Recycling of pneumatic scrap tyre into nano-crumb rubber by pulsed laser ablation in different pH media

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Abstract. Nano crumb rubber from scrap tyre is synthesized via 1064 nm pulsed Nd:YAG laser ablation in three different pH media i.e. DI-water (pH~6.45), D-limonene (pH~3.47) and NaOH solution (pH~13.41). Field Emission Scanning Electron Microscope (FESEM) results show spherical morphology of crumb rubber with high degree of aggregation in DI-water and in D-limonene. However, dispersion of crumb rubbers is observed in NaOH solution. The smallest particle size is obtained in NaOH solution within the range of 10.9 nm – 74.3 nm. Energy-dispersive X-ray spectroscopy (EDX) and FTIR analysis confirmed the elements distribution and chemical bonding of rubber with DI-water, D-limonene and NaOH solution. The experimental findings shows that pulsed Nd:YAG laser ablation has potential for fabricating nano-crumb rubber in liquid media.

1. Introduction

Recently, scrap tyre wasted create adverse effects on the environment because waste tyre disposal process directly contributes towards the enhancement of biodiversity due to its insoluble and toxic compounds [1]. Numbers of researches have been carried out regarding to this particular matter [2-7]. Advent of industrial technology reported that waste tire crumbs have potential as recycled rubber-containing products ranging from construction to road pavement industry [8-10]. To date, there are several processes being practiced for manufacturing of crumb rubber. Two of the most common techniques are ambient grinding [11] and cryogenic processing [12]. However, ambient grinding technique refers to a series of processes that are carried out to yield the desired product and time consuming. Typically, granulation equipment or cracker mills are used in this process. Meanwhile, in cryogenic processing, liquid nitrogen is used to freeze or reduce the temperature of the scrap tyre. By this method, crumb rubber can be produced up to 50 μm in size [12]. However, this technique requires special designed chamber with high intensity instrument to produce finer rubber crumbs.

Crumb rubber manufacturing technologies are continuously focusing on a mechanism to yield finer crumb rubbers from scrap tyre ranging from 40 to 200 mesh. In this study, we proposed a new approach to synthesize finer crumb rubber from scrap tyre by pulsed laser ablation technique in liquid (PLAL). This technique offers green synthesis of nanoparticles or particles’ clusters without using any...
any toxic chemicals [13]. Several researchers reported the synthesis of nanoparticles from pure metal such as gold [14], zinc oxide [15], organic compound i.e. Eu(TMA) (H$_2$O)$_4$ [16] using PLAL. Basically, in PLAL technique, nano/or finer particles can be synthesized from hard target (metal) by focusing a pulsed laser on the target surface. High pressure and temperature of plasma as well as a stronger shockwave with a longer duration and a higher impact force leads the formation of finer particles compared to ambient air.

Lately, owing to hybrid approaches, different aqueous liquid solutions e.g., water, ethanol, isopropanol and acetone have been applied to assist laser ablation [17-19]. The D-limonene was chosen because of its environmental friendly nature, non-toxicity and naturally can be found in lemon and orange peels. To the best of our knowledge, we are reporting a new fast, non-toxic and easy approach i.e. PLAL (Nd:YAG 1064 nm laser) within different pH media such as DI-water (pH~6.45), D-limonene (pH~3.47), and NaOH (pH~13.41) to produce the crumb rubber within range of 117 nm – 10 nm.

2. Experimental

Pneumatic scrap tire (which is made of synthetic rubber, natural rubber, fabric, carbon black and C, O, Zn, Si and Si) is used as a target material. The scrap is cut into small piece with dimension of 2 cm x 2 cm x 0.5 cm and then cleaned it in acetone for 30 min using Branson ultrasonic bath and rinsed it thoroughly with de-ionized water. A 1064 nm pulsed Nd:YAG laser is used as a source in laser ablation, operating at a pulse width of 8 ns, repetition rate of 3-Hz, and maximum pulse energy at 311 J. The laser is focused via objective lens at a focusing length of 100 mm onto the rubber surface. The sample is immersed in 10 ml of DI-water (pH~6.45), D-limonene (pH~3.47) and NaOH solution (pH~13.41). After this, each solution is rotated individually by rotational plate (Newport®-UTR80) at 120 rpm driven by a stepping motor to avoid crater formation during the ablation processes. The solutions are processed within different time intervals i.e. 10 min, 20 min, 30 min, 40 min and 50 min at room temperature. Subsequently, variations in solutions color are observed by increasing/changing the pulse numbers. Figure 1 shows the schematic diagram of pulsed laser ablation in liquid to produce the crumbs rubber.

Figure 1. Schematic diagram of pulsed laser ablation for crumbs rubber producing from scrap tyre.
3. Characterization
Morphology of synthesized crumb rubber was observed using Field Emission Scanning Electron Microscope (FESEM) HITACHI SU8020. For FESEM analysis, one drop of each colloidal solutions was placed on 15 mm x 15 mm x 2 mm FTO glass slide. Each of the glass slide was then baked in an oven at 200 °C for 8 min. Then, the glass slides were coated using platinum by automated platinum sputter (QUOROM Q150RS) for about 5 min. The samples were examined through FESEM, operating at ultra-low accelerated voltage imaging resolution of 1.3 nm at 2.0 kV. The elemental analysis was also carried out by an energy-dispersive X-ray spectroscopy (EDX) spectra (Oxford Silicon Drift Detector [SDD]). The infrared spectra were recorded using a frontier FTIR (ATR) spectrometer, Perkin Elmer Series L160000A (USA) within the range of 600 to 4000 cm−1 at ambient temperature.

4. Results and Discussions
Digital pictures in Figure 2 (A, B, C) shows that the color varies in different solutions i.e. DI-water, D-limonene and NaOH within different ablation time intervals 10 min – 50 min. In DI-water [Figure 2-A (a – e)], concentration of crumb rubber particles is low even after increasing the ablation time as compared to D-limonene and NaOH. Whereas, [Figure 2-B (a - e)] shows that the concentration of crumb rubber particles increases by increasing the ablation time and gathered at the bottom of the falcon tube. After 50 min, high concentration of crumbs was obtained which can be clearly seen in [Figure 2-B (e)]. However, the crumb rubber particles are found to be dispersed in NaOH solution and the concentration of particles increases gradually after increasing the ablation time 10 min – 50 min [Figure 2-C (a – e)].
Figure 2. Crumb rubber into (A) DI-water (B) D-limonene (C) NaOH solutions, a, b, c, d and e is corresponding to 5 different ablation times 10 min, 20 min, 30 min, 40 min and 50 min, respectively. Whereas, (D) is the schematic illustration of laser processing, (a) plasma plume is ignited on the irradiated spot, (b) isothermally expansion of plasma plume by laser energy absorption, (c) plasma plume adiabatically expands and chemical reaction takes place at the liquid-material interface after laser pulse treatment.
From figure 2-B (a - e), it is observed that the production of crumb rubber is higher in D-limonene medium as compared to DI-water and NaOH solutions. The enhancement of pulsed laser ablation in d-limonene solution is due to the strong confinement of plasma plume [Figure 2-D (a-c)] and the assisted localized chemical etching forces that occurred within the surrounding medium [20, 21]. In mechanism of PLAL technique, focusing of high intensity laser beam on the sample surface (rubber) leads to excitation of electrons to a higher state as a result from inverse-bremsstrahlung process [22]. This process further yields a dense cloud of atoms and ions in excited state (C⁺, H⁺, O₂⁻) due to energy transfer from electron-ion and electron-neutral collision processes. Accordingly, transfer of energy from the laser pulse formed the plasma plume [Figure 2-D (a)] that consists a mixture of vapours containing those ions, atoms and electrons all together. The plasma plume then experienced an isothermal expansion due to continuous absorption from laser pulse energy [Figure 2-D (b)], resulting in relatively high speed increment in temperature and pressure. After the laser treatment, plasma plume continues to expand adiabatically with relatively high pressure and temperature [Figure 2-D (c)]. This expansion last for about few microseconds before it shrinks up and collapse. Under this extreme condition, thermal evaporation and decomposition of molecules, are excited, resulting in the generation of cavitation bubbles. Energetic expansion of plasma plume induced a shock wave with a relatively strong pressure. The plasma plume condensates into clusters and aggregates into smaller particles [23]. The smaller particles (ejected materials) distributed in the irradiated area. Furthermore, the chemical reaction around the irradiated area further increases the removal of target rubber. The size and the weight of the removal particles are apparently greater than the rest of other tested media, consequently the precipitation of the crumb rubber is obviously observed from the D-limonene solution.

Figure 3 shows the graph of crumb rubber concentration in three different solutions i.e. DI-water, D-limonene and NaOH versus ablation time. It can be observed that the concentration of rubber particles increases by the ablation time (10 min – 50 min). The D-limonene solution curve (b) has the highest concentration followed by NaOH solution curve (c) and the lowest concentration is in DI-water curve (a). The concentration of crumb rubber in D-limonene solution is higher than the DI-water and NaOH is due to the precipitation of rubber particles at the bottom of the container which also confirmed as shown in Figure 2(B). The lowest concentration is observed in DI-water because less crumb rubber particles produced in the solution. The average concentration of crumb rubber in D-limonene is 0.2211 g/mL, NaOH with 0.0346 g/mL, meanwhile for DI-water 0.0011g/mL.

**Figure 3.** Crumb rubber concentration in different solutions (a) DI-water, (b) D-limonene and (c) NaOH solution, versus ablation time.
The morphology and particles size of laser ablated crumb rubber after 50 min treatment were analysed by FESEM. Figure 4 (a, b, c) shows morphology of rubber particles in DI-water, D-limonene and NaOH solution, respectively. Figure 4 (a) shows spherical shape particles’ aggregation in DI-water is probably due to absorb water molecules on the surface of the crumb rubber. Meanwhile, Figure 4 (d) is the magnified image of Figure 4 (a). The observed particles size is in the range from 29.6 – 82.2 nm. Moreover, cluster formation (737.6 nm) with particles aggregation can be clearly observed in D-limonene as shown in Figure 4 (b) and its magnification for the circular area is shown in Figure 4 (e). Particles size are observed in the range of 23.8 – 117 nm. Particles size within the range of 10.9 – 74.3 nm are realized in NaOH solution as depicted in Figure 4 (c), and it corresponding magnification is shown in Figure 4 (f). The hydroxide ions from NaOH solution chemically break into mono-,
polysulfidic cross-linkages in rubber vulcanizate, resulted in small particles dispersion of crumb rubber [24].

Figure 4 (g), (h) and (i) shows the EDX spectrum of laser ablated crumb rubber in DI-water, D-limonene and NaOH solutions. The element composition in weight percentage (wt. %) of crumb rubber from each solution is tabulated in Table 2. The main component of crumb rubber is comprised of carbon C, oxygen O, silicon Si, zinc Zn, iron Fe, sulphur S and aluminium Al. The EDX analysis, suggest that there are no foreign elements detected from fabricated crumb rubber. However, the presence of sodium Na in Figure 4(i) is attributed from the NaOH solution. This finding indicates that pulse laser ablation in liquid technique has ability to induce crumb rubber.

![FTIR spectra of laser ablated crumb rubber in (a) DI-water, (b) D-limonene and (c) NaOH](image)

The broad absorption band at ~3300 cm\(^{-1}\) associated with hydroxyl group stretching in all three samples. A little intense peak around ~2965 cm\(^{-1}\) [Figure 5(a)], is due to C-H symmetric stretching of organic residue. Occurrence of sharp absorption band in all three samples around ~1639 cm\(^{-1}\) is characteristic of a C=O group [25]. The prominent peak at ~1053 cm\(^{-1}\) is attributed to the bending of =C-H bonds that indicates the presence of D-limonene in the solution [Figure 5(b)]. Prominent bands at ~1414 cm\(^{-1}\) and ~880 cm\(^{-1}\) correspond to the CH\(_3\) and =CH out of plane bending of cis-1,4-polyisoprene the component in natural rubber [26]. FTIR analysis confirmed that the rubber species have good interaction with different pH media.

5. Conclusion
Nanocrumb rubber (10 – 117 nm) was synthesized using PLAL technique in different pH media. The concentration of crumb rubber is found to be optimum in acidic solution like D-limonene with pH~3.47. The smallest nanoparticle of rubber is achieved when the crumb rubber is synthesized using basic solution like sodium hydroxide NaOH with pH~13.41. Beside the crumb rubber particles are realized to be more homogenized in this basic solution. However, the crumb rubber are very difficult to be achieved using deionized water (pH~6.45). FESEM images show the spherical morphology of crumb rubber within the range of particle size (DI-water, 29.6 – 82.2 nm, D-limonene, 23.8 – 117 nm, NaOH solution, 10.9 – 74.3 nm). EDX analysis confirms the presence of crumb rubber in the solutions from scrap tyre. FTIR analysis shows the chemical bonding between three different pH media (DI-water, D-limonene, and NaOH) and rubber species. The experimental findings demonstrated that
PLAL is a promising technique to fabricate nano-crumb rubber from a recycle scrap tyre compared to mechanical grinding methods.

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