

Reinforcement of Latex Rubber by the Incorporation of Amphiphilic Particles

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Latex rubbers are fabricated from latex suspensions. During the fabrication process, latex particles are bound together while water is removed from the suspension. This report shows that the mechanical properties of latex rubbers can be improved by incorporating a small amount of amphiphilic submicron particles as interface modifier. The incorporated particles were prepared from bovine serum albumin (BSA) and ethyl cyanoacrylate (ECA). These particles changed conformation while mixing with latex suspension, and bound to latex particles to induce aggregation of latex. The improved mechanical properties of the produced reinforced latex rubbers were characterised by mechanical analysis (stress-strain). Incorporation of microparticles into latex improved mechanical properties such as % elongation and energy at break up to ~250%. On the other hand, tensile strength and tensile modulus were not significantly affected by the incorporation of particles. Experimental results showed that the optimum BSA:ECA weight ratio for particles is 1:3, and the optimum percentage of particles is 3%. The mechanism for the reinforcement of latex rubber by microparticles has been elucidated by zeta potential analysis and optical microscopy.

Keywords: Microparticles; latex; tensile strength; zeta potential

Rubbers are used in a wide range of products, from tyres to medical products. The most common elastomers are synthetic rubber derived from petroleum and natural rubber from *Hevea* (*Hevea brasiliensis*). Because of the rubber elastomers excellent physical properties, rubber products are preferred for use in many applications worldwide for many years. The major property of latex polymers is their ability to form a flexible and homogeneous polymer after dehydration.

Latex is an aqueous suspension of colloidal polymer particles that consists mainly of poly (*cis*-1,4-isoprene) (natural rubber) or styrene-butadiene copolymer (synthetic rubber).

Regardless of its source, the stability of latex suspensions is determined by the balance between the electrostatic and steric repulsion forces and the van der Waals attraction forces¹. The role of the electrostatic repulsion forces and van der Waals attraction forces has been accounted for theoretically by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory^{2,3}. The DLVO theory suggests that the stability of a colloidal system is determined by the sum of van der Waals attractive and electrical double layer repulsive forces that exist between particles as they approach each other due to Brownian motion. This theory proposes that an energy barrier resulting from the repulsive force prevents two particles from approaching

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one another and adhering together. Therefore, if the particles have a sufficiently high repulsion, the dispersion will resist flocculation and the colloidal system will be stable. The electrostatic charges on the surface of latex particles are the major repulsion forces that govern the stability of latex suspensions. This force, however, renders the final product weaker than the particle without surface charges. To improve the mechanical properties of the final product, it is necessary to reduce the repulsive force between the latex particles during the manufacturing stage. In the actual manufacturing process, coagulants such as calcium chloride^{4,5} and calcium nitrate⁶⁻⁸ are used for this purpose. These divalent cationic metal salts screen charges and induce coagulation immediately upon mixing. In this report, we introduce submicron particles that are made up of amphiphilic block copolymers as a new type of coagulant that induces aggregation of latex particles slowly. This slow process will be useful for the manufacture of latex films where particles need to form an ordered array of particles during the film-forming process⁹. Upon introduction, particles will be mixed well with latex particles without significant interaction. As solvent is removed from the mixture, particles will be bound to the latex particles to form aggregates.

Alkyl cyanoacrylates are monomers that polymerise at room temperature. They are the major component of solvent-free, rapid curing adhesives¹⁰. During the last three decades, poly(alkyl cyanoacrylate) (PACA) particles drew attention with a view to their use as controlled release drug delivery materials^{11,12}. The majority of PACA particles are obtained through anionic polymerisation of alkyl cyanoacrylate by using hydroxyl ions in water as an initiator^{13,14}. In our previous research, amine groups of gliadin were utilised as initiator for the polymerisation of ethyl cyanoacrylates¹⁵. Gliadin is a wheat protein that belongs to prolamin. As its production cost is

low, this protein is suitable for the production of low-cost microparticles. However, the molecular-weight distribution of gliadin is broad, even after purification. Therefore, to minimise the number of factors that influence the particle effect, particles produced with the well-defined (*i.e.*, monodisperse) protein bovine serum albumin (BSA)¹⁶ were employed for this research. For the monomer of PACA, ethyl cyanoacrylate (ECA) was chosen because it is readily available, and its price is lower than other cyanoacrylates. The produced submicron particle is an assembly of copolymers consisting of two types of homopolymers: protein and poly(ethyl cyanoacrylate) (PECA). Since proteins are highly hydrophilic due to the charges on amino acids, the protein moiety works as the hydrophilic end in the resultant amphiphilic molecule, while the PECA moiety works as the hydrophobic end due to its aliphatic polymer backbone.

In this article, this amphiphilic submicron particle was utilised as a coagulant for latex particles to improve the mechanical properties of the produced rubber. For that purpose, the particles are mixed with a latex suspension during the fabrication stage. The optimum amount of particle inclusion, optimum length of the PECA chain, and the mechanism for this improvement were investigated. Since both BSA and poly(ethyl cyanoacrylate) are degradable polymers, the developed particles are degradable.

EXPERIMENTAL

Materials

BSA was purchased from Sigma (St. Louis, MO, USA). Ethanol and hydrochloric acid were reagent grade, and purified water (>18 M Ω) was used for all solutions. ECA monomer (E-Z Bond, viscosity = 5 cps) was

obtained from K&R International (Laguna Niguel, CA, USA). ECA contained ~0.5% hydroquinone as a free radical inhibitor that prevents the monomer from undergoing free radical-induced polymerisation upon storage. ECA was stored until use in a refrigerator at 4°C to further inhibit polymerisation. The latex (Rovene 9410) was a carboxylated styrene-butadiene emulsion obtained from Mallard Creek Polymers (Charlotte, NC). The glass transition temperature (T_g) of the rubber was -56°C, and the styrene-butadiene ratio was 25/75. The latex, as received, had ~50% solids and a pH of 8.6.

Preparation of Submicron Particle Suspension

Particles were prepared by polymerisation of ethyl cyanoacrylate on the surface of BSA aggregates. The standard preparation of the particle suspension for BSA:ECA = 1:3 by weight was as follows: 1.5 mL of 4N hydrochloric acid was added to 289.7g of 35% (w/w) ethanol solution. Next, 2.2g BSA was added to this solution with vigorous stirring. Once the BSA was fully dissolved, 6.6g of ECA was slowly added with constant vigorous stirring to make a 3% particle solution. The solution was stirred for 2h until the polymerisation reaction was fully completed, and was used to make the composites. To prepare the microparticle suspensions with varying chain lengths of surface modifier, the amount of BSA and ECA was varied accordingly. All of the other parameters of the solution were the same as listed above.

Particle Size and Zeta Potential Measurement

The size of the particles (BSA only or particles prepared from ECA and BSA) was determined by dynamic light scattering (DLS)

instrument equipped with a 658 nm diode laser and an avalanche photodiode detector (NanoBrook Omni Particle Sizer and Zeta Potential Analyzer, Brookhaven Instruments Corporation, Holtsville, NY, USA). For each sample, ten DLS measurements were conducted ten times and each run lasted 10 s or 20 s depending on the data quality. All the data were processed using the software supplied by the manufacturer (9kpsdw, v.5.31). Zeta potential measurement was conducted ten times for each sample and all the data were processed using the software supplied by the manufacturer (palsw32.exe, v.5.73). Both measurements were conducted at 23°C.

Preparation of Rubber Composites

Before mixing with the particle suspension, the latex emulsion was diluted with water at a 1:1 ratio to yield a solution of ~25% latex. The particle suspension was added to ~25% latex (100g) as follows: for the particle suspensions where the ECA chain length was varied, the particle suspension was added at a 3% level. In other words, 25.7g of the particle suspension was added to the latex. After addition of the particle suspension, each mixture was stirred for 30 minutes. For the particle-latex composites where the chain length of the modifier was constant, the amount of particle suspension added to the latex was as follows: 0 (control), 1, 1.5, 2, 3, 5, 10, and 20%.

After stirring, each micro-latex composite solution was treated in a BUCHI R-205 Rotavapor (Buchi Labortechnik AG, Flawil, Switzerland) to remove the ethanol. The conditions of the rotavapor treatment were as follows: vacuum was maintained at 77-85 kPa; bath temperature was 50°C; rotation speed was 75 rpm; maximum vapour temperature was ~40 °C; and time of treatment was 30-45 minutes. Next, the sample was freeze-dried to obtain the solid latex rubber.

Compression Moulding

Samples of freeze-dried latex-particle composite (16g) were torn into small pieces, then placed in a custom disc-shaped mould (12.7 cm diameter) consisting of a circular aluminum top and bottom plates, and a stainless steel ring as the border. Mylar sheets were placed between the sample and the top and bottom plates of the mould to prevent the sample from sticking to the mould. The mould was then placed in a Carver Model 3889 Hot Press (Carver, Inc., Wabash, IN) which had been preheated to 130°C. After 5 min, 2,270 kg of force was applied to the mould, and the sample was heated under this pressure for 2 h at 130°C. After 2 h, the sample was cooled to ambient temperature by running cold water through the press for 10-12 minutes. The mould was then removed from the press, and the sample was extracted from the mould. This treatment yielded a “disc” of moulded material with a diameter of 12.7 cm and a thickness of 1.0-1.2 mm.

Mechanical Properties – Tensile Strength

All the composite samples were prepared for testing according to *ASTM Method D412*, cut ring specimen. A die was used to cut Type 2 (100 mm circumference, 2 mm radial width) O-rings from the compression-moulded sample sheet. Prior to cutting, each sample sheet was cooled using dry ice to avoid irregular cuts from the die. A total of six O-rings were cut from each sample sheet for testing. Cut ring samples were tested on an Instron 5500R Universal Testing Machine (Norwood, MA) according to *ASTM Method D412*, Method B using a test speed of 500 mm/min. At least five O-rings from each sample were tested, and the average of the results with standard deviation showing the range of error was reported.

Microscopic Observation of Latex-Particle Interaction

The interaction between latex and particle was observed using a phase-contrast microscope. Microscopic images were then taken using a digital camera (Model D90, Nikon Corp., Tokyo, Japan) that was fit to an inverted microscope (Zeiss, Merz Optical Instruments, Chicago, IL, U.S.A.) through a relay lens. The obtained images were transferred to a Mac computer and processed with image software (Photoshop v. 7.0; Adobe Systems Inc., San Jose, CA, U.S.A.) for optimum brightness/contrast control.

RESULTS AND DISCUSSION

Preparation of Particles

The particles to be used as an interface modifier are composed of amphiphilic macromolecules. These macromolecules have been prepared by attaching poly (ethyl cyanoacrylate) chains on the surface of BSA aggregates. Attachment of poly (ethyl cyanoacrylate) chains to each BSA molecule is done by utilising amine groups on the surface of BSA as an initiator of the polymerisation reaction of cyanoacrylate monomers. As a result of this reaction, particles comprised of block copolymers are produced¹⁶. The schematic of particle produced by the reaction of BSA aggregate and ethyl cyanoacrylate monomers is shown in *Figure 1*. This particle is produced in an aqueous ethanol medium, and it undergoes inversion as the water content increases in the environment. This topic will be discussed in detail in a later section.

For the preparation of particles that will be stable in the suspension medium, the size of BSA aggregates needs to be as small as possible. Therefore, the solvent composition at which the hydrodynamic diameter of the aggregates is smallest needs to be chosen, and

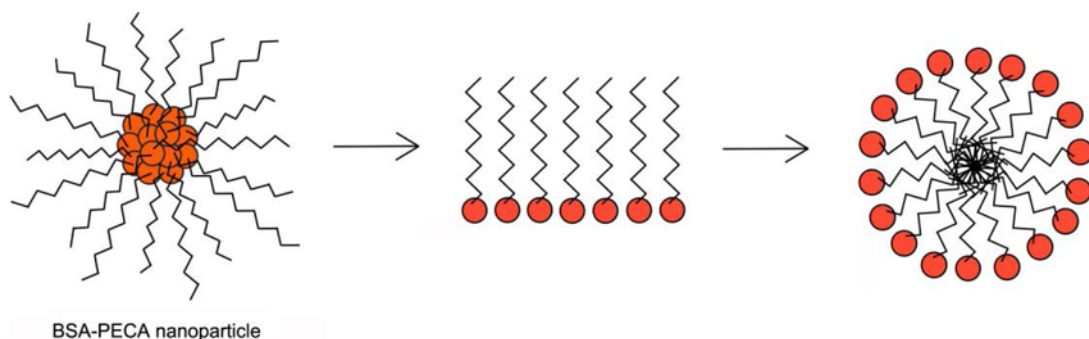


Figure 1. Schematics showing the structure of BSA-PECA microparticle and its inversion in the environment with lower ethanol content. BSA molecule and polymerised ethyl cyanoacrylate (PECA) are represented by spheres and zig-zag lines, respectively.

this composition will be used throughout the polymerisation reaction. BSA molecules form aggregates when the solvent medium contains ethanol, and the size of aggregates depends on the content of ethanol in the medium. The variation of hydrodynamic diameter of aggregates measured by DLS is shown in Figure 2. The size of aggregates decreases and increases again as the content of ethanol is increased from 25% to 50% by weight. The reason for the inflection at around 37% ethanol is due to the conformational change in the structure of the aggregates. More specifically, the surface of aggregates formed in lower than 37% ethanol is hydrophilic, while that formed in higher than 37% ethanol is hydrophobic. In other words, BSA aggregates show micellar inversion at 37% aqueous ethanol solution. This type of micellar inversion is not unusual for proteins: zein shows an inflection point at around 90% ethanol^{17,18} while gliadin shows an inflection point at around 62% ethanol¹⁹. Since the size of BSA aggregates is smallest in ~35% ethanol, this solution was chosen as a solvent medium for the preparation of particles (Figure 2).

PECA/BSA Ratio

The relative size of PECA (hydrophobic moiety) to BSA (hydrophilic moiety) in the

produced amphiphile can be controlled by varying the ECA/BSA ratio in the reaction mixture. As the ECA/BSA ratio increases, the PECA/BSA ratio in the reaction product increases until the ECA/BSA ratio reaches 8. After that, the produced particle becomes unstable and forms aggregates. This behaviour was investigated by measuring the size of the particles at each ECA/BSA ratio with DLS (Figure 3). The instability at high ECA/BSA ratio should be due to the formation of aggregates caused by the interaction between the long PECA chains on the surface of the produced particles. For this type of system, aggregation between particles is well known²⁰. To avoid this problem, a polysaccharide-based surfactant (dextran) has been widely used as a stabiliser for cyanoacrylate particles²¹. According to the data shown in Figure 3, the ECA/BSA ratio should not exceed 8 for the preparation of particles since no stabiliser was used for the current research.

Mechanical Properties of Latex Rubber with Particle

Latex rubbers were prepared by mixing the latex suspension with the microparticle suspension. To obtain a rough idea about the desirable experimental condition, trial samples were prepared by mixing 0.5 -

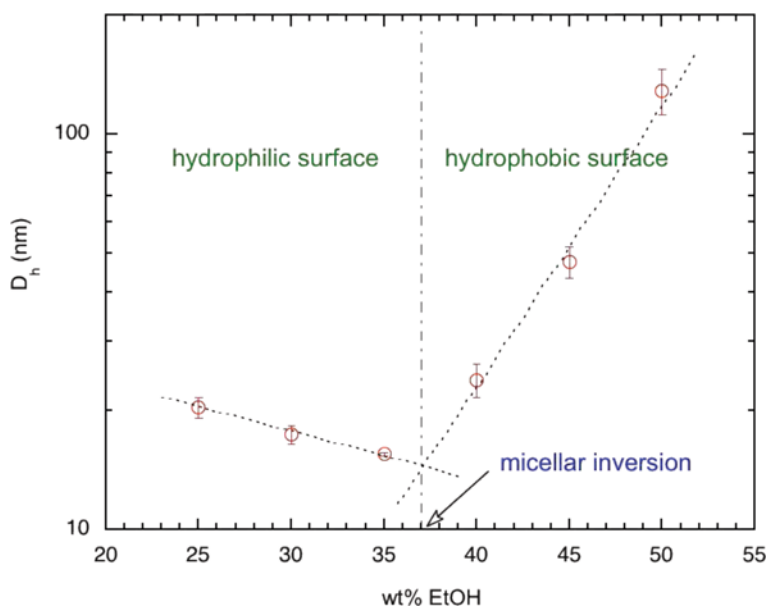


Figure 2. Hydrodynamic diameter of BSA in aqueous ethanol with various ethanol contents.

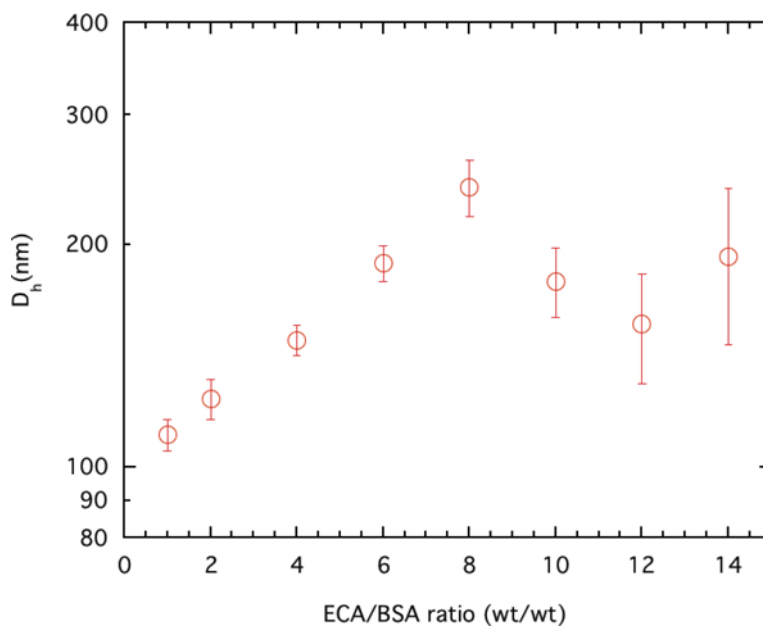


Figure 3. Hydrodynamic diameter of the microparticles formed at different ECA/BSA ratios.

30% particles that were prepared from an ECA/BSA ratio of 4. Mechanical property measurement of these samples showed that inclusion of 3% particles showed the most improved mechanical properties. Based on this finding, for systematic data acquisition, a series of rubber samples were prepared by incorporating particles with different chain lengths (ECA/BSA ratio = 1 to 8) keeping the amount of particles to 3%. In *Figure 4*, the mechanical properties are presented as a function of ECA/BSA ratio. Four types of mechanical properties, tensile strength, tensile modulus, energy at break, and %

elongation, were shown. The data range for the latex without particle is indicated by two solid lines in each graph. Since all the particles are built by attaching PECA chains on top of the same size core, *i.e.*, BSA aggregates, larger ECA/BSA ratio implies larger particle size and thus longer hydrophobic chain. All the mechanical properties were improved over those of the rubber prepared without particles. In the end, it is concluded that particles with ECA/BSA ratio of 3 have the optimum structure for the improvement of mechanical properties in the given experimental condition.

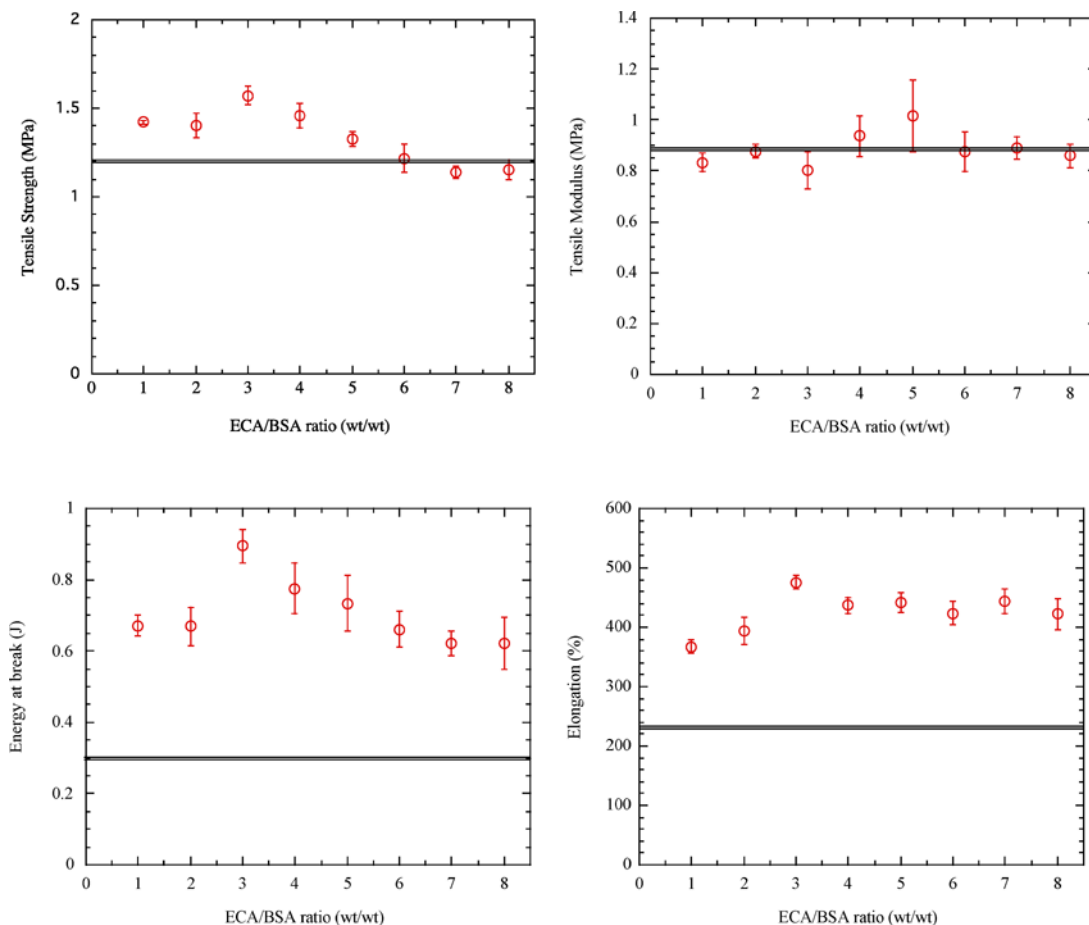


Figure 4. Mechanical properties of latex rubber with microparticles as a function of ECA/BSA weight ratio of microparticles. The added microparticles were 2% by weight. Data range of the latex without microparticle is indicated by the two solid lines.

In the next experiment, a series of latex rubbers were fabricated by varying the relative weight of incorporated particles from 1% to 20% keeping the ECA/BSA ratio to 3 to find an optimum percentage of particles (*Figure 5*). It is clear that no mechanical properties of the product are decreased by the inclusion of particles. The properties were improved or remained at the same level as those of neat latex. Both energy at break and % elongation were greatly improved (200-300% with 3% particles). Tensile strength was improved by 10%. In general, the mechanical properties were most favorable when the percentage of incorporated particle was 3%.

Overall, the incorporated particles reinforced the interaction between latex particles leading to the production of latex rubber with improved mechanical properties. As a conclusion, the optimum processing condition for the production of latex rubber is incorporating 3% particles that were prepared with ECA/BSA ratio of 3:1 into the latex suspension. It is quite impressive that inclusion of only a few percent of particles improves several mechanical properties without any negative impact. To understand the reason for this drastic effect of particles, the mechanism of how particles improve the mechanical properties are further investigated.

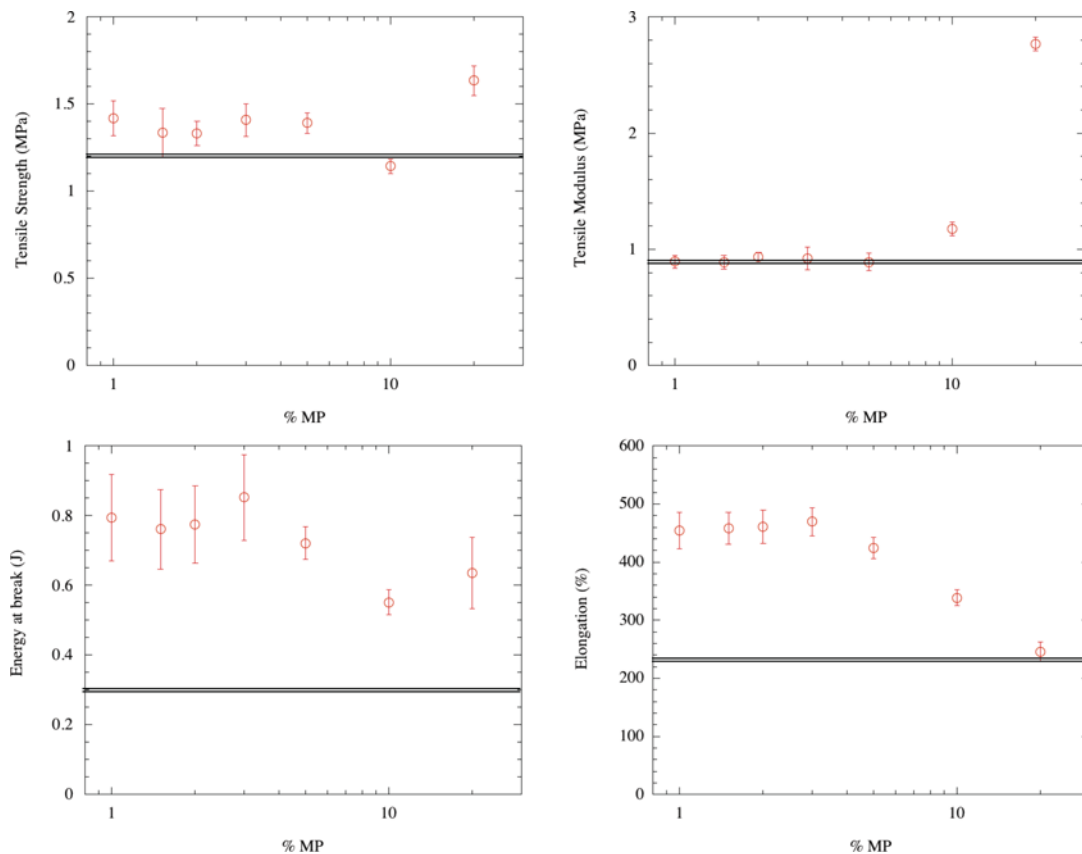


Figure 5. Mechanical properties of latex rubber with microparticles as a function of percentage of added microparticles that were prepared with ECA/BSA weight ratio of 4. Data range of the latex without microparticle is indicated by the two solid lines. MP stands for microparticle.

Mechanism for the Enhancement of Mechanical Properties

While latex particles are suspended in aqueous solution, particles are suspended in aqueous ethanol. During the processing, a small volume of particle suspension is added to a larger volume of latex suspension. This means that the particle is exposed to an environment with very low percentage of ethanol content, *i.e.*, to a highly hydrophilic medium. This change in the hydrophilicity of medium will lead to micellar inversion of the particles as illustrated in *Figure 1*. After the micellar inversion, the surface character of particles is expected to change from hydrophobic to hydrophilic. Actually, this change was identified by a simple experiment: particles in 35% aqueous ethanol adhere to the surface of hydrophobic materials (*e.g.*, plastic sheets) while those in much lower content (*e.g.*, 5%) aqueous ethanol did not adhere to the same surface. Investigation of the variation

of the size, zeta potential, and mobility of particles in different ethanol contents provided a better insight into the inversion process. DLS experiments showed that the hydrodynamic diameter (D_h) of the particles increases significantly as the ethanol content of the suspension medium decreases from 35% to 20% (*Figure 6*). In the same ethanol content range, zeta potential measurements show a significant increase in the surface charge (*Figure 7*).

This behaviour of particles can only be explained by inversion of the particles. In other words, microparticles disintegrate to the constituent amphiphilic block copolymers and reassemble in a different conformation by arranging the hydrophilic moiety (*i.e.*, BSA) pointing outward while hiding the hydrophobic moiety (*i.e.*, PECA chains) inside the particles. In this new conformation, the overall size is supposed to be larger than the previous size because, unlike PECA chains, BSA molecules

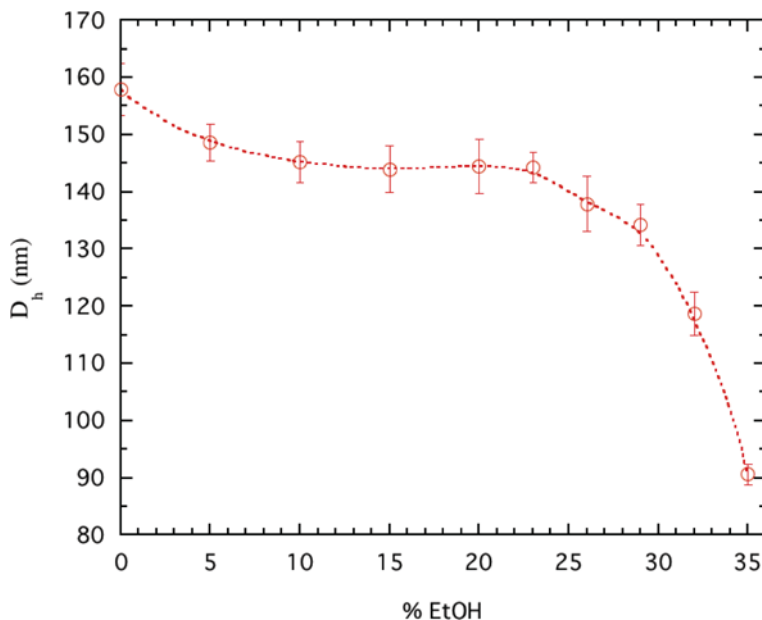


Figure 6. Size variation of microparticles in different ethanol contents of the suspension medium.

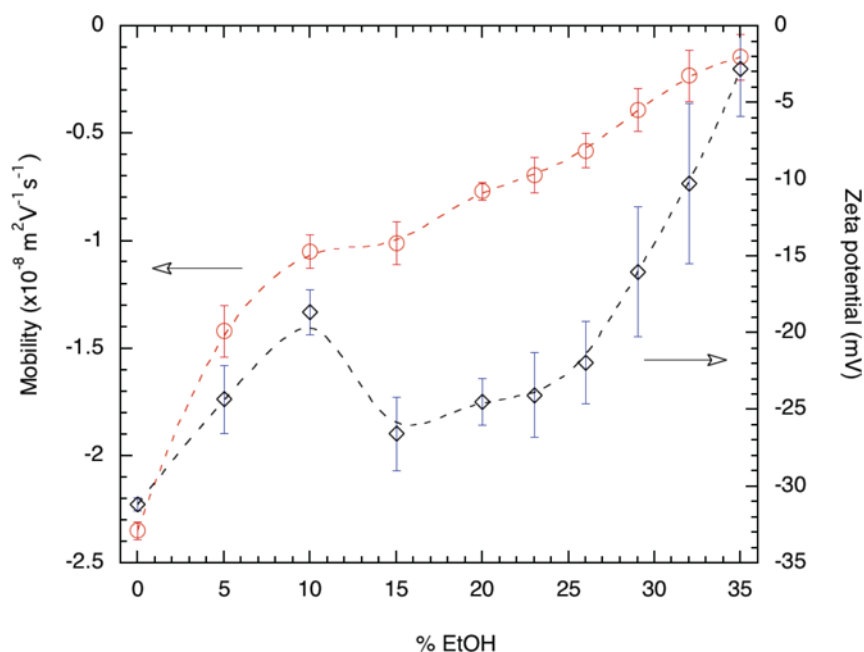


Figure 7. Variation of mobility and zeta potential of BSA/ECA microparticles in different ethanol contents of the suspension medium.

will repel each other by electrostatic force. Figure 7 clearly demonstrates that the surface charge of the particles increases as the ethanol content of the suspension medium decreases. In 35% ethanol, both the mobility and zeta potential are close to zero, indicating that the surfaces of the particles are covered with non-ionic material, *i.e.*, PECA chains. The surface charges are developed and increased as the ethanol content is decreased to 15%. According to the data shown in Figure 6, the inversion process is terminated at around 20% of ethanol as D_h the of particle does not expand further at lower ethanol content. Further decrease in ethanol content is supposed to lead to more ionisation of charged groups on the surface of the particles. Therefore, it is understandable that the mobility keeps on increasing while D_h does not increase much as the content of ethanol decreases to 0% (Figure 6). The strange decrease in the zeta potential at 10% ethanol is speculated to

be due to the variation in the permittivity of aqueous ethanol; the relationship between zeta potential and mobility is expressed by

$$\zeta = -\frac{\eta\mu}{\varepsilon} \quad \dots 1$$

where μ is the mobility, ε is the permittivity of the medium, ζ is the zeta potential, and η is the viscosity of the medium²². The viscosity of aqueous ethanol monotonously increases in 0 – 40% range of ethanol content.

In the above experiment, the behaviour of pure particles was investigated. In the actual situation, however, latex particles coexist in the same solution. Therefore, the interaction of particles with latex needs to be considered as the content of ethanol in the solution medium decreases. With the latex particles present in the same medium, inverted microparticles will not be formed even at low content of ethanol,

because the disintegrated particle (*i.e.*, the constituent amphiphilic block copolymers) will be bound to latex particles before they assemble as inverted-particles. Since the zeta potential of the latex particles was measured to be 48 ± 1 mV in aqueous medium, the amphiphilic block copolymers will readily bind with latex particles because of the charges on the surface of BSA molecules. Once they are bound together, the effective surface-charge of the latex particles will be decreased. Thus, the repulsion force between latex particles that had played a pivotal role in the stability of the suspension of particles will be weakened. The more particles are incorporated, the greater the charge cancelling effect, and this effect will lead to the formation of aggregates. The

microscopic observation of this effect is shown in *Figure 8*. The optical microscopic images clearly demonstrate the aggregate formation of latex with 10% particles. Since the particle suspension contains ethanol, this aggregate formation could be attributed to the presence of ethanol. However, addition of the ethanol solution that does not contain particles did not show aggregate formation. For more demonstration, 1%, 5%, and 10% particle mixtures in the latex suspension were prepared and stored for a week at room temperature. *Figure 9* shows that 1% particle is not enough to induce large aggregates. In the case of latex with either 5% or 10% particle, large aggregates were formed in the vial, as seen in their tendency to form agglomerates and segregate from the suspension.

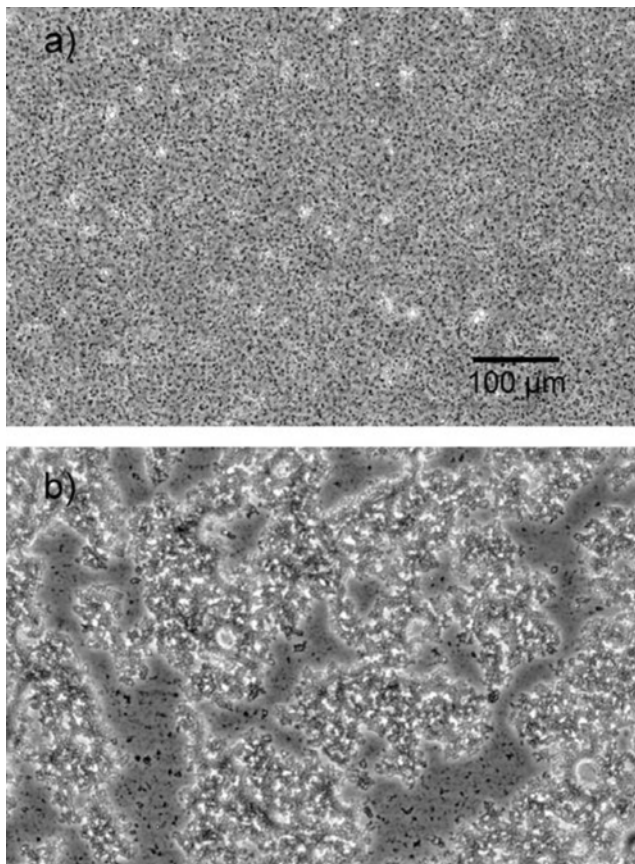


Figure 8. Optical microscopic images of a) Pure latex and b) Latex with 10% microparticles.

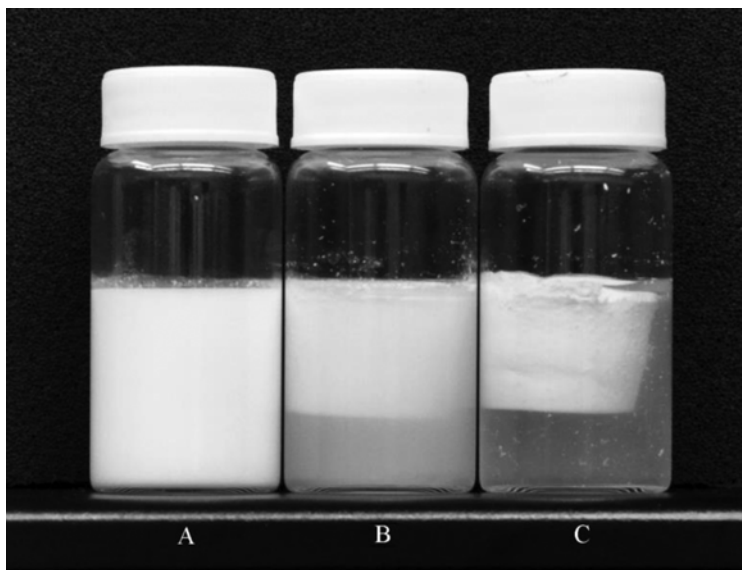


Figure 9. Demonstration of the induced aggregation by microparticles: latex with a) 1%, b) 5%, and c) 10% microparticles.

CONCLUSIONS

The mechanical properties of latex rubber were greatly improved by the incorporation of only a few % of protein-based submicron particles. The reason for this dramatic effect of particle was explained by the development of charges on the surface of particles that interact with the existing charge on the surface of latex particles when they are mixed together. This interaction reduces the electrostatic repulsion between latex particles, thus improving the inter-particle binding force between latex particles. Since this particle effect does not improve the strength of latex particle itself, tensile strength is not much affected by the inclusion of particles, while other properties, such as energy at break and % elongation, that are influenced by inter-particle attracting forces are improved appreciably. This research showed that the presented amphiphilic particles can be used as a coagulant, and its slow action is expected to be useful for the manufacture of latex films where particles

need to form an ordered array of particles during the film-forming process.

Date of receipt: July 2016

Date of acceptance: December 2016

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