A novel core/shell latex particle was successfully prepared by seeded emulsion polymerization. The rubbery core was made of poly (butyl acrylate) (PBA) with a slight cross-linked structure, while the glassy shell was poly (methyl methacrylate) (PMMA) containing a small amount of itaconic acid (ITA). The resulting core/shell latex particle PBA/P(MMA-ITA) should possess the function both of toughening the PBA core and the compatibilization of P(MMA-ITA) shell as well. The latex particles were characterized by transition electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and non-aqueous acid-base titration. The results showed well-defined core/shell morphology with the diameter of 50~65 nm and the cross-linkers diethylene glycol diacrylate (DEGDA), diallyl phthalate (DAP), and trihydroxymethylpropyl triacrylate (TMPTA) appeared the highest cross-linking efficiency. The monomer ITA has copolymerized with MMA successfully, and P(MMA-ITA) copolymer has been linked onto the surface of PBA core both by chemical bond and physical adsorption. The PBA/P(MMA-ITA) latex particles were core/shell structure indeed, and varying the ITA dosage and core/shell proportion, its size, T_g, and ITA content in shell layer would change relatively.

INTRODUCTION

It is well known that polyamide 6, as an important engineering plastic, is extensively utilized for its outstanding mechanical strength, abrasion resistance and easy processibility. However, the severe brittleness limits its application. Much effort has been paid on blending it with various elastomers to improve its brittleness. In most cases, the super-tough PA 6 is derived when the average particle size of the elastomers is ranged from 200 to 300 nm, but this is unobtainable. So many techniques have been attempted for the ultrafine dispersion of the elastomers into the polymer matrix. For example, some
graft copolymers compatibilizer, such as polystyrene-
\( b \)-poly(ethylene-\( \text{ran} \)-butylene)-\( b \)-polystyrene (SEBS) grafted with maleic anhydride (SEBS-\( g \)-MA), were
added to the blends. In this ternary system the com-
patible effect was attributed to the reaction of maleic
anhydride with the amine groups of polyamide 6 [1].
In recent years [2-4], impact modifiers with core/shell
structure have attracted great interest for their special
structure in which the elastomer as the core is encap-
sulated with a hard shell, and exhibits synergistic
effect derived from the two components. Such materi-
als including poly(n-butyl acrylate)/poly(methyl
methacrylate) (PBA/PMMA) [5], polyethylene-octene
elastomer/semi-crystalline polyolefin blend
(TPEg) [6,7] and polybutadiene/poly(methyl
methacrylate) (PB/PMMA) [8,9] have been devel-
oped. The particle size of the above-mentioned impact
modifiers with core/shell structure can be controlled
by adjusting polymerization condition, but there are
no reactive groups with the amine groups of
polyamide 6 in shell layer. Therefore the compatibi-
lizer containing MA component must be introduced
into blend of PA 6, where the blend is also a ternary
system.

In this study, we have designed a novel core/shell
latex particle used as impact modifier with a slight
rubbery cross-linked poly(n-butyl acrylate) (PBA)
core and a glassy poly(methyl methacrylate-itaconic
acid) (P(MMA-ITA) ) shell containing small amount
of itaconic acid [10-26], which have been prepared by
seeded emulsion polymerization method via batch
procedure. The PBA/P(MMA-ITA) impact modifier
should possess toughening and compatibilizing func-
tion simultaneously. Thus, we can change the blend
from a ternary to a binary system and make the disper-
sion of impact modifier in polyamide 6 matrix more
symmetrical, process the blend more easily and
toughening it more effectively.

Generally, the functional monomer MA was used
for preparing compatibilizer in the previous works
due to one MA molecule containing two carboxyls in
being more efficient as the compatibilizer of PA 6
than a monobasic acid. Comparing with MA, the
functional monomer ITA is also a dicarboxylic acid. It
is avirulence and flavourless, moreover its carboxyl
content/price ratio is higher than acrylic acid. The
polymerization procedure, the effect of the types and
dosage of cross-linkers on gel content of core were
investigated. The structure and morphology of
core/shell latex particles were characterized by non-
aqueous acid-base titration, FTIR, DSC, light scatter-
ing (LS), and TEM.

EXPERIMENTAL

Materials
Methyl methacrylate (MMA) and n-butyl acrylate
(BA), purchased from Tianjin Kemiou Chemical
Regent Development Center, were distilled under
reduced pressure to remove inhibitors and stored in a
refrigerator at 4°C. Itaconic acid (ITA) was supplied
by Tianjin Chemical Regent Plant. Divinylbenzene
(DVB), 1,4-butanediol diacrylate (BDA), neo-pen-
tene glycol diacrylate (NPGDA), diethylene glycol
diacrylate (DEGDA), diallyl phthalate (DAP), tri-
hydroxymethylpropyl triacrylate (TMPTA), and eth-
ylene glycol dimethacrylate (EGDMA) were all pur-
chased from Aldrich and used as received. Initiator
ammonium persulphate (APS), emulsifier sodium
dodecyl sulphate (SLS), and other materials were
obtained from Shanghai Reagents Co. and used with-
out further purification. Deionized (DI) water was
used throughout the experiments.

Preparation of Seed Latex
The seed particles were synthesized in a 500 mL four-
neck round-bottom flask equipped with a mechanical
stirrer, reflux condenser, feeding device, and nitrogen
gas inlet system via emulsion polymerization process.
The mixed solution of SLS, 2/3 of the dosage BA in
recipe, cross-linker and deionized water was stirred
for 30 min in the flask in nitrogen to remove oxygen
from the system. Stirring speed was controlled at 230
rpm. Then the polymerization was initiated by drip-
ing the aqueous solution of APS into reaction vessel
at 60°C. The rest of BA was introduced into the reac-
tion mixture and the reaction was maintained at 80°C
for 2 h under stirring. The polymerization reaction
formula was shown as Scheme I.

Preparation of Core/Shell Latex
The core/shell latex particles were prepared by seed-
ed emulsion polymerization method. In the reactor
where the seed PBA was prepared, stirring device controlled the stirring speed at 230 rpm, the mixture of MMA and ITA was added dropwise, and the polymerization was maintained at 80 in nitrogen for 2.5 h under stirring. By this method, the graft polymerization occurred because of some living radicals on the surfaces of PBA core particles, and the resulting shell layers of core/shell microspheres were hairy as no cross-linker was used in the second stage. The polymerization reaction formula was shown as Scheme II. CaCl₂ aqueous solution (1 wt%) was charged into the emulsion for coagulating. The prepared core/shell samples were purified by repetitive centrifugation, decantation, redispersion and freeze-dried, subsequently. A series of core/shell impact modifiers samples can be obtained by varying the type and dosage of cross-linker, core/shell proportion (w/w), and ITA dosage in shell layer (wt%) with the same processes mentioned above.

**Characterization**

The latex particles size and morphologies were characterized by Laser Particle Sizer (LS-800) and transmission electron microscopy (TEM, JEM-100CXII) using phosphotungstic acid as staining agent. The T_g of shell layer was performed by differential scanning calorimetry (DSC, Netzsch DSC 204 F1) from room temperature to 250ºC at a heating rate of 10ºC/min under a nitrogen atmosphere. The PBA core particles were extracted successively with acetone for 24 h using Soxhlet apparatus and the gel content was calculated by the following formula, which is described as gel content = (m_1/m_2)×100%. Here m_1 is the sample weight after extraction and m_2 is the sample weight before extraction. The core/shell latex particles were extracted with ethanol and acetone for 24 h, respectively. Then, the ITA content was determined by non-aqueous acid-base titration method and the structure was investigated by Fourier transform
infrared spectra (FTIR, Perkin Elmer Spectrum-one). The ITA content in shell layer can be written:

\[
\text{ITA content}\% = M \times (C_1V_1-C_2V_2)/(m \times \alpha) \times 100\%
\]

where \( M \) is molecular weight of ITA (g/mol), \( m \) is the sample mass (g), \( \alpha \) is weight percent of shell layer in core/shell latex particle, and \( C_1, C_2 \) are the concentrations of base, acid in ethanol solution (mol/mL). \( V_1, V_2 \) are the volumes of base, acid solution used in titration (mL), respectively.

RESULTS AND DISCUSSION

Effect of the Types and Dosage of Cross-linkers on Gel Content

The PBA/P(MMA-ITA) latex particles with core/shell structure were prepared by seeded emulsion polymerization via a two-stage batch procedure [10-26] which has been reported in our previous work [23]. After BA or MMA/ITA introduced into the reaction kettle, the reaction was maintained at 80°C for 2 h, the conversion of BA reached over 96 wt%, and the MMA/ITA over 95 wt% for 2.5 h. The above described results confirmed that the monomer which was introduced into the reaction kettle almost all participated in polymerization. Figure 1 showed the dependence of gel content on the type and dosage of cross-linkers. The gel content increased with increase in cross-linkers dosage and its value was up to 90 wt% even with small amount of cross-linkers, and the cross-linking efficiency of DEGDA, DAP, and TMPTA was better than others. The cross-linking degree of rubbery core cannot be too high otherwise it will harden and would be unfavourable for toughening [26]. According to the above described experimental results the dosage of cross-linker was fixed at 3 wt% of BA. The DVB was chosen as a cross-linker for the following test considering the cross-linking efficiency/price ratio determined by light scattering (LS). The particle size of PBA/P(MMA-ITA) latex particles was greater than that of PBA latex particles when ITA dosage varied between 2 wt% and 10 wt% of shell monomer. This result confirmed that the shell monomer copolymerized successfully on the surface of PBA core. The polymerization was carried out according to the seeded emulsion polymerization mechanism. But the particles size of PBA/P(MMA-ITA) was smaller than that of PBA core as ITA dosage up to 12 wt% indicated that the secondary nucleating phenomenon occurred during the second stage of seeded emulsion polymerization. Monomer ITA is water soluble and the secondary particles are produced via compatibili-
lizing and polymerizing inside the new micelles formed by agglutination of P(MMA-ITA) copolymer in aqueous phase when the ITA/MMA proportion increases to a certain extent. It was for the above reason that the average particle size of polymerization system decreased due to the small secondary particles being formed.

Functional monomer, ITA, was introduced into polymerization system at the shell polymerization stage, it copolymerized with monomer MMA and the P(MMA-ITA) copolymer was formed. Some ITA copolymer content was high and some others were low. The copolymer with particular high ITA content was water soluble. It was also possible that a few ITA did not participate in copolymerization. Therefore, the ITA content of PBA/P(MMA-ITA) latex particle specimens was inconsistent with ITA dosage in synthesis. In other words, the ITA content of latex particle was less than ITA dosage in synthesis. Otherwise, there are two kinds of connection mode between PBA core and P(MMA-ITA) shell layer, one is P(MMA-ITA) copolymer in shell layer connected with PBA core by chemical bond, and another is physical bond. In order to investigate the effect of ITA dosage on ITA content of latex particle and identify how many P(MMA-ITA) copolymers are connected by chemical bond or physical bond, the non-aqueous acid-base titration method was used to analyze the PBA/P(MMA-ITA) particle specimens in this work. Before the titration analysis, latex particle specimens were firstly extracted by ethanol so to remove the remaining ITA, MMA, as well as other alcohol extractives. The ITA content for extracted specimens represented the total ITA amount in copolymer. Then, the specimens were extracted by acetone once again, so to remove P(MMA-ITA) copolymer connected with PBA core by physical bond. Here, ITA content for extracted specimens represented the ITA amount connected with PBA core by chemical bond. The detailed change of extraction process is shown as Scheme III.

After extraction by ethanol, ITA content in shell layer increased with the increasing of ITA dosage in the range of 2-6 wt% and decreased when the dosage was over 6 wt% (Figure 2). Despite these results which confirmed the presence of component ITA in shell layer, the utilization coefficient of monomer ITA appeared as parabola-shaped varieties with increasing of ITA dosage. After extraction by acetone once again,

![Scheme III](image)

**Scheme III.** The process illustration of PBA/P(MMA-ITA) latex particle specimens extracted by ethanol and acetone, respectively.

![Figure 2](image)

**Figure 2.** Influence of ITA dosage on ITA content 1, ITA content of specimens after extracted by ethanol; 2, ITA content of specimens after extracted by ethanol and acetone, respectively.
The extraction result was almost the same as that of ethanol. The maximum ITA content in shell layer corresponded to 8 wt% ITA dosage, which meant that the effect of ITA dosage on ITA content was due to linking by chemical bond and physical bond as well. The above results illustrated that ITA really participated in copolymerization with MMA. One part of P(MMA-ITA) copolymer accumulated on the PBA shell because of the physical adsorption, and another part of which inarched on the PBA core by chemical bond.

The reason of ITA content anomaly with varying ITA dosage may be explained as follows: The ITA is a water soluble monomer, it can increase the water-solubility of P(MMA-ITA) copolymer. This copolymer with high ITA content would be dissolved in polymerization process or extracted by ethanol easily. The ITA amount participated in copolymerization and P(MMA-ITA) copolymer amount dissolved and extracted should both increase with increasing of ITA dosage shown as Figure 3 (curves 1 and 2). But when ITA dosage was higher than 6 wt%, the latter increased rapidly and curve 2 appeared as a turning point due to ITA content in P(MMA-ITA) copolymer reaching critical value, which resulted in more copolymer dissolved or extracted. In fact, after extracted by ethanol, the ITA content in curve 1 and curve 2 is different. This is the reason for ITA content varying with ITA dosage in Figure 2 (curve 1). In addition, the ITA content of P(MMA-ITA) copolymer increased gradually with increasing of ITA dosage. But when ITA dosage was above 8 wt%, the ITA relative amount in shell layer reached a definite value and the P(MMA-ITA) copolymer with high ITA content anomaly with varying ITA dosage.

Table 1. The recipe for the synthesis of core/shell latex particles.

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BA (g)</td>
<td>60</td>
<td>60</td>
<td>55-75</td>
</tr>
<tr>
<td>SLS (g)</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>APS (resolved in 10 mL of H2O) (g)</td>
<td>0.0710</td>
<td>0.0710</td>
<td>0.0710</td>
</tr>
<tr>
<td>DVB (DAP, EGDMA, BDA, NPGDA, DEGDA, TPTNA) (g)</td>
<td>0.48-3.00</td>
<td>1.8</td>
<td>1.8</td>
</tr>
<tr>
<td>H2O (deionized water) (g)</td>
<td>150</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Shell</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MMA (g)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ITA (g)</td>
<td>0.0-4.8</td>
<td>1.5-2.5</td>
<td></td>
</tr>
<tr>
<td>APS (resolved in 10 mL of H2O) (g)</td>
<td>0.0260</td>
<td>0.0260</td>
<td></td>
</tr>
</tbody>
</table>

Note: Sample 1, the DVB, DAP, EGDMA, BDA, NPGDA, DEGDA, and TMPTA used as cross-linker, their dosage varied as 0.8, 1.5, 2.0, 2.5, 3.2, 4.0, and 5.0 wt% of the BA dosage, respectively, then the PBA latex particles were prepared; Sample 2, the core/shell proportion fixed as 60/40 the ITA dosage varied as 2, 4, 6, 8, 10, and 12 wt% of the MMA dosage, respectively, then the PBA/P(MMA-ITA) latex particles were prepared; Sample 3, the ITA dosage fixed as 6 wt% of the MMA dosage, the core/shell proportion varied as 55/45, 60/40, 65/35, 70/30, and 75/25, respectively, then the PBA/P(MMA-ITA) latex particles were prepared.
content began to be dissolved in polymerization process and the dissolution increased with increasing of ITA dosage. The lower the amount of P(MMA-ITA) copolymer in shell layer, the less P(MMA-ITA) copolymer grafted onto PBA core. In fact, the amount of ITA in P(MMA-ITA) copolymer of shell layer is different in curves 1 and 3. This is the reason for ITA content varying with ITA dosage in Figure 2 (curve 2). The illustration of extraction process using ethanol and acetone for latex particle specimens is shown as Scheme III.

Lu et al. [8] used 20 wt% of core/shell elastomer as toughening agent and 3-5 wt% of styrene and maleic anhydride copolymer (SMA, 8 wt% of MA) as compatibilizer. Then blended them with PA 6 to obtain super-tough PA 6 alloy. Calculating in terms of the above proportion, there would be 0.9-1.6 g of MA in 100 g blend of elastomer and compatibilizer, i.e. 0.9-1.6 wt%. When the core/shell proportion was fixed at 60:40 and ITA dosage at 6 wt%, the ITA content in shell layer for the PBA/P(MMA-ITA) latex particle prepared in our laboratory reached 4.38 wt%. The average ITA content in PBA/P(MMA-ITA) latex particle was 1.75 wt%, in which 1.3 wt% of ITA connected with PBA core by chemical bond. This meant that the PBA/P(MMA-ITA) latex particle was satisfactory for preparing super-tough PA 6 alloy.

The PBA/PMMA latex particle exhibits lower Tg (110.0) relative to that of pure PMMA (123.9) owing to the existence of rubbery PBA core. The Tg value of PBA/P(MMA-ITA) latex particle is found between that of PMMA and PBA/PMMA (Table 1 and Figure 4), but the influence of ITA content on Tg of P(MMA-ITA) copolymer was not obvious. Compared with PBA/PMMA latex particles, the increasing of Tg value of PBA/P(MMA-ITA) latex particles may be attributed to the enhancement of intermolecular force caused by the introduction of polar monomer ITA.

Preparation of PBA/P(MMA-ITA) Latex with Various Core/Shell Proportions
After extracted by ethanol, the ITA content of specimens increased gradually with increasing core/shell proportions under ITA dosage fixed at 6 wt% of shell monomer, and approached the maximum (4.51 wt%) when core/shell proportion was 65:35. Then, the ITA content decreased obviously when core/shell proportion was more than 65:35. After extracted by acetone once again, the ITA content of specimens showed the same rule with that extracted by ethanol (Figure 5), which implied the existence of P(MMA-ITA) copolymer connected with PBA core by chemical bond and the utilization coefficient of monomer ITA appeared a parabola-shaped with increasing of core/shell proportion. The Tg values of PBA/P(MMA-ITA) latex particles decreased gradually with increasing of core/shell
proportion owing to the existence of rubbery PBA core which could increase the flexibility of molecular chain as shown in Table 2 and Figure 6.

The particle size of PBA core enlarged and the thickness of P(MMA-ITA) shell diminished gradually along with increasing of core/shell proportion. The shell layer was thick and ITA absolute amount was great when core/shell proportion was low. ITA tended to move to the outside layer of shell due to its water solubility and ITA content of P(MMA-ITA) copolymer in the outside layer of shell was higher than inside layer. Because P(MMA-ITA) copolymer in the outside layer of shell had higher ITA content and greater water-solubility, so it was easily dissolved in polymerization process. In addition, the large size of PBA core and thin P(MMA-ITA) shell layer was propitious P(MMA-ITA) copolymer with high ITA content to diffuse and dissolve in the polymerization process when core/shell proportion was high. For the specimens extracted by ethanol, the decrease in ITA content was caused by the dissolution of P(MMA-ITA) copolymer with high ITA content in shell layer. The ITA relative amount in shell layer decreased due to the loss of P(MMA-ITA) copolymer with high ITA content, which resulted in the decreasing of ITA content grafted onto PBA core, so that ITA content of shell layer reduced correspondingly when the core/shell proportion was low or high for the specimens extracted by acetone. Only when core/shell proportion was appropriate (65:35), the dissolved P(MMA-ITA) copolymer was less and ITA content of shell layer was the highest both for the specimens extracted by ethanol(1) or/and acetone(2) shown as Figure 5.

**Morphology Analysis of PBA/P(MMA-ITA) Latex Particle**

Figure 7 shows the IR spectrum of latex particles. The peaks at 1690.32 cm\(^{-1}\) (specimen 2, 3) and 1736.36 cm\(^{-1}\) are associated with carboxyl (–COOH) characteristic stretching vibrations, whereas the peak at 2957.17 cm\(^{-1}\) corresponds to aliphatic(C–H) stretching vibrations. Compared with latex particles 1, 2 and 3, the weak stretching vibrations of carboxylate group (–COO–) were detected at 1587.76 cm\(^{-1}\) and 1588.05 cm\(^{-1}\) in latex particle 4 and 5, respectively. This indicated that ITA had been copolymerized successfully with MMA in shell layer and the presence of P(MMA-ITA) copolymer, some of which linked onto

![Figure 6](image-url)
Figure 7. Infrared spectra of latex particles: 1, PBA/PMMA; 2, PBA/P(MMA-ITA) extracted by ethanol; 3, PBA/P(MMA-ITA) extracted by ethanol and acetone, respectively; 4, sodium salt of PBA/P(MMA-ITA) extracted by ethanol; 5, sodium salt of PBA/P(MMA-ITA) extracted by ethanol and acetone, respectively.

Figure 8. Transition electron micrographs (TEM) of core/shell latex particles. a, b and c represent the core/shell proportions of 55/45, 60/40 and 70/30 PBA/P(MMA-ITA) latex particles, respectively.

Table 3. Analysis data of PBA/P(MMA-ITA) latex particles with various core/shell proportions.

<table>
<thead>
<tr>
<th>Core/shell proportion (wt%)</th>
<th>ITA contentb (wt%)</th>
<th>ITA contentc (wt%)</th>
<th>Tg (ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>55:45</td>
<td>3.88</td>
<td>2.85</td>
<td>116.0</td>
</tr>
<tr>
<td>60:40</td>
<td>4.38</td>
<td>3.26</td>
<td>111.5</td>
</tr>
<tr>
<td>65:35</td>
<td>4.51</td>
<td>3.64</td>
<td>111.2</td>
</tr>
<tr>
<td>70:30</td>
<td>3.36</td>
<td>1.90</td>
<td>91.3</td>
</tr>
<tr>
<td>75:25</td>
<td>2.01</td>
<td>0.82</td>
<td>79.4</td>
</tr>
</tbody>
</table>

Note: (a) The ITA dosage in shell layer was fixed at 6 wt%; (b) analysis results after extracted 24 h by ethanol; (c) analysis results after extracted 24 h by ethanol and acetone, respectively.

the surface of core by chemical bonds.

TEM micrographs of PBA/P(MMA-ITA) latex particles prepared under different core/shell proportions are shown in Figure 8. The particles are spherical with diameter of 50-65 nm approximately. With
careful staining of the latex particles using 2 wt% phosphotungstic acid, the core/shell nanostructure is clearly revealed where PBA appears as bright areas and P(MMA-ITA) lies in the dark regions circling the cores independent of the core/shell proportion. The shell layer thickness increased as the core/shell proportion decreased which could be observed in Figure 8a, b and c. In most cases, however, when the average particle size of elastomer lies between 200 to 300 nm, the best toughening effect is obtained for blends with polyamide 6 matrix. Therefore, much work should be done for the increase of the particle size in the future.

CONCLUSION

A novel core (PBA)/shell (P(MMA-ITA)) latex particles was successfully prepared by seeded emulsion polymerization via batch procedure. The cross-linkers DEGDA, DAP, and TMPTA have shown the highest cross-linking efficiency through analyzing the effects of the type and dosage of cross-linkers on gel content. The monomer ITA has copolymerized with the monomer MMA successfully and one part of P(MMA-ITA) copolymer linked by chemical bond with PBA core and another adsorbed by physical bond. The PBA/P(MMA-ITA) latex particles were core/shell structure indeed, and varying the ITA dosage and core/shell proportion, its size, T_g and ITA content in shell layer are changed to various extent.

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