Development of aqueous biomass containing emulsions

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1. Introduction[1), 2)]

From the viewpoint of sustainability, the utilization of biologically derived resources having less environmental impact is gaining momentum these days. Especially, utilization of biomass materials derived from plants is said to be effective way in reducing the use of petroleum resources and carbon dioxide emissions to reach a carbon neutral. Therefore, manufacturers are trying to differentiate themselves by obtaining biomass-use certificates from accreditation bodies or establishing self-standards regarding environmental contribution of their products. For example, according to the criteria for "Biomass Mark" certified by the Japan Organics Recycling Association, environmental products are specified as follows, those containing a minimum of 10% biomass on a dry weight basis, which is known to be one of the most widely acceptable criteria on low environmental impact products. This biomass mark is used in many fields such as inks, paints, adhesives, textiles, containers, and daily necessities. The number of certified products for this mark was 632 as of March 1, 2020, 845 as of September 1, 2020, and continued to increase to 1387 as of March 10, 2022, indicating that the use of biomass is expanding in various fields.

However, the use of biomass resources often has a negative impact on product performance compared to existing fossil fuel-derived materials, thus leading to extremely difficulty in meeting the market's demand, namely, achievement of both increased biomass usage and keeping its high quality as before. To overcome the trade-off between biomass utilization and product performance, we here introduce water-based biomass containing emulsions with performance equal to or better than conventional styrene acrylic emulsions, utilizing core-shell typed styrene acrylic emulsion technology cultivated in the process of developing ink resins.

2. Plant-derived biomass feedstock

Figure 1 shows examples of typical plant-derived biomass feedstocks. Plant-derived biomass feedstocks can be roughly classified into hydrophilic and hydrophobic materials. Plant-derived biomass feedstocks classified into hydrophilic substances are starch and cellulose, and its hydroxyl group modified derivatives. Oxidated and aminated starches are used as chemicals to improve the strength of paper.

Figure 1. Typical biomass feedstock Left : Starch, Center : Rosin, Right : Soybean oil

Nitrocellulose has been used as a material for gravure inks, and cellulose nanofibers, which are obtained by fibrillating wood pulp into nano-level fibers, are used as a thickener or a material of resin reinforcements.

On the other hand, typical biomass classified into hydrophobic substances are rosin, fatty acids, natural rubber, and lignin. Alkali salts of rosin and fatty acids are used as emulsifiers and chemically modification derivatives of their carbon-carbon double bonds are employed as various functional chemicals. Natural rubber has a polymer with high molecular weight and is easily soluble in organic solvents. Natural rubber and its derivatives are used as additives for tires, rubber gloves, and adhesives. Sodium lignin sulfonate is used as a surfactant and a water reducer in concrete.

3. Aqueous biomass emulsion

3-1. "HIROS－XE"series of core-shell emulsion

Our "HIROS-XE" series are styrene acrylic or acrylic core-shell emulsions obtained by emulsion polymerization in an aqueous system using polymeric surfactants. In the presence of organic amine or metallic alkali salt of carboxyl-group containing polymers as polymeric surfactants, an emulsion polymerization gives rise to a core-shell emulsion containing hydrophobic core polymer particles surrounded by polymeric surfactant. This core-shell emulsion polymerization technology can give highly concentrated aqueous emulsions without the use of low-molecular-weight surfactants or organic solvents. These obtained core-shell emulsions exhibit excellent coating ability due to their low thixotropic property despite their high concentration.

Leveling and drying ability of coated layer of the core-shell emulsions highly depend on chemicals to neutralize carboxylic acid group of polymeric surfactants and designing chemical structure of shell part. In addition, the physical properties of the coated film such as rub resistance and water resistance are adjusted by combining various factors such as the ratio of core and shell parts, affinity between them, polymer compositions, Tg, and molecular weight to meet requirements of application and purpose.

3-2. Basic concept of product development

Most of existing water-based coating products with higher biomass content often show poor coating ability, lower gloss and inferior adhesiveness. These existing high biomass content coating emulsion is probably manufactured by simply mixing conventional polymers with biomass feedstock (Details are given in section 3-3 and thereafter). Furthermore, biomass feedstocks are natural products of varying quality, thus requiring several pretreatments such as purification and chemical modifications.

Based on the above understanding, we have developed emulsion products with biomass content of 20-50% showing equal performance or more than those of conventional styrene acrylic resins through chemically hybridizing them with biomass materials.

3-3. Starch-based biomass emulsion「HIROS－X・QE-2229」

While starch is an inexpensive hydrophilic polymer and a raw material with excellent solvent resistance, it has the disadvantages of coloration (lower whiteness) and poor water resistance. To overcome these drawbacks, we explored preferable modification methods of starch and optimized its molecular weight to lessen coloration. Water resistance property has been improved by adjusting the chemical composition of core part and rheological behavior of the emulsion has been improved by modifying the shell part structure. We have developed QE-2229, a styrene acrylic/starch composite emulsion containing 30% biomass by integrating those above mentioned technologies. Table 1 shows the results of water absorption test (Cobb test, 120 seconds) for emulsion coated papers.

QE-2229 shows superior water resistance which is equivalent to that of our existing styrene acrylic emulsion (Emulsion A), whereas the comparison emlsion having the same biomass content (30%) as QE-2229 obtained by mixing Emulsion A with a starch shows significantly poor water resistance.

This indicates that our proprietary hybridization technology has made a significant contribution to solve several problems caused by incorporation of starch into coating emulsion.

Table 1. Cobb water absorption measurement results

Product	Cobb120
Emulsion A	0.8
Emulsion A／Starch mixture	5.8
QE-2229 (Styrene acrylic/Starch composite emulsion)	1.0

3-4. Rosin-based biomass emulsion「HIROS－X・PE-2189」

While a wide range of chemical modifications of rosin is possible due to its acid group and double bonds, it has some disadvantages such as working as an inhibitor in radical polymerization, yellowing, its faint piny odor and wide variability in quality. We have developed PE-2189, a styrene acrylic/rosin hybridized emulsion through optimizing chemical modification of rosin and polymerization conditions. PE-2189 has a high biomass content of 50% and it imparts high gloss and excellent printability when used as a binder resin for water-based printing inks. Figure 2 and 3 show the test results of PE-2189 used as a varnish for paper and as a resin binder for water-based printing ink, respectively. As comparative samples, we employed our existing water-based styrene-acrylic emulsion (Emulsion B) and the mixed product of Emulsion B and the modified rosin varnish with the same biomass content (50%) as PE-2189.

The slight increase in gloss is observed by simply mixing emulsion B and rosin varnish compared to the use only Emulsion B and meanwhile, the styrene-acrylic / modified rosin hybridized emulsion, PE-2189 shows a significant improvement of gloss. PE-2189 shows excellent color development of printing as well as Emulsion B. Whereas, the mixture of Emulsion B and modified rosin gives lower print density. These results suggest that hybridizing styrene acrylic resin with modified rosin is the key factor to improve performance

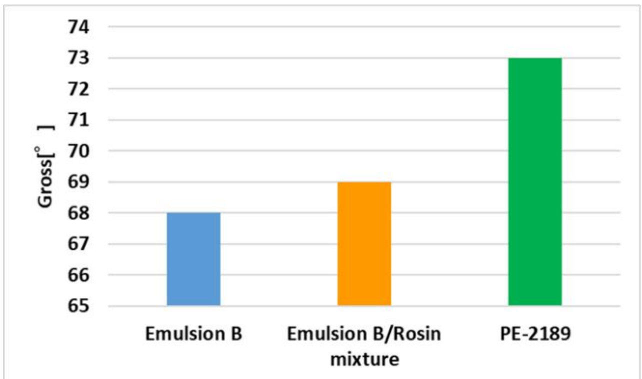


Figure 2: Gloss measurement results

※Gloss Evaluation Method：Emulsion viscosity is adjusted to ZC #4, 25s, coated on coated paper, and gloss of the coated surface is measured with a gloss meter.

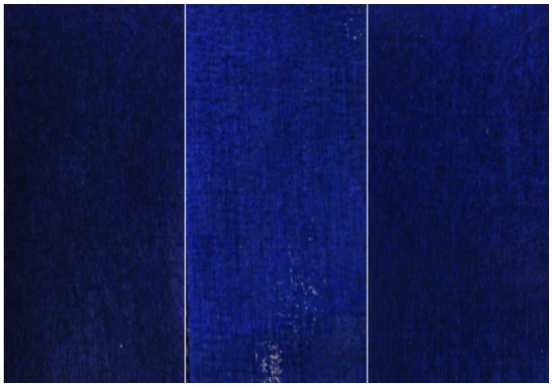


Figure 3: Photographs of the coating film during inking (left: Emulsion B, middle: Emulsion B / Rosin mixture, right: PE-2189)

※Inking formulation：Base ink (indigo)/emulsion ＝ 7/3 (as available) mixed and coated on liner paper.

as a varnish and an printing ink binder.

3-5. Fatty acid-based biomass emulsions「HIROS－X・NE-2309」

Fatty acids have long alkyl chains with low polarity, so, we tried to develop fatty acid containing emulsion for water-based printing inks showing superior adhesiveness toward non-polar films such as OPP. However, it is difficult to obtain stable and long-storable fatty acid containing emulsion due to its high crystallinity.

We have designed the polymeric surfactants suited to emulsifying fatty acid and modified fatty acid to keep the emulsion stable during storage. Furthermore, by designing the core part composition to mitigate bleedings of modified fatty acids, we developed emulsion NE-2309 with a biomass content of 20% and excellent film adhesiveness.

Figure 4 shows the results of adhesion test to various films. As a comparison, we employed our existing acrylic emulsion (Emulsion C) and the mixture of an Emulsion C / modified fatty acids with the same biomass content (20%) as NE-2309. NE-2309 shows excellent adhesiveness not only to low-polarity substrates such as OPP and OPS, but also to polar substrates, PET compared to Emulsion C and the mixture of Emulsion C and modified fatty acid.
We are expecting that the use of this product will make it possible to increase the biomass content of printing inks for flexible packaging films.

4. Summary

The physical properties and characteristics of QE-2229, PE-2189, and NE-2309 are summarized in Table 2. Using a variety of biomass raw materials, we have developed water-based biomass containing emulsions having excellent performance as well as or better than our existing products. Using the knowledge gained through development of these products, we will continue to contribute to the realization of a sustainable society by utilizing new biomass feedstocks and further increasing in biomass content.

＜References＞

1) Japan Organic Resources Association HP
2) Michio Yabuno・Ryo Sugawara, J. Jpn. Soc. Colour Mater., 93 [6], 182-188 (2020).

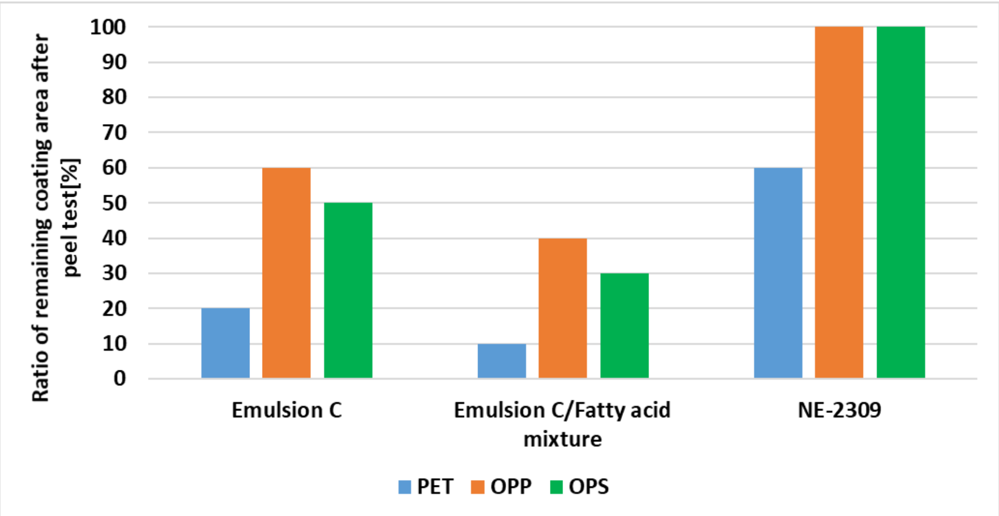


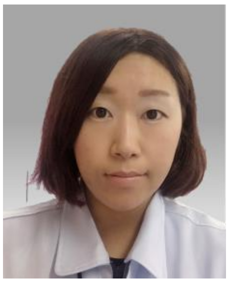
Figure 4. Film adhesion test results

※Adhesion test method：Mix base ink (white)/emulsion = 1/1 (presence) and apply to film.
After drying, peel off the cellophane tape and calculate the remaining area

Table 2. Summary of physical properties (typical values) and characteristics of biomass emulsions

Product	**QE-2229**	**PE-2189**	**NE-2309**
Biomass feedstock type	Starch	Rosin	Fatty acid
Viscosity [mPa·s]	250	600	800
pH	8.5	8.3	8.5
Nonvolatile content [mass.%]	48	45	40
Particle size [nm]	100	100	60
Theoretical acid value [mgKOH/g]	49	155	51
Minimum film-making temperature [℃]	＜5	＜5	＜5
Biomass rate [%]	30	50	20
Advantages	・Good water resistance ・Good alcohol resistance	・High biomass rate ・high gloss ・Good IPA dilution stability	・Good film adhesion

Profile



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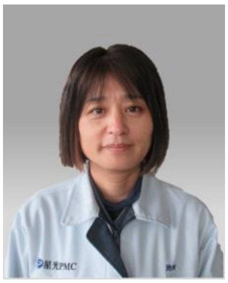

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