

# SUSPENSION-SWELLING GRAFT COPOLYMERIZATION—SYNTHESIS OF ACS RESINS\*

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## ABSTRACT

Acrylonitrile (AN)-chlorinated polyethylene (CPE)-styrene (St) (ACS) terpolymer was synthesized by suspension-swelling graft copolymerization method, in which two key factors such as dispersing system and swelling time were studied. Highly effective complex dispersing system was chosen and determined, and two-layer protection model<sup>1</sup> was put forward to clarify the stable effect mechanism. Varying the swelling time of CPE in AN and St monomer mixture, some results such as grafting effect, particle characteristics, rubber particle morphology and its size distribution, and properties of ACS resins were investigated, thus the optimum swelling time was proposed.

## INTRODUCTION

ACS resin is a terpolymer in which acrylonitrile and styrene are graft-polymerized onto chlorinated polyethylene. It possesses superior weather-, fire- and static electricity-resistance to that of ABS caused by the substitution of CPE for PB or SBR<sup>[1]</sup>. Techniques of graft copolymerization for ACS resin introduced in literatures included such methods as the bulk, solution and suspension polymerization<sup>[2]</sup>. The former two have been already obsolete owing to high bulk viscosity or solvent recovery operation. Suspension-swelling graft copolymerization is a satisfactory method and has been used for industrial production. This method was developed by modifying the conventional suspension polymerization. Wherein CPE is suspended in the dispersant aqueous solution, then monomers and initiators are added. The base polymer and monomers are brought into contact by agitation, thus CPE is swollen, finally temperature is raised and grafting reaction takes place. In the polymerization parameters, dispersing system and swelling time are two key factors for polymerization process and product properties.

## EXPERIMENTAL

### *Synthesis*

ACS resin was synthesized in a 2-litre stainless steel autoclave with oil heating jacket at the temperature of 100 to 150 °C.

CPE powder with chlorine content of 29% and particles of 16—80 mesh size amounted to 98% weight, was from Weifang Chemical Works. St monomer was treated with anion exchange resin and AN purified by rectification.

### *2. Characterization*

Free SAN was separated from ACS resins with dimethyl sulfoxide as a selective

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solvent, thus grafting degree ( $Gd$ ) and grafting efficiency ( $Ge$ ) were measured.

$$Gd (\%) = \frac{\text{SAN grafted}}{\text{CPE rubber}} \times 100$$

$$Ge (\%) = \frac{\text{SAN grafted}}{\text{SAN grafted} + \text{free SAN}} \times 100$$

Sieving test was carried out using XSB-70B type sieve shaver to analyze weight average particle size and particle size distribution of ACS resins, taking weight fraction as the frequency function  $\psi$ . Particle surface was observed with Cambridge S-600 scanning electron microscope. Super-thin slices of ACS resins were observed with Olympus BH2 Series phase contrast microscope to study rubber particle morphology and its size distribution.

Determination of melting index was conducted according to HG 2-1171-77<sup>[3]</sup> at 220 °C under 5 Kg load. Impact strength was determined according to GB 1043-79 (state standard) at 25 °C.

## RESULT AND DISCUSSIONS

### 1. Dispersing system

Such types of suspension stabilizers as water-soluble polymers and insoluble powders of inorganic salts are widely used in suspension polymerization. A small amount of surfactant is usually added to increase dispersing effect.

#### (1) Organic stabilizer with surfactant

Polymeric compounds such as PVA-124, CH-23 and KH-20 (three types of polyvinylalcohol) and sodium salts of methacrylate-type copolymer (SSMC) etc., were not effective even if assisted by sodium dodecyl benzene sulfonate (SDBS) when used at high-temperature synthesis of ACS resins. This is due to the low cloud points for PVA series organic dispersants. While for SSMC, the colloid-protected ability decreases at high temperature though their cloud points are higher, which results in low film strength on droplet surface, and thus dispersing particles coalesce together when collide with one another in polymerization process.

#### (2) Inorganic stabilizer with surfactant

Dispersing system of hydroxyapatite (HAP) with SDBS was examined in the experiment. HAP was prepared from reaction of  $\text{CaCl}_2$  with  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  as follows:



Polymerization results were directly affected by preparation conditions of  $\text{HAP}^{[4]}$ . The main factors were arranged in the order of importance as: concentration of  $\text{CaCl}_2$  and  $\text{Na}_3\text{PO}_4$ , reaction temperature and charge style. Experiments were carried out under different preparation conditions, where aggregation of the suspension took place to convert it into a lumpy mass and severe foul was formed.

It is apparent that HAP dispersing system is high temperature resistant but not very stable. HAP and SDBS molecules are both adsorbed on the surface of oil droplets and complex layer is still formed by adsorption of HAP powders on the external layer of SDBS. However complex film is unstable and hard to form because SDBS molecule is shorter and less charged even if HAP can be easily moistened in the presence of SDBS. HAP powder is apt to be peeled off under vigorous agitation owing to weak interfacial

adhesion with oil droplets<sup>9</sup>.

### (3) Organic-inorganic complex with surfactant

Satisfactory results are obtained when complex stabilizers of PVA and HAP are used in the presence of SDBS for GH-23- and KH-20-type PVA, however narrow complex ratio of the former to the latter followed. Results are presented in Table 1.

Table 1 Effect of complex dispersing system on polymerization results<sup>a)</sup>

| Exp. No. | PVA in % <sup>b)</sup> | HAP in % <sup>b)</sup> | PVA/HAP wt. ratio | Agitation speed in rpm | Polymn. result |
|----------|------------------------|------------------------|-------------------|------------------------|----------------|
| 90419    | 0.52G <sup>c)</sup>    | 0.58                   | 1/1.1             | 750                    | lumpy mass     |
| 90420    | 0.39G                  | 0.88                   | 1/2.2             | 750                    | less foul      |
| 90417    | 0.52G                  | 1.17                   | 1/2.2             | 750                    | less foul      |
| 90416    | 0.52G                  | 1.17                   | 1/2.2             | 800                    | less foul      |
| 90422    | 0.61G                  | 1.36                   | 1/2.2             | 750                    | less foul      |
| 90424    | 0.52G                  | 1.46                   | 1/2.8             | 750                    | lumpy mass     |
| 90801    | 0.52K <sup>d)</sup>    | 1.17                   | 1/2.2             | 650                    | less foul      |

a) SDBS was charged to the amount of 8.6% of complex stabilizers including PVA and HAP

b) Weight fraction based on oil phase

c) GH-23-type PVA

d) KH-20-type PVA

He et al.<sup>[6-7]</sup> have pointed out that HAP is a sort of hydroxy phosphate crystal, which includes  $\text{Ca}(\text{OH})_2$ . Thus  $\text{Ca}^{++}$ ,  $\text{Ca}(\text{OH})^+$  and  $(\text{OH})^-$  etc. are probably formed in aqueous dispersion.  $\text{Ca}^{++}$  and  $\text{Ca}(\text{OH})^+$  are preferentially adsorbed by  $n[3\text{Ca}_3(\text{PO}_4)_2]$  colloid particle to show positive electricity, and solvated film is formed around particles as displayed in Fig. 1.

It was demonstrated by IR analysis that hydroxy group exists in HAP, which could be seen from its infrared spectra in Fig. 2 that strong and wide band appeared at characteristic frequency  $3450\text{ cm}^{-1}$  attributed to hydroxy vibration back and forth. Absorption peak was also found at  $1350\text{ cm}^{-1}$  corresponding to  $\text{PO}_4^{3-}$ . Based on above, the stable effect mechanism of PVA/HAP/SDBS ternary system can be clarified by two-layer protection model as shown in Fig. 3. PVA protection film is first formed on oil droplet surface owing to strong adhesion and then HAP powders are adsorbed on.

It was considered that hydrogen bonding is formed between internal PVA molecule and external hydroxy in HAP which result in firm combination. Furthermore, positive charge accumulated on the external surface of protection film, thus suspension system was stabilized with electricity isolation besides mechanical segregation by HAP. SDBS is added to decrease oil-water interfacial tension and to make CPE and HAP moisten easily. Complex ratio is probably related to the structure of the two-layer protection film.

## 2. Swelling time

When ACS resins are synthesized by suspension-swelling graft copolymerization

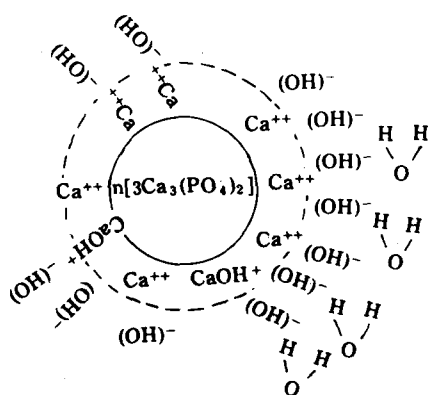


Fig. 1 Structural model of individual HAP

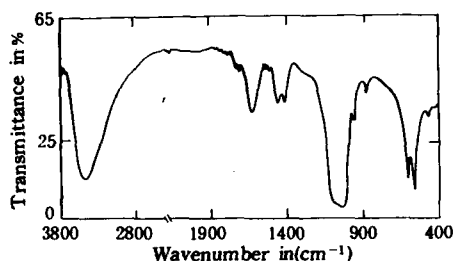
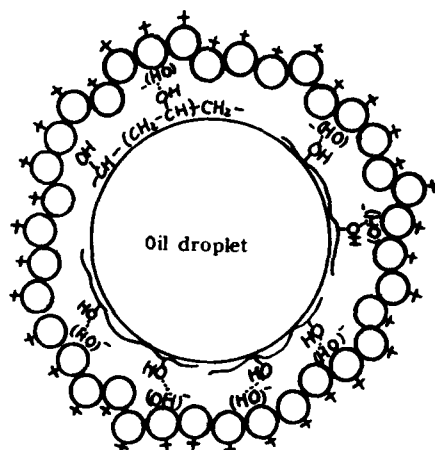


Fig. 2 FTIR spectral diagram of TCP-KBr pressed slice



O — Individual HAP particle  
Fig. 3 Two-layer protection model

method, monomers were adsorbed on and penetrated into CPE particles while copolymerization reaction was carried out. Preswelling was necessary before graft copolymerization in order to make monomers well adsorb on and penetrate into base CPE particles to obtain high-quality graft copolymer. Microstructure and properties of the ACS resins are affected by swelling time distinctly.

#### (1) Grafting degree and grafting efficiency

Gd and Ge are influenced by swelling time as shown in Fig. 4 at 40 °C. Both Gd and Ge increase with the increase of swelling time until 0.5 hr, then level off. It was considered that monomer amount on or into CPE particles increases with the increase of swelling time before 0.5 hr, then tends to be in swelling equilibrium (exactly time to raise reaction temperature should be added).

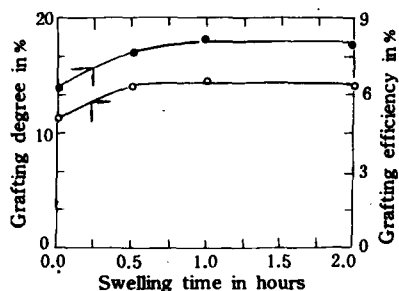


Fig. 4 Variation of Gd and Ge with swelling time at 40 °C

Particle size distribution (PSD) for ACS resins is probably two-peak as a result of free AS copolymer. Base CPE powders are predominantly distributed over 16–80 mesh size and free AS over 100–200. Thus the fine-particle size distribution is mainly corresponding to that of AS copolymer and the coarse to CPE and its graft product.

The fine and coarse particle are specially separated by 80 Tyler mesh size in order to characterize the two-peak distribution.  $w_1$  is defined as weight fraction of fine particles to signify free AS, and  $\bar{d}w_2$  as weight average particle size of the coarse to characterize grafted CPE.  $\bar{d}w$  is taken as overall weight average particle size of ACS resins.

Particle characteristic value is affected by swelling time as listed in Table 2. Both  $\bar{d}w$  and  $\bar{d}w_2$  increase with the increase of swelling time until 0.5 hr, then tend to be constant, whereas  $w_1$  decreases. It showed that swelling of monomer mixture in CPE inclined to be in phase equilibrium.

AS copolymer on CPE particle surface was observed in scanning electron micrographs

Table 2 Variation of particle characteristic values with swelling time at 40 °C

| Swelling time in hr              | 0     | 0.5   | 1.0   | 2.0   |
|----------------------------------|-------|-------|-------|-------|
| $\bar{d}_w$ in $\mu\text{m}$     | 0.50  | 0.70  | 0.73  | 0.75  |
| $w_1$ in %                       | 12.1  | 9.8   | 10.1  | 9.6   |
| $\bar{d}_{w_2}$ in $\mu\text{m}$ | 0.549 | 0.806 | 0.830 | 0.818 |

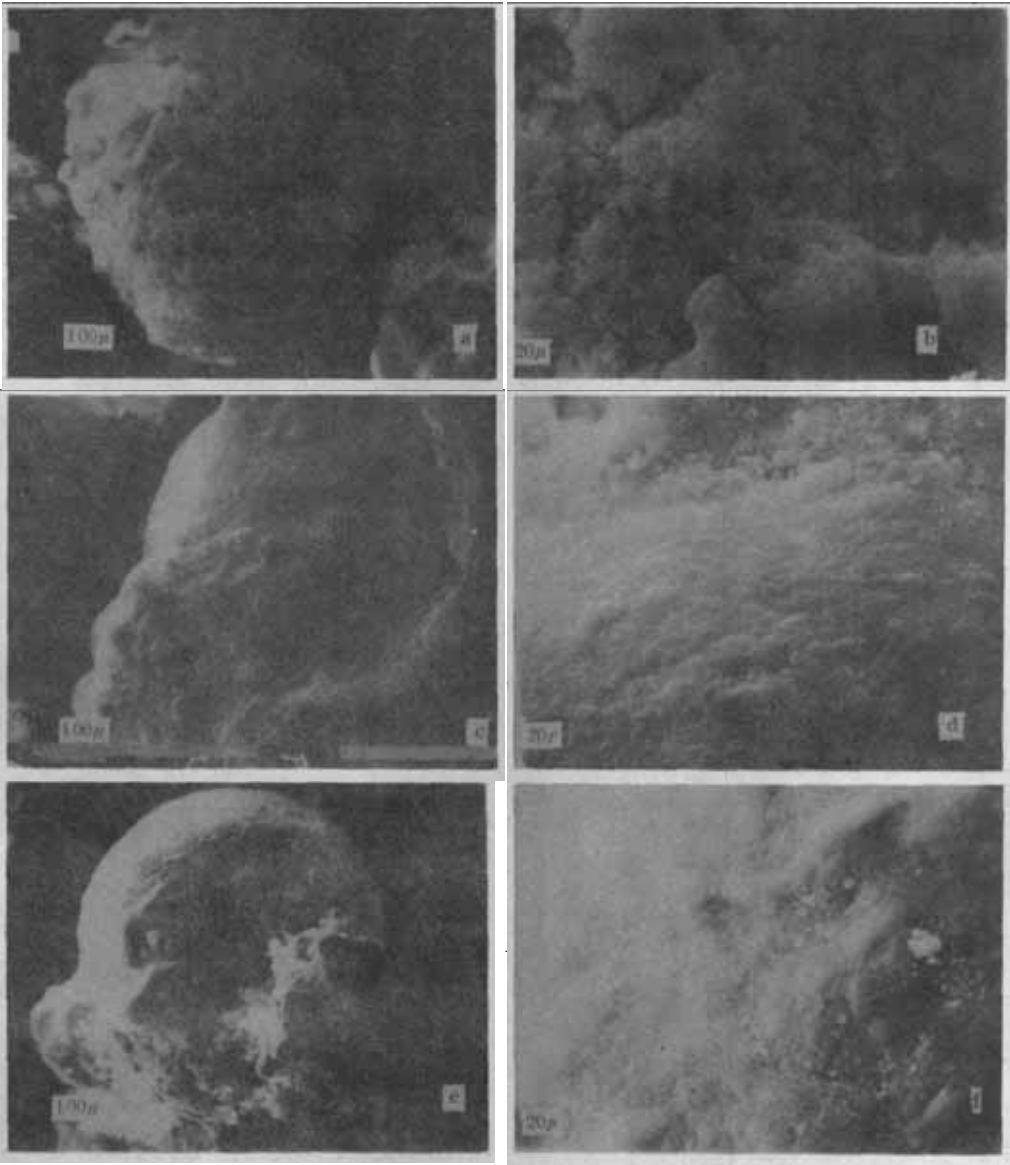


Fig. 5 SEM photographs of ACS particles  
a, b non-swelling; c, d swelling 0.5 hr;  
e, f swelling 2 hr

as shown in Fig. 5. There is partial exposure on CPE particle surface if only partially swollen and a thick layer after 0.5 to 2 hour swelling.

(3) Rubber particle morphology and distribution

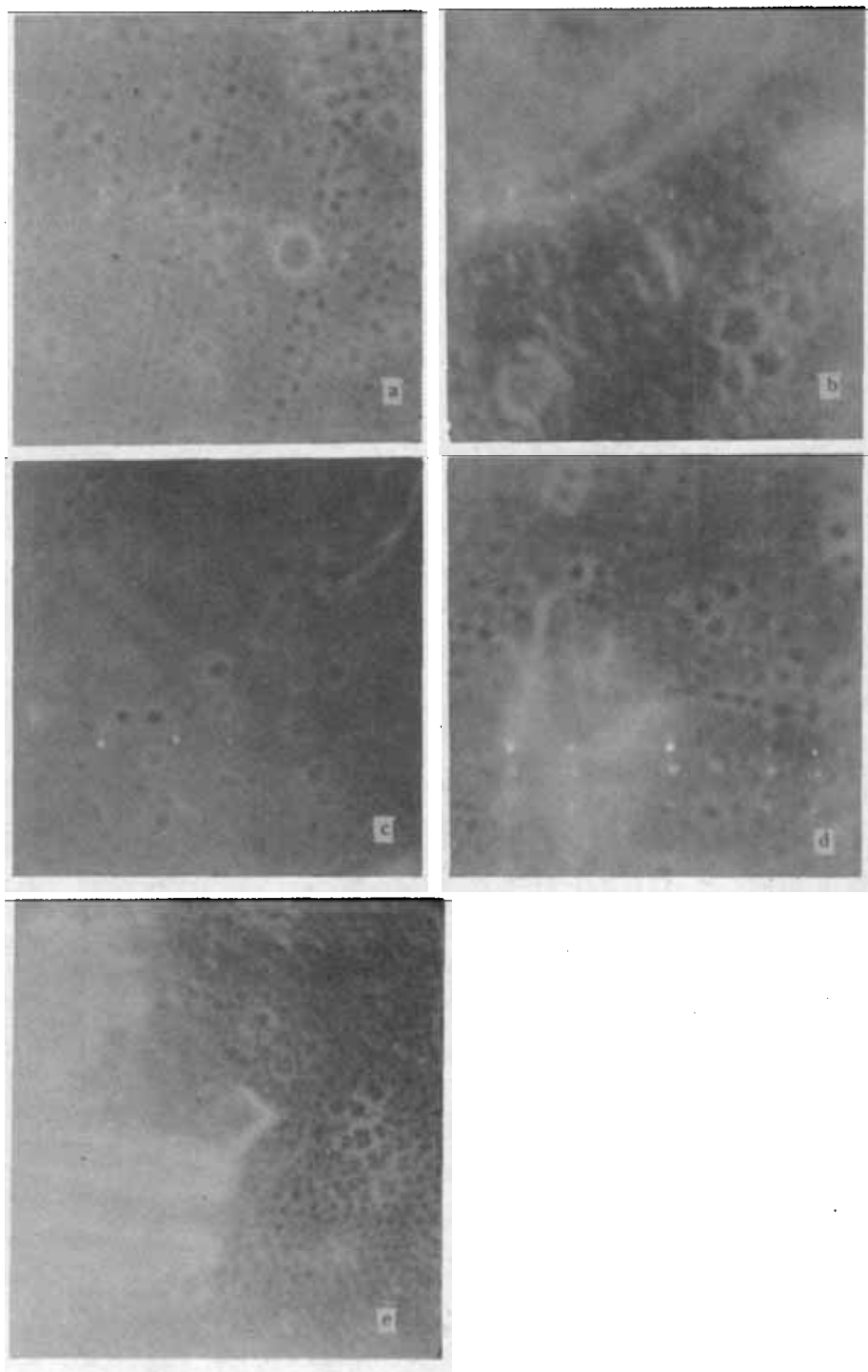


Fig. 6 Phase contrast micrographs (magnifying power 665)

a)ABS b) ACS non-swelling c) ACS swelling 0.5 hr, d) ACS swelling 1 hr, e) ACS swelling 2 hr

Phase contrast micro-observation demonstrated that dispersing situations of CPE rubber in ACS resins are similar to that in HIPS and ABS, being "sea-island" structure, as shown in Fig. 6. Where "island" stands for CPE rubber and "sea" for plastic continuous phase and its miscible parts. There is a great disparity in rubber particle size and particles are not well-dispersed in non-swollen or blend-type ACS resins. However particles were well-dispersed spheroids with the size of 1—2.5  $\mu\text{m}$  if CPE was swollen for 0.5—2 hours.

#### (4) Properties

Both impact strength and melt index are affected by swelling time as shown in Fig. 7. Both of them reached the maximum when swelling time was 0.5 hr. Thus pre-swelling is necessary before polymerization and swelling time is recommended to be 0.5 hr at 40  $^{\circ}\text{C}$ . There is a great disparity in rubber particle size and particles are not well dispersed in non-swollen ACS resins, which results in low impact strength. Solubility parameters for CPE (29%Cl), St and AN are  $18.6 \times 10^3$ ,  $19.0 \times 10^3$ , and  $21.5 \times 10^3$  ( $\text{J}/\text{m}^3$ )<sup>1/2</sup> respectively, thus St is adsorbed on or penetrated into base CPE preferably. As a result of above, there would be a fairly great difference in composition between free AS and AS-grafted when CPE was swollen for more than 0.5 hour, which brought about weak interfacial combination, and thus low impact strength.

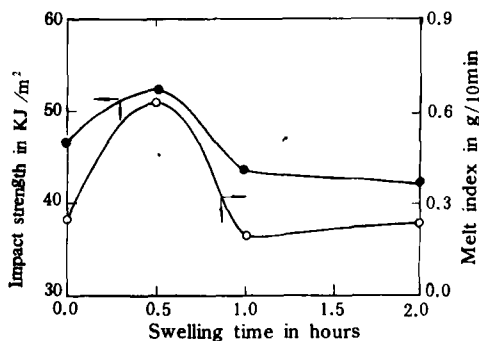


Fig. 7 Curves of impact strength and melt index versus swelling time at 40  $^{\circ}\text{C}$

## CONCLUSIONS

ACS resins are synthesized by suspension-swelling graft copolymerization method at temperature above 100  $^{\circ}\text{C}$ , the conclusions can be drawn as follows.

1. Complex stabilizers of organic and inorganic ones should be used in the presence of surfactant such as SDBS, however narrow complex ratio of the former to the latter followed. Two-layer protection model was put forward to clarify the stable effect mechanism.
2. Pre-swelling is necessary before polymerization and swelling time is recommended to be 0.5 hour at 40  $^{\circ}\text{C}$ , which will give products the highest impact strength and melt index.

#### Keywords:

Complex stabilizers; Two-layer protection; Swelling time; Acrylonitrile-chlorinated-polyethylene-styrene

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