Study of Plasma Electrolysis Method on Starch-Based Hybrid Latex Synthesis

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Abstract. The plasma electrolysis is a rich source of free radicals, it commonly induces unusual chemical reaction. This paper focus to study plasma electrolysis induces grafting reaction between latex and starch to prepare a functional material – ether bond – with radicals as the initiator to produce hybrid latex which presume has acoustic property. By the method of plasma electrolysis, the reaction can take place and the difference of polarity between the reactants can be overcome. The synthesis – both by using anodic and cathodic plasma – is said to work qualitatively when the characterization results by using Fourier Transformation Infrared Spectroscopy (FTIR) arises a new ether bond waves at around 1560 cm\textsuperscript{-1}. The synthesis processes – both by using anodic and cathodic plasma – were investigated more specifically by looking at the effect of electrolyte, Na\textsubscript{2}SO\textsubscript{4} concentration used with variations of 0.02; 0.03; 0.04 M to the efficiency of synthesis. The applied operating voltage of the process are 567.5 and 340.5 volt for anodic and cathodic, respectively. The reaction time is 10 minutes, and the efficiency of synthesis is represented by % yield of hybrid latex per kJ of electric energy consumption. The obtained efficiencies – from anodic and cathodic – were 0.04; 0.02; 0.01 and 0.18; 0.13; 0.12, for each of electrolyte concentrations, respectively.

1. Introduction
Latex (natural rubber) is the main commodity owned by Indonesia. In accordance with data obtained in 2014, shows that Indonesia is the 2\textsuperscript{nd} largest rubber producer country in the world after Thailand, with productivity around 3.2 million tons of natural rubber [1]. These overflowing resources certainly encourage the development of rubber industry in Indonesia. Currently, many rubber is manufactured into such as rubber carpets, pipes, car tires and others. Car tires are the most developed applications caused by the needs of public transport. The increase in transportation needs is evident from BPS data, where an increase in vehicle volume from 8,145,278 in 2012 to 8,988,506 in 2013 [2].

Latex is a polymer of isoprene monomer (C\textsubscript{5}H\textsubscript{8}) under the IUPAC name of cis 1,4-polyisoprene with general formula (C\textsubscript{5}H\textsubscript{8})\textsubscript{n}. Latex is a material with excellent mechanical characteristics in terms of flexibility, but poor in terms of Young’s modulus of stiffness. The low value of Young’s modulus is a weakness of rubber, consequently vehicle tires that is dominantly composed of latex tend to have a low grip strength, thus shortening the tire's lifespan when high friction frequencies is constantly contacting the tire. The Young’s modulus is one of several parameters for measuring the stiffness of a material expressing its response to linear voltage; one of them in the form of friction. On the other hand, starch, which is a polymer of the glucose monomer arrangement, has mechanical properties of a high Young’s
modulus of stiffness but poor in flexibility. Starch based latex modification or grafting, as hybrid latex, is the solution to the problem. Modification or grafting of latex and starch is potentially carried out, by looking at the bonds present in each of the polymers. The possibilities is visible from the latex having two double phi bonds and the starch having an alcohol group [3]. Both groups are potentially to be combined or grafted to form an acoustic or mute hybrid latex.

It is expected, by grafting, the combination of each material’s perk properties is applied. This study focuses on the subject of plasma electrolysis as a method of inducing the grafting reaction of both materials. The transplanting reaction is the reaction of combining large molecules into much larger molecules. Hybrid latex synthesis can be done by grafting or combining latex, which is a polymer of isoprene, and starch, which is a polymer of glucose, through chemical reactions. Conventionally, polymerization reactions (in this study referred to as grafting) are performed by the addition of a chemical initiator to produce the radical substance that initiates the reaction. Conventional methods have some disadvantages that depend on the number and concentration of initiators used and the physical properties of the two reacted substances. Periodic addition of initiators and intermittent physical properties of the reactants [4] are required.

The method of plasma electrolysis is an alternative method that can be used to overcome the weaknesses of the conventional method. This method is rich in radicals that can induce reactions, by generating energetic species such as electrons, ions, ultraviolet light, and meta-stable (radical) groups. The resulting energy is sufficient to break the bonds between atoms (force breaking bond) to produce hydroxyl radicals (\(\cdot\)OH), hydrogen radicals (\(\cdot\)H), and other active radicals, depending on the compound subjected to the energy. Such radicals can initiate polymerization reactions [5].

In plasma electrolysis, the problem of reacting reactants that were not intermingled, due to differences in polarity, can be forced to bind through a radical reaction mechanism. That is, each particular reactant has a particular reaction mechanism also in reaching the final product. In addition, the reaction induced by the plasma electrolysis method can overcome and replace the role of the chemical initiator required when using conventional methods [5]. Plasma electrolysis produces radical species without the addition of a chemical initiator due to the plasma itself is a continuous, relatively safe and easy source of radical in terms of operation [6,12].

Plasma electrolysis is closely effected to the mobility of ion, electron, and radical species in solution. Therefore, it is necessary to add an electrolyte with a certain concentration to maintain the conductivity of the solution and ensure that the species can move freely in the solution. The higher electrolyte concentrations used result in greater conductivity. This increase in conductivity can increase the size of the plasma formed and trigger the production of hydroxyl radicals (\(\cdot\)OH) to be increased [7]. If this reaction uses the Faraday electrolysis concept, then plasma electrolysis can be performed either cathodically or anodically. The fundamental difference is cathodic and anodic, that is, in the process of electrolysis of cathodic plasma produced more hydrogen (\(\cdot\)H) radicals, whereas in the more produced anodic electrolysis is radical hydroxyl (\(\cdot\)OH). The objective of this study specifies in the effect of plasma formation position (cathode or anode) on the acquisition of hybrid latex using plasma electrolysis method.

2. Material and Method
Electrolysis plasma reactor, shown in Figure 2, is a modified 1 liter beaker glass that jacketed with plastic container. This container is used as cooling water space that allows water to recirculate from water reservoir back to the reactor. Beside, plastic is used as jacket due to its nice thermal resistance. Used electrodes are stainless steel (SS-316) with 6 mm in diameter as cathode, and wolfram with 0.5 mm in diameter as anode. The depth of anode that contacts to solution is around 5 mm. The source of electricity is come from PLN (Electricity supplier in Indonesia). The electricity from PLN is controlled by using regulator slide, step-up transformer, and diode-bridge. Electrical circuit is shown by Figure 1.
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Figure 1. Schematic view of electric position to generate plasma.

Figure 2. Schematic view of plasma electrolysis reactor

1. Reactor cap. 2. Anode (SS-316). 3. Thermometer. 4. Cathode (Wolfram). 5. Free air hole. 6. Baffle. 7. Cooling water space. 8. Cooling water inlet. 9. Magnetic stirrer. 10. Reaction zone.

The raw materials are diluted latex, starch, and electrolyte. The synthesis process was investigated more specifically by looking at the effect of the Na$_2$SO$_4$ electrolyte concentration used with variations of 0.02; 0.03; 0.04 M, the influence of plasma formation (cathodic or anodic), on the acquisition of hybrid latex using plasma electrolysis method. The latex concentration used in the reaction of 1% -wt obtained by diluting the latex 55% -wt (around 9.1 mL in volume) using aquadest to 500 mL volume, the used latex is also protein free, starch used at 3% of the 9.1 mL latex mass. The ratio was chosen after doing trial and error. The operating voltage of the process with anodic and cathodic plasma respectively was 567.5 and 340.5 volt for 10 minutes reaction. From the above variables, we obtain each efficiency of synthesis which represented by % yield per kJ of hybrid latex electric energy consumption using anodic and cathodic plasma (with electrolyte addition).

The gross product – just after plasma electrolysis is done - it is purified by dried it in a vacuum dryer to make it free from water. The product is still considered as gross product and need to be purified to
the next purification steps. About 0.03 grams as solid aliquot is taken and solute in a chloroform solution for 48 hours. After that, filtered, and pondered. The final step is re-drying for half hour, and pondered. The yield calculation is based on ratio latex hybrid that was obtained per used initial latex. Need to know that this research to modified latex and starch is a new research for preparing functional material: hybrid latex.

The energy of the species and UV radiation produced in electrolysis plasma are greater than the binding energies in organic molecules of common bonds (shown in Fig. 5). Thus, the energies both by particle bombardment and by UV radiation can provoke random chains scissions, C-radical formation, auto-oxidation, crosslinking, etc. in polymers [5].

3. Result and Discussion

3.1. Confirmation of Functional Group
The wavelengths that appear on the reactants are compared (see Figure 3) with the number of waves present in the product to ensure the existence of new ether bonds. The result of reaction to be obtained by reacting latex and starch using plasma electrolysis method is the formation of ether bond between latex and starch. In another similar study, that modified starch with poly-methyl-methacrylate, it was found that the ether bond formed between starch and poly-methyl-methacrylate appeared at a wave number of about 1576 cm\(^{-1}\) [8]. In this hybrid latex synthesis study, the ether (C-O) linking between latex and starch is thought to occur in the range of 1530 - 1560 cm\(^{-1}\) waves not far from the ether bond wave numbers formed between starch and poly-methyl-methacrylate from the study that modified starch [8].

Figure 4 in hybrid latex samples there are many peaks that appear on the fingerprint area. Among them are 1086 cm\(^{-1}\), 1232 cm\(^{-1}\), 1373 cm\(^{-1}\), 1442 cm\(^{-1}\), 1545 cm\(^{-1}\), and 1644 cm\(^{-1}\). Peak in the range of 1086-1235 cm\(^{-1}\), identified as an ether functional function (C-O), alkyl group identified at 1373-1442 cm\(^{-1}\), and an alkene group (C=C) at 1644 cm\(^{-1}\). All identified peaks have similarities to the reactants, which is starch chain as well as pure latex. However, a new peak appears on 1545 cm\(^{-1}\) which is thought to be the ether linking the latex and starch as previously described. If referring to the reference table FTIR wave number, then the wave number 1545 cm\(^{-1}\) should be identified as an amine bond [9,10]. However, since the latex used in this study is a depepted latex (the protein has been removed; the protein itself has an amine bond) - as evidenced by the absence of amine group wave numbers from proteins at the time of latex FTIR characterization at the start of the study - the wave number 1545 cm\(^{-1}\) was not identified as an amine bond (NH) arising from amine-bonding of the protein, but was identified as a novel bond derived from the ether bonds linking the latex and starch. At this stage it is said that the method of plasma electrolysis can be used to synthesize hybrid latex or modify starch with latex.
Figure 3. Functional group of latex, starch, and hybrid latex respectively.

Figure 4. Latex hybrid’s new wavenumbers appear on 1530-1560 cm\(^{-1}\) (top: anode and bottom: cathode).

3.2. Presumption of Reaction Mechanism

Plasma electrolysis commonly induces unusual chemical reactions in aqueous solution. The energies of energetic species produced in electrolysis plasma and UV-radiation can break existing bonds in compounds and easily establish new chemical bonds. Table 1 shows the approximation of energies generate by electrolysis plasma [5].

Due to energy of the energetic species in electrolysis plasma can break existing bonds in compounds, which means there is so much possible mechanism. Yet, Figure 5 is the close presumption for reaction mechanism to yield the hybrid latex.
Table 1. The energy of the energetic species in electrolysis plasma.

| Energetic Species      | Energy (eV) |
|------------------------|-------------|
| Electron               | 0–20        |
| Ions                   | 0–2         |
| UV Light               | 3–40        |
| Metastable Groups      | 0–20        |

The electrolysis plasma is a rich source of energetic species which contains hydrated electrons ($e_{eq}$), radicals ($\cdot$OH, $\cdot$H, HO$^-$), ions (H$_2$O$_{gas}$) and molecules such as H$_2$, H$_2$O$_2$ and O$_2$. It is noteworthy that the whole processes takes place in aqueous solution [6,12]. It can be seen in Figure 6 that electrolysis plasma lead to break water bond at initiation step and resulting some radical products such as $\cdot$OH, $\cdot$H, and other species. By the time of reaction, radical products increase [11]. Thus, lead a chain reaction to yield product, latex hybrid. It also can be seen that hydrogen radical, $\cdot$H, having more impact to yield the hybrid latex due to it existance in each step of reaction mechanism and it will also impact to the yield of product if we generates plasmas at different plasma zone (cathodic or anodic).

3.3. Effect of Electrolyte Concentration
It is seen that the increase in electrolyte concentration of Na$_2$SO$_4$ with 0.01 M increment is likely followed by increasing yield. Yield (anodic) for 0.02 M electrolyte concentration; 0.03 M; 0.04 M respectively that is 2.20%; 1.61%; 2.88% and% yield (cathodic) for 0.02 M electrolyte concentration; 0.03 M; 0.04 M respectively that is 23.72%; 41.97%; 48.86%. The tendency to increase yield, either anodic or cathodic, is based on the theory that electrolyte concentrations have an important effect on the conductivity of the formed solution. The higher the electrolyte concentration, the higher the conductivity.
of the solution. This conductivity greatly affects the mobility of electrons, radicals, and other active species in solution. The higher the electron mobility, the radical, and the active species are dissolved, the higher the probability of contact the species with the reactants to initiate the reaction to form a hybrid latex product [11].

![Figure 6](image1.png) Effect of electrolyte concentrations on yield.

![Figure 7](image2.png) Effect of electrolyte concentrations on production efficiency.

At electrolyte concentration of 0.03 M with anodic plasma there was a slight decrease in yield. This happened because in the interval of fourth minute to the fifth minute the reaction takes place, the hybrid latex product is observed attached to the electrode where the plasma is produced so that plasma production becomes inhibited, as a result the plasma capable of exciting electrons, producing radicals and active species that act to initiate the transplant reaction into reduced. The attachment of the product to the electrode on which the plasma is produced is indicated by a sudden drop of current from about 0.70 amperes close to about 0.02 amperes over that time span. Even though after the time span the plasma again looks normal, but at the end of the reaction obtained less yield due to the above reasons.

In this study, yield of hybrid latex formed against the consumption of electrical energy, for 10 minutes of reaction, is also compared. Increased electrolyte concentration can increase electrical conductivity in the solution. However, this increase is also proportional to the consumption of electrical energy in the process of plasma electrolysis. Figure 7 shows the yield of hybrid latex per kilojoule (kJ) of electrical energy consumed. It can be seen that there is a decrease in yield for every electrical energy consumed (rising electric current in the solution due to an increase in electrolyte concentration). In other words, the cause of this can happen is the rate of formation of the product is smaller than the rate of consumption of electrical energy itself.

3.4. Effect of Plasma Zone Position

It is seen in Figure 8 that the electrode position of the plasma at a particular electrolyte concentration greatly affects the yield% of the hybrid latex obtained. For comparison, the efficiency of synthesis which is represented by the yield per kJ of energy consumed between cathodic for a concentration of 0.02 M; 0.03 M; 0.04 M is 4.53 respectively; 5.14; 8.72 times greater than the% yield per kJ of energy consumed in anodic plasma processes. It can be understood from the existing reaction mechanism.
Cathodic plasma electrolysis tends to produce more hydrogen radicals, whereas anodic plasma electrolysis tends to produce more hydroxyl radicals. The hydrogen radical is required as a radical at the reaction propagation stage to form at the intermediate product and termination stage to form hybrid latex. Yet, neither hydrogen radicals nor hydroxyl radicals can both initiate transplant reactions to synthesize hybrid latex. Therefore, a hybrid latex product to be found both as a cathodic and anodic product.

If both are compared, the efficiency of the cathodic plasma process is higher than the anodic plasma. Evident from the larger yield in cathodic plasma process with the use of an electrolyte concentration of 0.02 M compared with the yield on anodic plasma processes with electrolyte concentrations of 0.04 M. In other words, for higher energy consumption in anodic plasma than cathodic plasma, will not make it superior to the hybrid latex yield efficiency results compared to cathodic plasma. This phenomenon confirms that the production of hydrogen radicals is more responsible in the termination stage.

4. Conclusion
The plasma electrolysis method - both anodic and cathodic - can be used to synthesize hybrid latex. The ether bonds connecting the latex and starch appear at a wave number of around 1545 cm\(^{-1}\). The hybrid latex synthesis process is included in the type of reaction modification or grafting between latex and starch initiated by radicals produced by plasma electrolysis. Increasing electrolyte concentration in solution tends to increase hybrid latex yield and electric energy consumption. The higher the electrolyte concentration, the higher the hybrid latex obtained, as well as the consumption of electrical energy. The cathodic plasma yields a greater yield than the anodic plasma and the cathodic plasma is more advantageous in terms of the product produced for every electrical energy consumed.

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