Ionically crosslinked core-shell particles for waterborne humidity-sensitive coatings

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Using conventional functional monomers, such as methylacrylic acid (MAA), styrene (St), methyl methacrylate (MMA) and butyl acrylate (BA), the core-shell styrene-acrylic ionomer particles (PSA) are prepared by two-step emulsion polymerization. Then, using zinc ion as ionic crosslinker of the carboxylate groups from the shell layer, a novel self-crosslinked core-shell ionomer latex (PSA-Zn) has been successfully prepared and characterized by dynamic light scattering and transmission electron microscopy, whose components were also confirmed by FT-IR and TGA. After mixing pigments and porous fillers, the cheap, readily available and environment friendly coatings (PSA-Zn-C) has been prepared. Compared to PSA and EF-AAC coatings, the adhesive force, hardness and thermal stability of PSA-Zn film are better. Moreover, the core-shell ionomer coating (PSA-Zn-C) can significantly decrease or increase relative humidity in response to environmental humidity in the artificial climate box, and this is a promising candidate for development of waterborne humidity-sensitive coatings.

Keywords: Polymer, Ionomers, Emulsion polymerization, Core-shell ionomers latex, Zinc crosslinking particles, Smart coatings, Humidity-sensitive coatings

Research on waterborne smart coatings has increased in the recent past, focusing both on novel latex systems and investigations of their unique properties. These materials have been widely employed as building coatings, metal/alloy coatings and wood paints. As is well known, indoor humidity seriously affects human health and life quality because most of us spend more than 80% of a day indoors. Too high or low relative humidity (RH) of indoor environment causes the occupant experience problem, such as respiratory discomfort, allergies, etc. Humidity also causes metal surface corrosion and material deterioration. Compared with humidifiers and air conditioners for adjusting indoor humidity, we found that the waterborne humidity-sensitive coating is a simple, energy saving and environmentally friendly material for controlling reasonable RH of indoor. Towards this, the silicylactylate copolymer core-shell nanoparticles could be used to prepare humidity-sensitive coatings. However, there are some problems in the finished products of such coatings, such as poor thermal stability, wearability and low temperature toughness. Therefore, some novel film forming materials and fillers, such as modified acrylate latexes with organic silicon compounds, polyurethane, organic fluorine compounds and inorganic nanoparticles have been investigated.

The ionomer, a polymer containing ionic groups (typically up to 10-15 mol%) in the side chains, easily forms metal crosslinked ionomer latexes (Na+, Cu2+, Zn2+), and their mechanical properties and thermal stability can be significantly enhanced. While synthesis of zinc ion self-crosslinkable polyacrylate latexes has been reported, there are no reports on the humidity-sensitive coatings. Also, it was found that the copolymer with core-shell structure not only improving wearability, weather ability and adhesive ability of coatings, but also solves the counteraction of film-forming ability and constructability. However, there are few reports about preparation of ionomer core-shell nanoparticle. In order to investigate the relationship between Zn2+ content with properties of core-shell styrene-acrylic ionomer latexes and humidity-sensitive coatings, herein core-shell ionomer latexes, have been prepared and applied to humidity-sensitive coatings. Firstly, using styrene (St) and methylacrylic acid (MAA) as core monomers, methylacrylic acid (MAA), methyl methacrylate (MMA) and butyl acrylate (BA) as shell monomers, core-shell styrene-acrylic ionomer latexes (PSA) were prepared by two-step emulsion polymerization. Then, using Zn2+ as cross-linker, the self-crosslinked zinc styrene-acrylic ionomer latex
(PSA-Zn) was successfully prepared. Further, after mixing pigments and porous fillers, self-crosslinked zinc styrene-acrylic humidity-sensitive coating (PSA-Zn-C) was also achieved and its properties were investigated.

Materials and Method
Methyl methacrylate (MMA), butyl acrylate (BA), methylacrylic acid (MAA) and styrene (St) were purchased from Tianjin Guangfu Chemical Industry Research Institute, China. Potassium persulfate (KPS), ammonium carbonate ((NH₄)₂CO₃), sodium hydroxide (NaOH), zinc oxide (ZnO) and ammonium hydroxide (NH₃·H₂O) were purchased from Tianjin Sitong Chemical Co., China. Sodium dodecyl sulfate (SDS) and OP-10 were obtained from commercial sources. Diatomite (CD02), diatomite (CD05), bentonite, kaolin, talc and titanium dioxide were all industrial grade compounds. Dispersant agent DA-01 (Beijing Yakeli Chemical Co., Ltd.) and defoaming agent 3016 (Shanghai Changfeng Chemical Co.) were used as coating additives. Distilled water was used throughout.

Preparation of core-shell zinc styrene-acrylic ionomer latex (PSA-Zn)
The core latex was obtained by conventional emulsion polymerization. Firstly, the surfactants (0.10 g OP-10 and 0.10 g SDS) were mixed with 50 mL distilled water in a three-necked flask equipped with a reflux condenser, a thermometer, a mechanical stirrer and dropping funnels. After being heated to 80 °C, 5 mL of KPS aqueous solution (4 mg/mL) was added with stirring. Then, core monomers comprising 9.6 g St and 0.4 g MAA, and the residual 20 mL KPS aqueous solution were simultaneously added to the reaction flask at 80 °C over a period of 1.5 h. Finally, the reaction system was stirred at 80 °C for a further 1 h to ensure complete monomer conversion, which afforded the blue-white core latex (PS).

To prepare the core-shell latex (PSA), the shell monomers, comprising MAA (1.0 g), MMA (2.0 g) and BA (7.0 g), and 20 mL of KPS aqueous solution (5 mg/mL) were added dropwise to the above core latex (PS) simultaneously at 80 °C over a period of 1.5 h. After reacting for another 1 h, the reaction was complete and afforded the blue-white core-shell latex (PSA).

The zinc styrene-acrylic ionomer latex (PSA-Zn) was prepared as follows: (NH₄)₂CO₃ (0.565 g) and NH₃·H₂O (0.188 g) were dissolved in 10 mL water. Then, ZnO (0.188 g) was added to the solution with stirring. After being heated to 60 °C, the core-shell latex was slowly added into the reaction system within 1.5 h. Finally, the white zinc styrene-acrylic ionomer latex (PSA-Zn) was obtained.

Preparation of self-crosslinked zinc styrene-acrylic coating (PSA-Zn-C)
The self-crosslinked zinc styrene-acrylic coating (PSA-Zn-C) was prepared by mixing PSA-Zn latex, pigments and porous fillers in distilled water. Firstly, the pigments and fillers (CD02: CD05: bentonite: kaolin: talc: titanium dioxide = 9:3:2:1:1:4) were dispersed in water under stirring. Then, PSA-Zn latex was added and the mixture was ground for 1 h with an attritor filled with glass balls at room temperature, to afford the humidity-sensitive coating (PSA-Zn-C).

Characterization and properties of PSA-Zn latex and film
Solids content (Solids %) was calculated by Eq. (1),

\[
\text{Solids}(\%) = \left( \frac{M_{\text{dl}}}{M_l} \right) \times 100
\]

where \(M_{\text{dl}}\) is the mass of dry latex, \(M_l\) is the mass of latex.

PSA latex (10.0 g) was dispersed in 20.0 g of distilled water, and neutralized by adding NaOH aqueous solution (0.1 mol/L). The concentration of acid bound at the surface of PSA latex particles \(S_a\) (mol/g) was estimated by conductometric titration, and calculated by Eq. (2),

\[
S_a (\text{mol/g}) = \left( \frac{V_b \times c}{M_{\text{dl}} \times \text{Solids}\%} \right) \times 10^{-3}
\]

where \(M_{\text{dl}}\) is the mass of latex, \(c\) and \(V_b\) are the concentration and volume of NaOH solution, respectively.

The average particle size and particle size distribution of latex particles were measured by dynamic light scattering (DLS) (Nano series, Malvern Instruments Ltd, UK) at 25 °C. The sample was highly diluted (< 0.01 %) to prevent multiple scattering. Micrograph and particle size of the PSA-Zn particles were obtained by transmission electron microscopy (TEM, JEM-1230 from JEOL) at an acceleration voltage of 200 kV. The microstructure was observed by scanning electron microscopy (SEM, ULTRA Plus, Germany).

The PSA-Zn film was prepared by drying latex at room temperature. FT-IR spectra were recorded on a
Digital FTS3000 spectrometer. Thermogravimetric analysis (TGA) was performed on a Pyris Diamond (Perkin Elmer) instrument under the nitrogen atmosphere at a heating rate of 10 °C/min from 20 °C to 650 °C.

To study the film-forming ability of different component latexes, the latex was painted on a clean glass at room temperature for 24 h to obtain natural dried films. The films which were flat, smooth, transparent, were used for further studies, while wrinkled and cracked samples were discarded.

Results and Discussion
Preparation of PSA-Zn latex

As a physical crosslinker, the ionic groups can modify the final mechanical and thermal properties of coatings, adhesives and textiles materials to a large extent. To investigate the influence of zinc ion in self-crosslinked core-shell styrene-acrylic ionomer latex, we have synthesized PSA-Zn ionomer particles. The preparation of core-shell latex (PSA) and formation process of PSA-Zn particles are described in Scheme 1. Firstly, the core-shell styrene-acrylic nanoparticles (PSA) were prepared by two-step emulsion polymerization. In the second step, the zinc ammine complex was obtained through the reactions of ammonium carbonate ((NH₄)₂CO₃), zinc oxide (ZnO) and ammonium hydroxide (NH₃·H₂O) in water phase. Then, PSA-Zn particles were prepared by mixing dispersions of zinc ammine complex and core-shell styrene-acrylic particles in a film-forming process.

As is known, during the preparation of polymer latex, the structure and properties of monomers are very important. We have to not only select hydrophilic-hydrophobic monomers, but also considering hard and soft monomers. Here, MAA was used as hydrophilic monomer in core and shell, and BA was used as soft monomer in shell, while MMA, a hard non-elastic monomer, played an important role in increasing the hardness and tensile strength of the target product with durability and waterproof characteristics.

The influence of MAA content, $m_{core}/m_{shell}$ ratio and Zn$^{2+}$ content on mechanical properties and thermal stability of the latex were investigated. An artificial climate box was built to simulate humid environment and investigate humidity-sensitive properties of coatings.

The hydrophilic MAA content greatly influence stability of the core latex. The appropriate MAA content in polymer chain can improve stability of the latex and adhesive force of films. However, latex particles are easy to aggregate coagulum when the polymer chain contains several units of MAA. The influence of MAA content on particle size of PS latex is showed in Fig. 1. It is found that particle size distribution is low and the average particle size is approximately 74 nm when MAA content is 4 wt%. When MAA content is more than 6 wt%, there are
two peaks, because MAA is easily homopolymerized when present in high amounts. Hence, 4 wt% was selected as optimal reaction condition.

The $m_{\text{core}}/m_{\text{shell}}$ ratio of PSA particles not only affects properties of latex, but also is directly related to film-forming ability. The soft monomer can improve film-forming ability, while hard monomer can enhance hardness of films. Here, using styrene (St) as hard core monomer and butyl acrylate (BA) as soft shell monomer, the film-forming ability under $m_{\text{core}}/m_{\text{shell}}$ ratios in PSA particles, as 1/1, 1/1.5, 1/2, 1/2.5 and 1/3, was studied (Supplementary Data, Fig. S1). It was found that the film-forming ability improves on increasing the content of shell monomers. The obtained film was peeling and cracked when $m_{\text{core}}/m_{\text{shell}}$ ratio was 1, while films with ratios of 1/1.5 and 1/2 were corrugated and rough. Figure 2 shows the average particle size and particle size distribution of PSA latex when ratio was 1/2.5. The PSA latex with a 108 nm particle size is bound to have a 34 nm shell layer of core-shell structure. Therefore, based on good film-forming ability and suitable hardness, the $m_{\text{core}}/m_{\text{shell}}$ ratio of 1/2.5 was chosen to prepare the PSA particles.

Self-crosslinked metal ionomer particles can greatly improve the final mechanical properties of films. In the present study, the zinc ammine complex provided aqueous Zn$^{2+}$ ions, which neutralized the carboxylate groups from MAA repeat units and imparted ionic crosslinking. The PSA particle was stabilized by hydration layer, and the $p$H value of reaction system was adjusted by ammonium ions. By casting PSA-Zn latex on a clean tinplate, the adhesive force of the films was measured by electric scratch method under Chinese Standard (GB/T 1720-79). Figure 3 shows the influence of molar ratio of Zn$^{2+}$/MAA on the adhesive force of films. The adhesive force of film was poor without any Zn$^{2+}$ ions. When the molar ratio was lower than 0.3, the Zn$^{2+}$ ions imparted ionic crosslinking of carboxylate groups and enhanced the interaction of the films with substrates. When the molar ratio is below 0.3, it is difficult to obtain the film because the crosslinking degree was high and some of the Zn$^{2+}$ ions were possibly converted to ZnO. Therefore, the optimal molar ratio of Zn$^{2+}$/MAA was 0.2, which provide the best adhesive force.

In addition, it was found that the molar ratio of Zn$^{2+}$/MAA significantly influences the hardness of the obtained films. The film hardness was determined by Buchholz indentation test (Supplementary Data, Fig. S2). Buchholz indentation hardness values of films with different molar ratios are given in Fig. S3 (Supplementary Data). The result shows that addition of Zn$^{2+}$ ions can effectively enhance hardness of the films. The hardness of the film was improved with increasing the ratios of Zn$^{2+}$/MAA until the ratio of Zn$^{2+}$/MAA was 0.4.
Characterization of PSA-Zn latex and film

The concentration of acid bound at the surface of the PSA particles (“surface bound”) is of great importance to both the properties of latex as well as the degree of crosslinking, despite carboxylate groups consisting of “surface bound” PSA particles, “free” acid in the water phase and acid “buried” within latex particles in emulsion polymerization. The concentration of “surface bound” was determined in a single conductometric titration (Supplementary Data, Fig. S4). In the first stage, the conductivity value decreased sharply as $H^+$ ions with higher conductivity ability from “free” acid in the water phase were replaced by $Na^+$ ions. In the second stage, the “surface bound” PSA particles began to be neutralized with NaOH aqueous solution (0.1 mol/L). Since the concentration of $Na^+$ ions was higher than that of $H^+$ ions from –COOH groups, the conductivity value increased slowly. In the final stage, there was a significant increase in conductivity value due to the addition of NaOH solution. The volume of NaOH solution neutralized by the “surface bound” was about 6.0 mL. Therefore, according to the Eq. 2, the concentration of “surface bound” of PSA latex was found to be approximately \((3 \times 10^{-4})\) mol/g.

The FT-IR spectra of the PSA spheres and PSA-Zn particles are shown in Fig. 4. In the spectra of PSA and PSA-Zn, the peak for C=C stretching vibration (1620 ~ 1680 cm\(^{-1}\)) was not observed since vinyl monomers copolymerization reaction has taken place. The peaks observed between 3000 cm\(^{-1}\) and 3100 cm\(^{-1}\) confirm the existence of polystyrene chains. The peaks at 2874 cm\(^{-1}\) and 2956 cm\(^{-1}\) are ascribed to the C-H stretching vibrations of -CH\(_2\) and -CH\(_3\) groups. The peaks at 1722 cm\(^{-1}\) and 1452 cm\(^{-1}\) are due to the presence of C=O and -COO\(^-\) groups. Compared to the spectrum of PSA film, a new peak observed at 1580 cm\(^{-1}\) in PSA-Zn film. This is due to the presence of ionic crosslinking between Zn\(^{2+}\) ions and carboxylate groups, which proves that self-crosslinked zinc styrene-acrylic ionomer particles have been prepared.

Thermogravimetric (TG) curves of PSA and PSA-Zn films are showed in Fig. 5. It is found that the weight loss of PSA film is about 5 wt. % below 293 ºC, while that for PSA-Zn is 316 ºC. Their maximum decomposition temperatures are about 440 ºC and 450 ºC,
respectively for PSA and PSA-Zn film. In general, the thermal stability of copolymer is influenced by monomer unit and polymerization method. As reported by De et al.\textsuperscript{25}, the chain scission of polymer backbone in PMMA occurs in the range of 375–450 °C. Herein also, the polymer chain was decomposed before 450 °C. Compared with PSA film and emulsifier-free acrylate copolymer film (EF-AAC)\textsuperscript{26}, the thermal stability of PSA-Zn particles was improved significantly by the self-crosslinked ionomers.

The microstructure of PSA-Zn particles was characterized by transmission electron microscopy (TEM). As shown in Fig. 6, the spheres with dark and light regions show the presence of core-shell structure in PSA-Zn particles. The particle size is about 110 nm, which is consistent with the result of DLS studies. Further, latex particles are closely packed, which indicating the crosslinking effect.

Properties of PSA-Zn latex and film

The solids content of blue-white uniform PSA latex got to 20 wt%. According to the standard of GB/T 20623-2006, basic properties of PSA-Zn latex met Chinese standard architectural coatings (Supplementary Data, Table S1), including mechanical stability, freeze-thaw stability, storage stability. Likewise, the properties of films were measured and results given in Table 1 show the improved adhesive force of PSA-Zn latex with good film-forming ability.

![Fig. 6 – TEM image of PSA-Zn latex.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface morphology</th>
<th>Surface drying time</th>
<th>Adhesive force</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSA film</td>
<td>Smooth, transparent</td>
<td>3 h</td>
<td>5 grade</td>
</tr>
<tr>
<td>PSA-Zn film</td>
<td>Smooth, transparent</td>
<td>3 h</td>
<td>1 grade</td>
</tr>
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</table>

Properties of PSA-Zn coating (PSA-Zn-C)

Using PSA-Zn as film-former, self-crosslinked zinc styrene-acrylic coating (PSA-Zn-C) was prepared. Its basic properties and humidity-sensitive property were compared with those of core-shell styrene-acrylic coatings (PSA-C) without any ZnO particles. Results show that the basic properties of the coating met the standards of interior wall coatings, GB/T 9756-2009 (Supplementary Data, Table S2). Moreover, the scrub resistance of PSA-Zn-C was improved effectively.

The dehumidifying and increasing humidity properties of the coating (PSA-Zn-C) were investigated in the artificial climate box (42 L) (Fig. 7). On the one hand, six glass panels (12x8 cm) coated with dry PSA-Zn-C decreased RH rapidly from 90% to 40% within 2 h (C-D), while the same six glass panels without dry PSA-Zn-C required 8 h for the same decrease in RH (B-D). On the other hand, after the six glass panels coated with dry PSA-Zn-C were immersed in the water, they could increase RH from 30% to 70% within 2 h (C-I). However, when the controlled experiment was conducted by replacing the coated glass panels with a

![Fig. 7 – Dehumidifying and humidity increasing properties of the PSA-Zn-C.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Alkali resistance (24 h)</th>
<th>Water resistance (48 h)</th>
<th>Scrub resistance</th>
</tr>
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<tbody>
<tr>
<td>PSA-C</td>
<td>Normal</td>
<td>Normal</td>
<td>360</td>
</tr>
<tr>
<td>PSA-Zn-C</td>
<td>Normal</td>
<td>Normal</td>
<td>440</td>
</tr>
</tbody>
</table>
dish-like glass vessel filled with water, with surface area equal to glass panels, it needs 6 h (B-I). Therefore, PSA-Zn-C can evidently control reasonable relative humidity in response to humidity of the environment. The humidity controlling mechanism of PSA-Zn-C was similar to emulsifier-free acrylate cross-linkable copolymer coating.

The surface microstructure of PSA-Zn-C studied by SEM and shows a coral-like structure (Fig. 8). Due to the presence of fillers and hydrophilic groups, such as –COOH and –COOR of styrene-acrylic copolymer, PSA-Zn-C is like an excellent water-absorbent material, which can store a lot of water. The large amount of voids in PSA-Zn-C can help to get moisture through.

Conclusions

Using conventional functional monomers and zinc ions, self-crosslinked core-shell ionomer latex (PSA-Zn) has been successfully prepared via emulsion polymerization. After mixing pigments and porous fillers, the cheap, readily available and environment-friendly coatings (PSA-Zn-C) was obtained. Compared to PSA and EF-AAC coatings, the adhesive force, hardness and thermal stability of PSA-Zn film were significantly improved by adding zinc ions. Moreover, the core-shell ionomer coating (PSA-Zn-C) could decrease and increase relative humidity significantly in response to humidity environment in an artificial climate box, which makes it a promising candidate for development of waterborne humidity-sensitive coatings.

Acknowledgement

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Supplementary Data

Supplementary data associated with this article, i.e., Figs S1-S4 and Tables S1 & S2, are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_55A(10)1167-1173_SupplData.pdf.

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