OBJECTIVE

- ***Ethylene-modified latexes were prepared by the emulsion polymerization using poly(ethylene-co-acrylic acid) (EAA) as a polymeric emulsifier.***

- ***To study the miscibility improvement of ethylene-modified latex film.***
  - Grafting Analysis
  - DMTA

- ***To study the barrier properties of ethylene-modified latex film.***
  - Water Permeability
  - Chemical Resistance

INTRODUCTION

◈ *Resin-Fortified Emulsion Polymer System*

- **System having most of the advantages of both bulk and emulsion polymer system without their disadvantages**
- **Fine particle size emulsions**
- **Excellent film property**
- **High gloss property**
- **Newtonian-like rheological property (viscosity is shear independent)**
- **Excellent mechanical stability and freeze-thaw stability**
- **Excellent pigment dispersity and wetting property**
- **Low foam production (desirable in roll coating operation)**

INTRODUCTION

◈ *Poly(Ethylene-co-Acrylic Acid) [EAA] Resin*

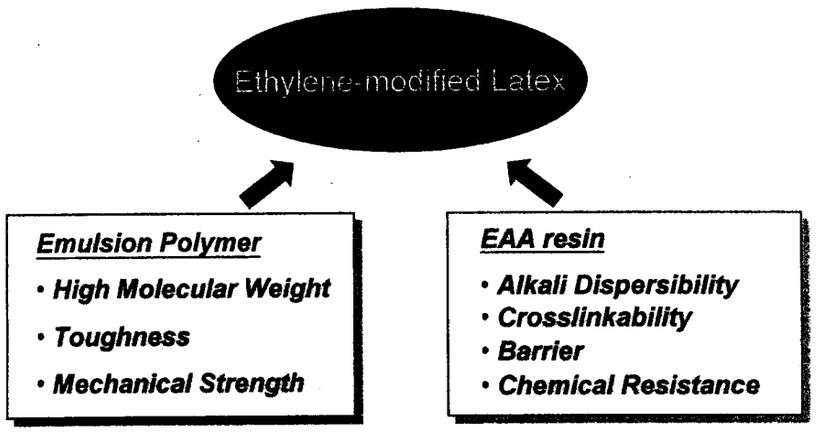
- **Number Average Molecular Weight : 18,800**
- **Weight Average Molecular weight : 111,000**
- **Acid Number : 140 mg KOH/gm**
- **Soluble or Dispersible in Water or Alkali**
- **Useful as Emulsifier, Leveling agent, and Film-former**
- **Barrier Properties similar to Low-Density Polyethylene (LDPE)**

◈ *Application of EAA Resin*

- **Foil Laminations**
- **Paper and Paperboard Coatings**
- **Medical Packing**
- **Binders for Nonwovens**

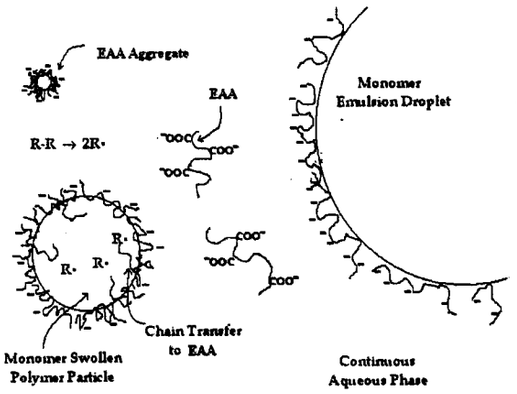
INTRODUCTION

◈ *Properties of Ethylene-Modified Latex*



THEORY

◈ *Emulsion Polymerization in the presence of EAA*



- In aqueous phase, EAA plays a role in *stabilizer.*
- The *grafting reaction* of PS and EAA would be occurred during emulsion Polymerization.

Schematic Representation of Emulsion Polymerization in the Presence of Ethylene-Acrylic Acid Resin.

THEORY

◆ Hildebrand equation $V_r/RT(\delta_1-\delta_2)^2$

in order to achieve molecular-level mixing of the blend constituents, < 0.002

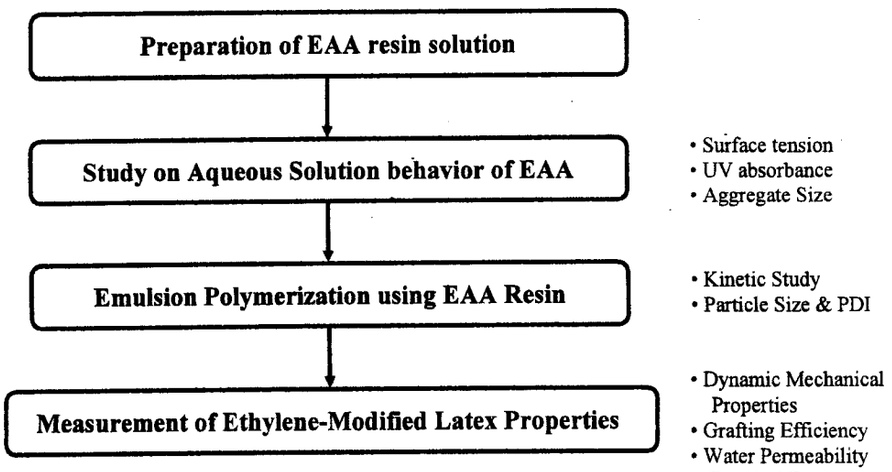
◆ Solubility parameter : Hoftyzer and Van Krevelen method (Group contribution)

Table. Physical Parameters of the Pure Constituents of the Blends

	Molar volume(cm^3mol^{-1})	Molar weight ($g\ mol^{-1}$)	Solubility parameter ($J^{1/2}\ cm^{-3/2}$)
polystyrene	98.0	104.1	8.90
polyethylene	33.0	28.1	8.00
poly(acrylic acid)	38.0	72.1	11.92
EAA			8.395

→ $0.043 >> 0$ → are completely

EXPERIMENTAL



EXPERIMENTAL

Table. Recipe for Emulsion Polymerization using Ethylene-Acrylic Acid Resin as a Polymeric Emulsifier.

Components	Amount (g)
D.D.I. Water	600
Ethylene-Acrylic Acid Resin (EAA)	20, 40, 50, 60
Sodium Hydroxide (NaOH) or Triethylamine (TEA)	variable[1]
Sodium Chloride (NaCl)	variable[2]
Monomer Styrene or Butyl Methacrylate	100
Initiator Potassium Persulfate	0.5

[1] NaOH was added in system in order to change the degree of neutralization of EAA.
[2] NaCl was added in system in order to change the ionic strength.

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RESULTS & DISCUSSION

◈ *Surface Tension & Pyrene UV Absorbance*

- **Pyrene absorbance and surface tension of ASR solution as a function of ASR concentration. (wt% based on EAA solution)**

- **The EAA molecules in aqueous phase seem to form aggregates at low concentration before they starts to transfer to air-water interface.**

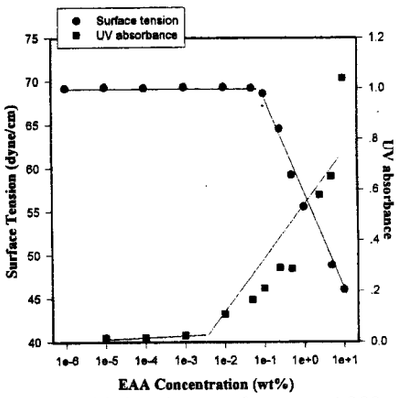

Figure. UV absorbance of pyrene at 360nm and surface tension of EAA solution as a function of EAA concentration(wt% based on EAA solution.

RESULTS & DISCUSSION

◈ *EAA Aggregates Size*

- **Effect of % neutralization of EAA**
  - **actual charge density of EAA**
  - **size of aggregate**

- **Effect of excess neutralization agent**
  - **increasing actual charge density of EAA.**
  - **→ induce the effect of screening of electrostatic repulsions between charges of along the EAA chain.**

- **% degree of neutralization of EAA : OH/COOH**

- **Size measured by light scattering.**

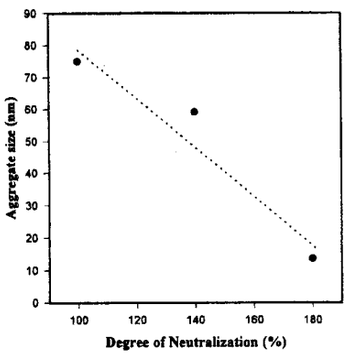

Figure. Aggregate sizes of EAA with different degree of neutralization of EAA.

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RESULTS & DISCUSSION

◈ *Latex Particle Size with Concentration of EAA*

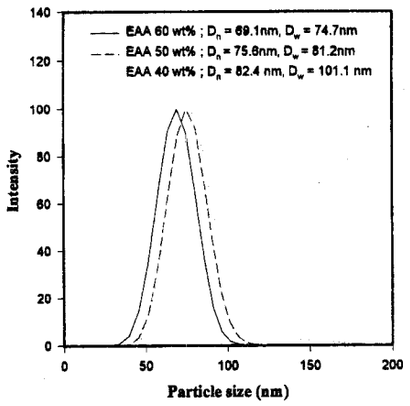

Figure. Particle size and size distribution of ethylene -modified polystyrene with different EAA concentration at 140% degree of neutralization of EAA.

- **As the *concentration of EAA* as a polymeric emulsifier increases, *particle size* is *smaller* and *size distribution* becomes *narrow*.**
- ***Polydispersity* is affected by :**
  - **water solubility of monomer**
  - **concentration of EAA as a polymeric emulsifier.**

RESULTS & DISCUSSION

◈ *Polydispersity Index with Degree of Neutralization of EAA*

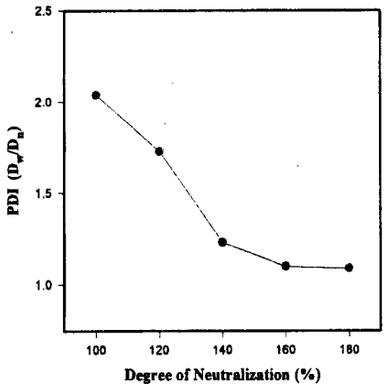

Figure. Particle distribution index of ethylene -modified polystyrene with different degree of neutralization of EAA.

- **As the *degree of neutralization* of EAA increases, *the particle size* is smaller and *size distribution* becomes narrow.**
- **Effect of excess neutralization agent**
  - **induce the effect of screening of repulsions between charges of along the EAA chain.**
  - **play a similar role of electrolyte.**
- **% degree of neutralization of EAA : OH/COOH**

RESULTS & DISCUSSION

◈ *Kinetic Study*

- Effect of EAA concentration of the rate of emulsion polymerization of styrene.

  - The increase of EAA concentration increases the number of aggregates providing polymerization loci and thus the rate of emulsion polymerization increases.

  - The result is similar to to conventional surfactant system

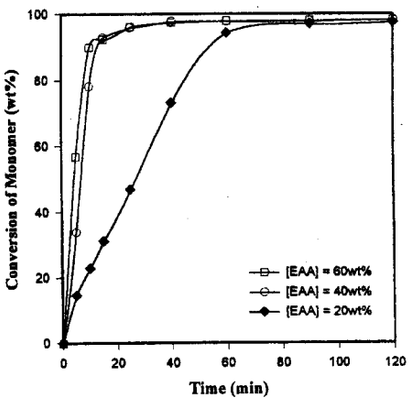

Figure. Conversion of monomer versus reaction time in emulsion polymerization of styrene with different concentration of EAA (wt% based on monomer).

RESULTS & DISCUSSION

◈ *Grafting Analysis*

Table. Characteristics of grafted EAA in ethylene-modified PS latex

	Grafting efficiency (%)
PS	20.2 % [a]
EAA	60.1 % [b]

[a] (Weight of total PS - weight of toluene-soluble PS) × 100 / (weight of total PS).
[b] (Weight of total EAA - weight of alkali-soluble EAA) × 100 / (weight of total EAA).

[redacted]

- **Hinder desorption of the EAA from the latex → improve the latexes' stability**

- **Prevent the migration and accumulation of EAA molecules**

- **Act as compatibilizers for the main polymer components.**

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RESULTS & DISCUSSION

◈ *Dynamic Mechanical Thermal Analysis Result*

Incompatibility between PS and EAA

The inhomogeneity between PS and EAA renders the product turbid

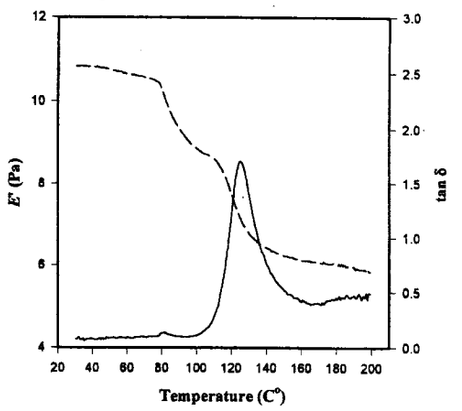

Figure. Dynamic mechanical properties of simple blending film of PS latex and 60wt% EAA based on PS as a function of temperature: storage modulus (E'), damping curves (tan δ).

RESULTS & DISCUSSION

◈ *Dynamic Mechanical Thermal Analysis Result*

Enhancement of compatibility between PS and EAA

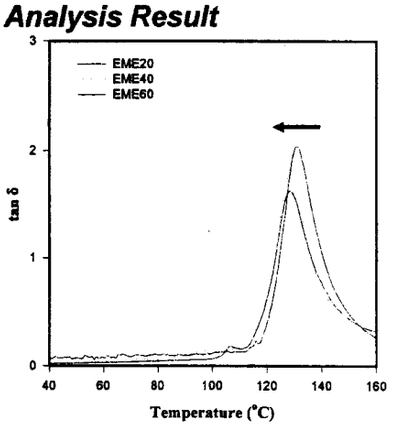

Figure. Dynamic mechanical properties of ethylene modified latex films with different EAA concentration as a function of temperature.

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RESULTS & DISCUSSION

◈ *Effect of EAA Concentration on Permeability*

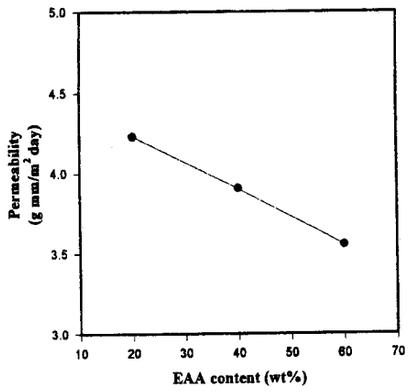

Figure. Permeability of ethylene-modified PBMA latex film with different EAA concentration.

Table. Permeability of PBMA Films and Pure EAA Film.

	Permeability[a] (g mm/m² day)
PBMA film	8.1267
EMPB-E20 film	4.2276
EMPB-E40 film	3.9046
EMPB-E60 film	3.5568
EAA film	0.2275

[a] measured at 20°C and 90% RH.
[b] % based on monomer.
* All sample drying at 40°C.

RESULTS & DISCUSSION

◈ *Chemical Resistance*

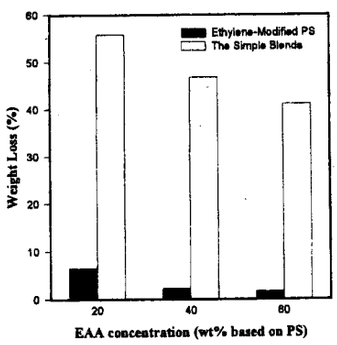

Figure. Weight loss of ethylene-modified PS and the simple blends of PS/EAA as a function of EAA concentration after their immersion to methyl ethyl ketone for 5 hours.

The chemical resistance of ethylene-modified PS films is about 20 times higher than that of simple blends.

Table. Percentage Weight Losses of Ethylene-Modified Latex Films and the Simple Blending Films of PS and EAA after Their Immersion to Methyl Ethyl Ketone for 5 Hours

	Weight Loss %		Weight Loss %
EMPS-E60	1.72	SBPS-E60	41.0%
EMPS-E40	2.26	SBPS-E40	46.8%
EMPS-E20	6.61	SBPS-E20	55.8%

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CONCLUSION

- **EAA in aqueous solution played role in polymeric surfactants.**
- **Misicibility between PS and EAA has been improved without any compatibilizer during ethylene-modified emulsion polymerization.**
- **The water barrier property of ethylene-modified latex film was improved with increasing the EAA concentration.**
- **The Chemical Resistance of ethylene-modified latex film was dramatically better than that of the simple blends.**