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RAFT-mediated radiation grafting on natural fibers in aqueous emulsion†

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Abstract: Using aqueous emulsion as the medium in radiation-induced graft polymerization (RIGP) offers an environment-friendly shift from organic solvents while increasing polymerization efficiency through known water radiolysis-based graft initiation. Here, we further extend the applicability of RIGP in emulsion under the influence of reversible addition-fragmentation chain transfer (RAFT) mechanisms. Emulsions prepared with Tween 20 showed good colloidal stability for several hours. Subjecting it to simultaneous irradiation with abaca fibers resulted in successful grafting, supported by gravimetric, IR, SEM, and TG analysis. A correlation was drawn between smaller monomer micelles and enhancement of grafting driven by diffusion and surface area coverage. RAFT mechanisms were also conserved based on molecular weight evolution. RAFT-mediated RIGP in aqueous emulsion shows good potential as a versatile and green surface modification technique for natural fibers for various functional applications.

Keywords: radiation-induced graft polymerization (RIGP); reversible addition fragmentation chain transfer (RAFT) polymerization; emulsion grafting; natural fibers

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1. Introduction

Emulsion polymerization involves the free radical polymerization of monomer molecules in large and discrete polymer particles dispersed in a continuous aqueous phase stabilized by surfactants. This aids in the utilization of water as the solvent for relatively hydrophobic monomers contributing to green chemistry as it significantly reduces organic solvent dependence and their corresponding VOC generation [1]. Because of the segregation of free radicals within the micelles formed in emulsions, the probability of bimolecular termination is reduced, leading to faster polymerization rates and higher molecular weights [2]. This technique has been successfully applied in various industries utilizing polymers that include coatings, adhesives, plastics, and synthetic rubber.

This has also been explored in graft copolymerization, particularly radiation-induced graft polymerization (RIGP). RIGP can be applied in the synthesis of functional materials as it involves the attachment of polymer chains with advantageous tailored properties to the surface of a base polymer with desirable bulk character. The general mechanism is illustrated in Scheme 1 [3]. The key advantage here is that graft reactivity is usually higher in water due to its radiolytic products, which participate in the initiation phase [4]. Glycidyl methacrylate (GMA), a widely used monomer in RIGP, is only soluble in water at concentrations less than 2%. In a previous work [5], emulsifying GMA with Tween 20 formed a milky emulsion that was stable for 48 h and gave sufficiently high grafting yield on polyethylene fibers at doses as low as 10 kGy. GMA concentrations can go up to 10% (w/w) which effectively enhances the degree of grafting [6,7].

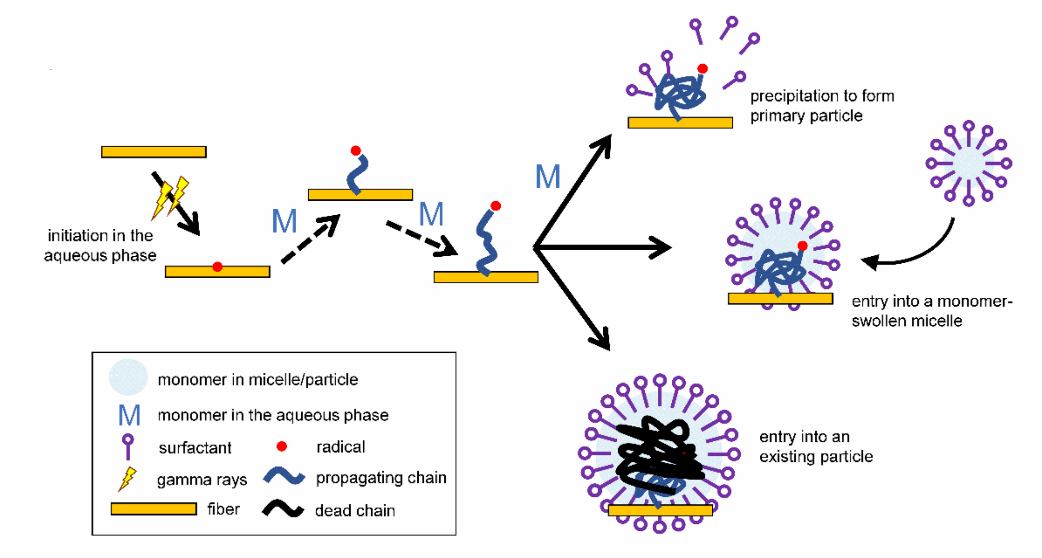


Figure 1. Proposed general mechanism of RIGP in emulsion [3].

In the preparation of diverse functional materials, control over polymer brush architecture leads to a significant influence over surface properties and often enhances its specific functionality [8]. Among controlled radical polymerization techniques, the reversible addition-fragmentation chain transfer (RAFT) mechanism is applicable involving both radiation-initiated reactions and emulsion systems [9–11]. The RAFT agent, initially dissolved in the monomer before emulsification, may be likely found inside the micelle where it can mediate chain growth through reversible deactivation of propagating chains [12]. Difficulties associated with the use of RAFT in *ab initio* emulsion systems such as low polymerization rates, broad molecular weight distribution, and loss of control are usually attributed to colloidal instability and RAFT transport [13]. In this work, RAFT-mediated radiation grafting in aqueous emulsion using Tween 20 as the surfactant for emulsion polymerization was assessed for its pseudo-living character and its potential as a green surface modification technique for natural fibers for various functional applications.

2. Materials and Methods

2.1. Emulsion preparation

The emulsion was prepared with the following components by weight: 10% GMA (>95%, TCI, Japan), 0.2% 4-cyano-4-(carbonothioylthio)pentanoic acid (CPPA, 97%, Strem Chemicals Inc., USA) and 0.5 – 2% Tween 20 (Kanto Chemical Co. Inc., Japan) in ultrapure water. The solution was homogenized at 6000 rpm for 10 min. Stability and micelle size was measured by dynamic light scattering using FPAR 1000 particle size analyzer (Otsuka Electronics Co., Ltd., Japan) at 25 ˚C.

2.2. Radiation grafting of abaca fibers

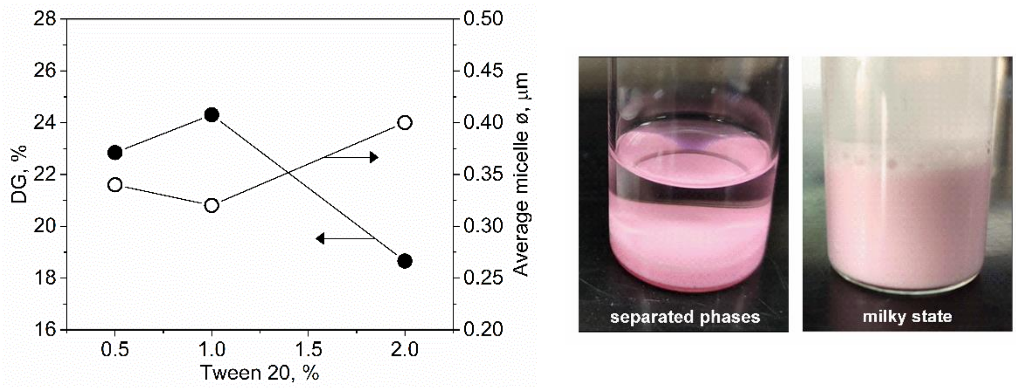
Pre-weighed abaca woven fabrics (1 x 5 cm^2) and 8 g of the emulsion were placed in a glass vial and purged with N_2 gas. The vial was placed in a Co-60 gamma irradiation chamber and polymerization was carried out at a dose rate of 1 kGy/h (in air). The fabrics were washed several times with methanol and tetrahydrofuran (THF) and dried to constant weight in vacuo. The homopolymers were then precipitated from the solution using methanol and weighed. The degree of grafting (DG, %) was calculated from the percent weight gain of the fabric, while conversion (%) was determined from the added weight of the collected homopolymer and weight gain of the fabric over the initial amount of monomer in the vial. A sample of homopolymers was dissolved in THF and analyzed using gel permeation chromatography (Chromaster, Hitachi HighTech, Japan equipped with Shodex Asahipak GF-16 7B guard and two GF-7M columns). Polymethyl methacrylate standards were used.

2.3. Characterization

The abaca fabrics before and after RIGP were subjected to several characterization techniques. The chemical information of the fabrics was examined by a Frontier FTIR Spectrophotometer (Perkin Elmer, Japan) in attenuated total reflectance (ATR) mode with 4 cm^{-1} resolution. Morphology and elemental composition of the fabric surface were examined by scanning electron microscopy with energy dispersive x-ray (SEM-EDX) taken by a Hitachi SU3500 scanning electron microscope (Hitachi HighTech, Japan) coupled to X-Max EDX spectrometer (Horiba Ltd., Japan) at vacuum conditions and acceleration voltage of 50 Pa and 10 kV, respectively. All fabrics were gold coated using JFC-1600 Auto Fine Coater (JEOL Ltd., Japan) prior to scanning. The thermal decomposition profile of the fabrics was examined using a TG/DTA 6200 Extar 6000 (Seiko Instruments Inc., Japan) under nitrogen atmosphere using a 5 mm aluminum sample pan, with the following heating program: (1) 25-130 °C at 20 °C/min; (2) 130 °C for 10 min; and continuing to 550 °C at 10 °C/min.

3. Results and Discussion

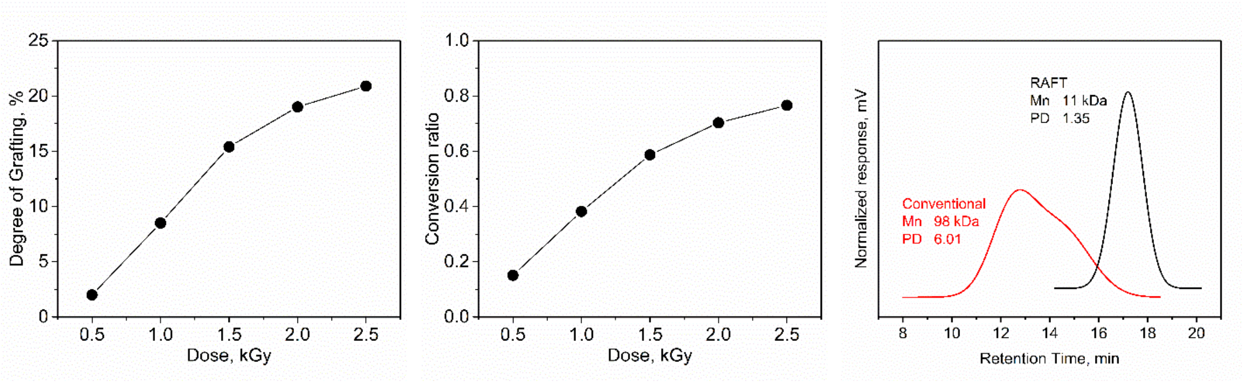
In the mechanism of emulsion polymerization via RAFT, the formation of oligomers at the initial phase can dramatically reduce the chemical potential of the nucleated particle and lead to a large amount of monomer to transfer from droplets to these particles [14]. This phenomenon, known as superswelling, ultimately destabilizes the emulsion and often leads to a loss of control of polymerization associated with the formation of a colored layer or coagulum. The use of a relatively higher surfactant concentration, preferably nonionic like Tween-20 above its critical micelle concentration (CMC), has been known to circumvent superswelling [15]. High amounts of surfactant (at least greater than their CMC) also ensure that most of the monomers, as well as the RAFT agent are in the stable micelles (<1 μm), which are considerably smaller than monomer droplets (>1 μm). This also aids in the rapid transport of RAFT agent to the growing particles owing to the larger surface area of the micelles [11].



(a) (b)

Figure 2. CTPA/GMA emulsion studies: **(a)** effect of surfactant concentration on the degree of grafting (DG) at 5 kGy absorbed dose and average micelle diameter ∅; and (**b**) representative images of solution during initial separated phases and emulsified milky state.

Emulsion systems with different surfactant-to-monomer ratios were observed. As seen in Figure 2a, the degree of grafting (DG) increased when the surfactant amount was changed from 0.5 to 1% and then proceeded to decrease at higher [Tween 20]. DG seems to correlate inversely with the observed micelle size of the emulsion. Smaller micelles may cover a wider surface area of the trunk polymer leading to an enhanced grafting efficiency [5]. Furthermore, smaller micelles usually diffuse better throughout the solution allowing them greater access to the site of graft propagation [4,5,16]. Based on these results, the surfactant concentration was fixed to 1% in further experiments as it exhibited the highest DG. At this concentration, the emulsion remained in a milky state (Figure 2b) with no phase separation and was relatively stable for at least 10 h.



(**a**) (**b**) (**c**)

Figure 3. Effect of absorbed dose on the (**a**) degree of grafting and (**b**) monomer conversion; and (**c**) representative GPC chromatograms for PGMA formed using the conventional technique and with CPPA at ~0.8 conversion.

Grafting in emulsion was further carried out at various absorbed doses. As seen in Figure 3a, there was an initial rapid increase in DG with absorbed dose as it correlates to radical production. Continuous chain growth is also a feature of RAFT-mediated polymerization, which minimizes irreversible chain termination (dead chains) through the reversible deactivation of propagating polymer radicals ("living" chains) [17,18]. Therefore, grafted polymer chains continue to grow and contribute to DG as long as monomers remain available. At higher absorbed doses, DG increase slowed down possibly due to the decrease in available monomer molecules during the course of the polymerization. This is reflected in monomer conversion values shown in Figure 2b. Similarly, monomer conversion showed a rapid increase with absorbed dose then slows down at higher doses due to restricted monomer diffusion with an increase in polymer concentration and viscosity. There was an initial linear increase in conversion values as a function of absorbed dose, which translates to polymerization time (h) as the dose rate is fixed to 1 kGy/h. To estimate the properties of the grafted polymers in terms of molecular weight and polydispersity, GPC analysis was performed on the precipitated homopolymers from the solution. As reported in previous works on RAFT-mediated radiation-induced grafting, the growth of surface grafted polymer chains exists in dynamic equilibrium with the free polymer chains (homopolymers) formed in the grafting solution [9,19]. Figure 3c shows the chromatograms of PGMA homopolymers formed using conventional (without CPPA) and RAFT-mediated RIGP. In contrast to the former's broad and multimodal molecular weight distribution, using RAFT polymerization demonstrated narrow and monomodal distribution with a polydispersity index of 1.35 and good correspondence with the calculated value based on the RAFT-monomer ratio and conversion [12]. These results suggests the pseudo-living characteristics of the polymerization, indicating that the RAFT mechanism was in effect in the emulsion [20].

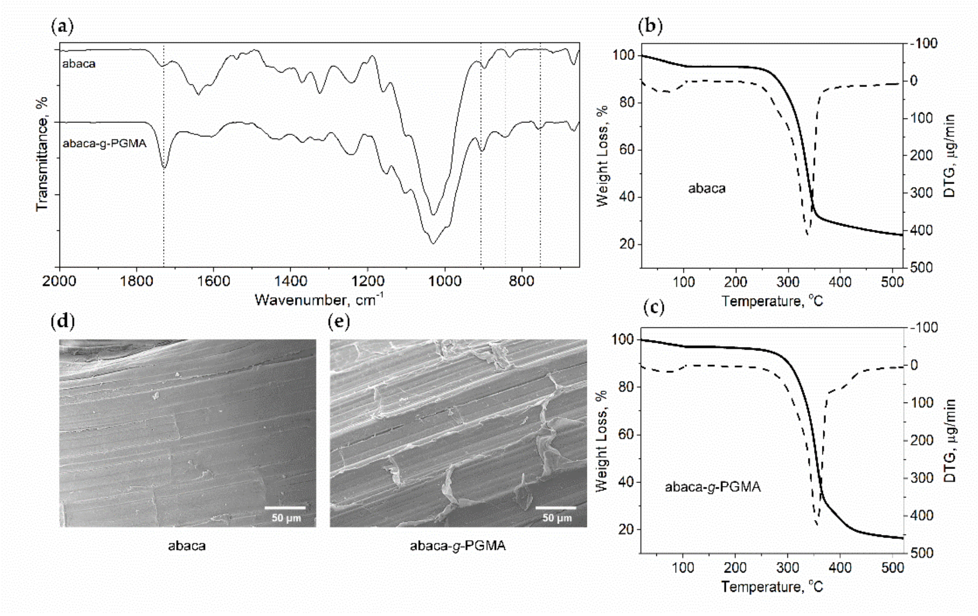


Figure 4. Evidence of grafting: (**a**) FTIR spectra highlighting the appearance of carbonyl and epoxide peaks on the (dashed lines); (**b-c**) weight loss and DTG (dashed lines) profiles; and (**d-e)** SEM micrograph of fiber surface of pristine and grafted abaca (DG ~ 20%).

Analyzing the fabrics using FTIR (Figure 4a), successful grafting is evident as supported by the appearance of C=O stretching bands at 1725 cm^{-1} and epoxide ring deformations at 750–950 cm^{-1}, in addition to the cellulose profile of the fiber shown as peaks at 1600, 1110 and 1040 cm^{-1} attributed to the glucose ring vibrations [21]. Figure 4b-c also show the extension of the degradation profile of abaca fiber after cellulose main chain 250–360 °C to 420 °C attributed to the degradation of the grafted polymers [22]. Finally, abaca fibers were examined using SEM-EDX. The pristine fiber showed a relatively smooth surface made of 60% carbon and 40% oxygen atoms (Figure 5c). Meanwhile, abaca-*g*-PGMA showed a much rougher surface due to the amorphous PGMA covalently grafted on its surface (Figure 4d). There is also an increase in the carbon content from the PGMA chain, shifting the composition to 70% C and 30% O. Trace amounts of sulfur (0.02 %) were also detected which can be attributed to the thiocarbonylthio end of CPPA which adds to the propagating chain during RAFT-mediated polymerization [9,12,23].

4. Conclusion

Graft polymerization reactions done in aqueous emulsion offer an environment-friendly alternative to the use of organic solvents. In this work, glycidyl methacrylate was successfully grafted from abaca fibers using radiation-induced graft polymerization mediated by reversible addition-fragmentation chain transfer mechanism. Stable milky emulsions were formed using Tween 20 as the surfactant and CPPA as the chain transfer agent. The emulsion remained stable for several hours and did not form an oily layer or coagulum indicative of unsuccessful RAFT polymerization. Instead, grafting proceeded with pseudo-living characteristics as supported by the increase in the degree of grafting with the linear increase of conversion, and the narrow and monomodal molecular weight distribution of generated homopolymers with good correspondence to the theoretic value. Evidence of grafting was verified using FTIR, TGA, and SEM-EDX, which all showed successful attachment of PGMA chains onto the abaca fiber. These results highlight the potential of RAFT-mediated RIGP in aqueous emulsion as a green surface modification technique for natural fibers. Studies on the further functionalization and characterization of the fibers for applications as adsorbents and composite reinforcement fillers are currently underway.

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