion height (H_t) and the bottom aqueous layer (H_s) height was taken upon standing and calculated as creaming index according to the Eq. (1) [13]:

$$\text{Creaming Index (\%)} = \frac{H_s}{H_t} \times 100 \quad (1)$$

2.5. Fourier Transform Infrared Spectroscopy (FTIR)

The infrared spectroscopy provides information on the polymer structure by measuring the vibrational properties of the functional group presence in the polymer compound. The emulsion of pure TPGDA and TPGDA/Tw-20 emulsion at an optimal condition were studied by FTIR Spectroscopy (Bruker, Tensor II). The FTIR spectrum was recorded in transmission mode with a resolution of 4 cm^{-1}. The emulsion was placed on the crystal and a total of 32 scans on average over a range of 650 cm^{-1} to 4000 cm^{-1}. The spectra of samples were collected and recorded in the OPUS software.

2.6. Microstructural analysis

The microstructure of the pure TPGDA and TPGDA/Tw-20 emulsion at optimal condition was determined by using optical microscopy (Primo Star, Carl Zeiss) at 20× magnification. One drop of each emulsion was placed on a slide under a glass coverslip. The glass coverslip was carefully placed in order to avoid trapping air bubbles. The images were then captured using Xenstar 2.3 software.

3. Result and discussion

3.1. Observation of phase separation

Emulsion properties depend highly on surfactant concentration and oil types [14]. Hence, it is essential to investigate the effect of the surfactant concentration of the TPGDA/Tw-20 emulsion on the emulsion stability. The emulsion state of 1 wt% TPGDA is obtained by adding water with the coexistence of Tw-20 at various concentrations. The resulting emulsions of TPGDA were in a milky form, and their homogenous forms of stability are summarized in TABLE 1. In the case of Tw-20

TABLE 1

Stability of TPGDA emulsion prepared by Tw-20 aqueous solution

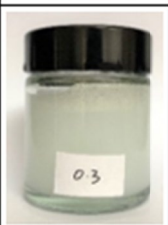
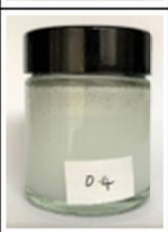
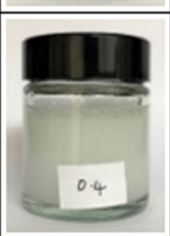
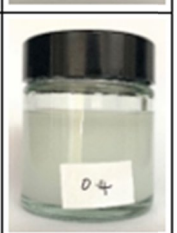
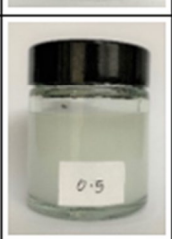
Concentration of Tw-20 (%)	Stability of milky state
0	<1 h
0.1	<3 h
0.2	<5 h
0.3	<8 h
0.4	48 h
0.5÷3.0	48 h

concentrations below 0.3 wt%, the emulsion solution maintained the milky state for some hours, which was less than 8h, and the heterolayer of TPGDA then appeared as a bottom layer. When the concentration of Tw-20 was increased to 0.4 wt%, the milky state was stable for 48 h. Further increment in the concentration of Tw-20 from 0.5-3.0 wt% presented no changes up to 48 h for the TPGDA/Tw-20 emulsion.

TABLE 2 displays the visual image of the phase separation of 1 wt% TPGDA/Tw-20 emulsion from 1 to 24 hours of storage. The effect of time was also investigated to test emulsification

TABLE 2

Visual image of phase separation of 1 wt% TPGDA/Tw-20 emulsion from 1 hour to 24 hours of storage

Concentration of Tw-20 (%)	Fresh Emulsion	1 hour	3 hours	5 hours	8 hours	24 hours
0						
0.1						
0.2						
0.3						
0.4						
0.5						

parameters on emulsion stability by observing phase separation. As shown in Table 2, all fresh emulsions exhibited good stability and emulsion; no apparent cream layer was observed. However, the TPGDA solution without Tw-20 surfactant presented rapid separation within 1 hour of storage. At low surfactant concentrations of <0.3 wt%, visible phase separation was observed in a very short time. The phase separation at low surfactant concentration began from 0.1 wt%, 0.2 wt%, and 0.3 wt% at <3 h, <5 h, and <8 h, respectively. This suggests that <0.3 wt% of surfactant concentration would be insufficient to cover the new surface of TPGDA monomer droplets [15]. As the surfactant concentration increased to >0.4 wt%, no phase separation was observed for up to 24 hours. These results suggest that the surfactant concentration of >0.4 wt% is sufficient to stabilize the emulsion. This is probably due to the droplet concentration being sufficiently high to create an aggregated droplet network to prevent creaming. At 0.5 wt%÷3.0 wt% concentrations of Tw-20, no phase separation was visible for up to 24 hours. In order to minimize material consumption, the Tw-20 concentration at 0.4 wt% was selected as the minimum amount of surfactant concentration needed to stabilize the TPGDA emulsion. It was also nominated as the most stable emulsion compared to 1 wt% of surfactant concentration, as in other studies [16]. The stabilization time of twenty-four hours is adequate for further treatment of the TPGDA grafting cycle since grafting time usually takes only several hours.

3.2. Creaming Index

The creaming index provides indirect information about the extent of the droplet aggregation in an emulsion. The more the aggregation, the larger the flocs and the faster the creaming. This is due to the gravitational force when the density of the dispersed phase is lower than that of the medium [17]. In the emulsion process, the TPGDA/Tw-20 emulsion is vigorously stirred with high energy homogenizer to disperse TPGDA within a continuous phase to water down into fine droplets. The resulting mixture becomes opaque and milky white due to the presence of small light scattering elements (TPGDA). However, after some time, creaming occurs in which a visibly separated emulsion with a droplet-rich cream layer and a droplet depleted watery layer can be observed [18].

Fig. 1 displays the creaming index (CI) of the emulsion prepared with 1 wt% TPGDA and different concentrations of Tw-20 surfactant over 24 hours of storage time. A thin layer of cream (CI at 4.2%) began to develop after 3 hours of storage for 0.1 wt% Tw-20 and a wider layer of cream (maximum CI at 20.8%) at 8 hours of storage. The higher degree of CI is probably due to the increase in the emulsion of agglomerated droplets. While for 0.2 wt% and 0.3 wt% of Tw-20, the thin layer appeared after 5 and 8 hours of storage time, respectively. From 0.4 wt% to 3 wt% Tw-20, the emulsion showed 0% CI for 24 hours of storage time. There was no visible cream layer observed for all emulsions. This phenomenon suggests that no flocculation and coalescence of the emulsion had occurred during storage. Chia C. L. mentioned in his paper that the ideal emulsion should have a CI of 0% where the emulsion can mix and avoid droplet aggregation to occur for some time [19].

The results show that the time for phase separation to be visible increases as the Tw-20 surfactant concentration increases. This is because the higher concentration of surfactant causes fine droplets to spontaneously experience interfacial turbulence [20]. Furthermore, a greater number of surfactant molecules are diffused from the oil phase to the aqueous phase, resulting in the formation of small particles that help create a stable emulsion. This observation of the CI result supports the emulsion stability in TABLES 1 and 2. Therefore, an optimum surfactant concentration for TPGDA/Tw-20 emulsion is recommended to be 0.4 wt% of Tw-20 compared to a higher surfactant concentration. Besides, the lowest concentration of Tw-20 is more favorable to avoid unnecessary chemical use.

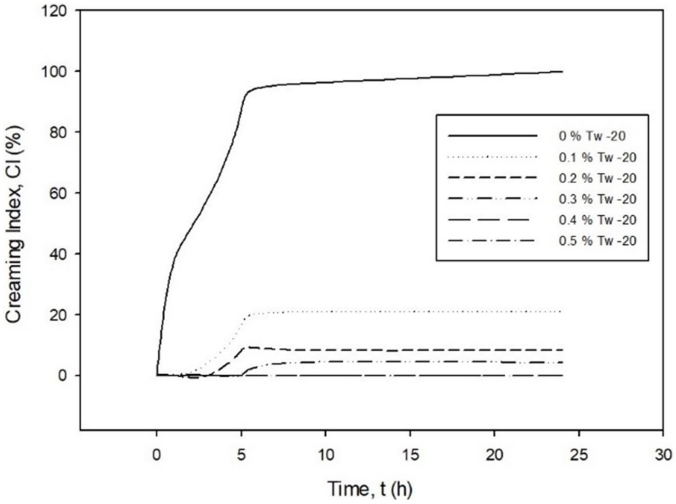


Fig. 1. Creaming index as a function of time for 1 wt% TPGDA emulsion using different concentration of Tw-20

3.3. FTIR Spectroscopy data

The structural changes of pure TPGDA and TPGDA emulsion system with Tw-20 surfactant were analyzed and displayed in Fig. 2. FTIR analysis of pure TPGDA shows a strong characteristic peak that is assigned to the carbonyl group, C=O, at 1720 cm^{-1} from the acrylate group [4]. The peaks at 1099 cm^{-1} and 1091 cm^{-1} both correspond to the C-O stretch peak [6]. The stretching band at 1271 cm^{-1} and 1193 cm^{-1} indicate the presence of C-O-C. The absorbance peak was present at 2977 cm^{-1} due to the -CH3 group [21].

The prepared emulsion of TPGDA/Tw-20 at the optimal condition, 0.4 wt%, was taken for FTIR characterization. The wide band located at 3332 cm^{-1} was attributed to the O-H stretching of Tw-20 surfactant and water solvent, indicating the presence of water in the emulsion [22]. The =C-H deformation of vinylidene hydrocarbon (983 cm^{-1} and 808 cm^{-1}) and the >C=C< stretching for vinylidene group which comes

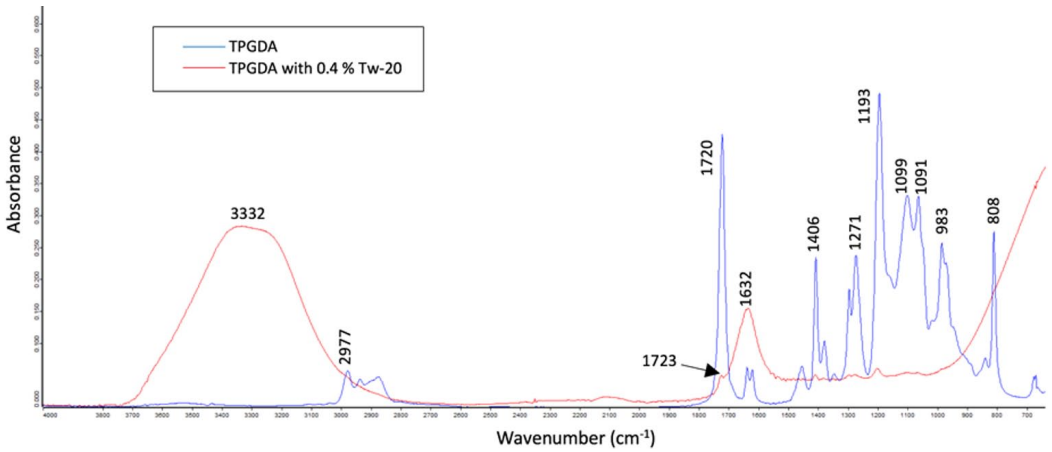


Fig. 2. FTIR spectra of TPGDA and TPGDA emulsion with 0.4 wt% of Tw-20

from TPGDA indicate that the emulsion has already reached stabilization and is fully mixed together [7]. The small peak at 1723 cm^{-1} shows the existence of the characteristic peak from the TPGDA in the TPGDA/Tw-20 emulsion. Compared to the TPGDA/Tw-20 emulsion, almost all the characteristic bands of TPGDA and Tw-20 had disappeared due to the aqueous coating phase. The result also showed a new peak visible at 1632 cm^{-1} of C=C, which suggests that the interaction of TPGDA with Tw-20 in the emulsion was effective and successful. With that, the stability of the TPGDA emulsion was achieved with the appropriate concentration of Tw-20.

3.4. Microstructure analysis

The microstructure of the TPGDA and TPGDA/Tw-20 emulsions at the optimal conditions of fresh emulsion and 24 hours after emulsion are displayed in Fig. 3. The images show that the droplet size is dependent on the type of surfactant in the O/W emulsion. From the microstructure analysis, some small droplets and large coalesced oil drops were observed at 0 and 24 hours of storage for the TPGDA emulsion. The droplet size after 24 hours was bigger with more flocculated droplets than the fresh emulsion. On the contrary, the emulsion prepared

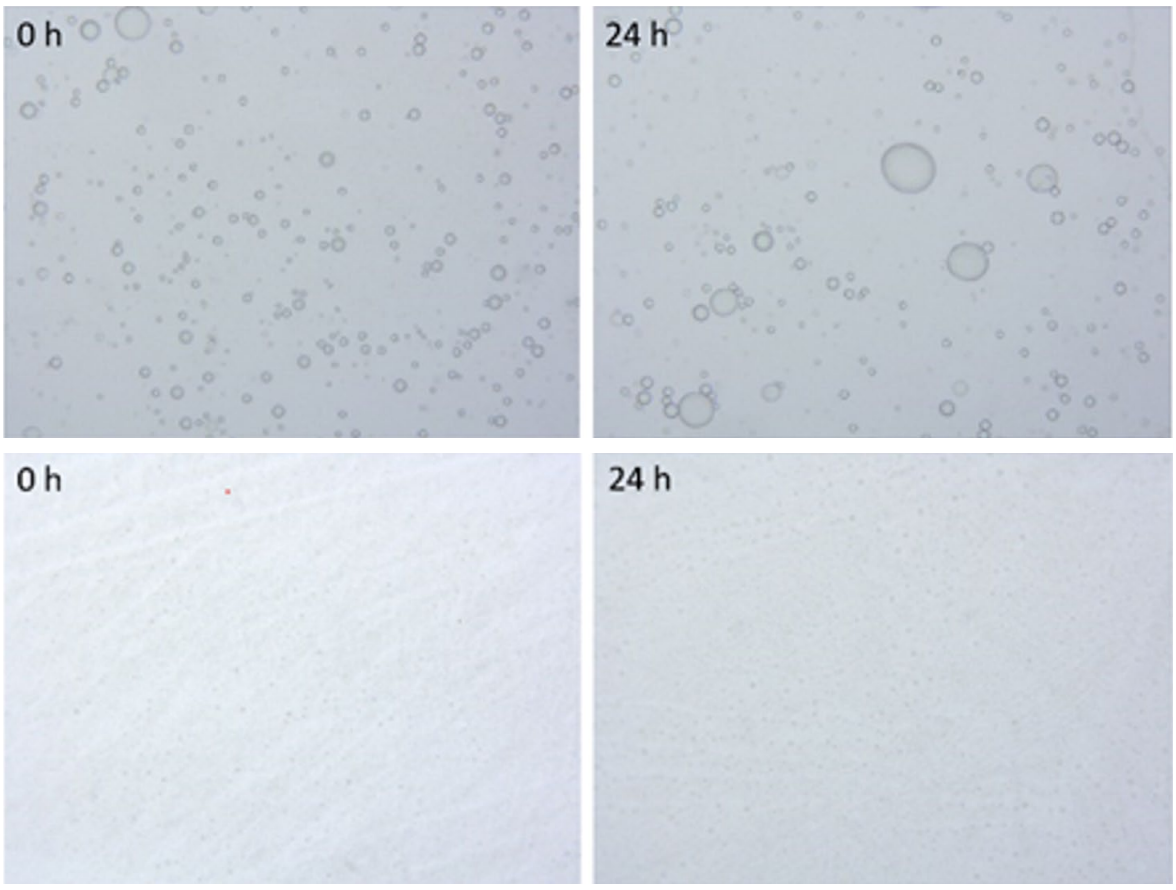


Fig. 3. Optical microscope images of emulsion droplets stabilized by Tw-20 (20× magnification)

with TPGDA and 0.4 wt% of Tw-20 surfactant concentration displayed a uniformity in droplet size throughout the 0 to 24 hours timeframe. The surfactant's presence has created a well-stabilized emulsion. This result is in agreement with Cory et al. and In Kwong Hong et al. [23,24], further validating the successful emulsification of TPGDA and Tw-20 emulsion.

4. Conclusion

This study evaluates the effect of Tw-20 concentration ratios, from 0.1 wt% to 3 wt%, in the TPGDA emulsion. The stability of the prepared emulsion was assessed through phase separation, creaming index, and FTIR. These emulsions exhibited different degrees of instability during 24 hours of storage. However, the most effective level for TPGDA/Tw-20 emulsion is at 0.4 wt% of Tw-20 when compared to lower concentrations of the surfactant and the control. The CI of the emulsion is 0%, and no phase separation was observed for up to 24 hours. The FTIR spectra found that the interaction of TPGDA and Tw-20 in the emulsion was successful with the presence of C=O band at 1723 cm^{-1} and C=C peak at 1632 cm^{-1}. Regarding the optical microscopy images of an optimum surfactant concentration, Tw-20 in the emulsion showed uniform droplet size during the storage period. These results are consistent with the phase observation and creaming index of 0.4 wt% surfactant concentration, which is the most ideal emulsification parameter prepared in this study. This work shows the stability of TPGDA emulsion was achieved at 0.4 wt% concentration of Tw-20 as a surfactant in the system.

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