



Relationship between Molecular Weight Distribution and Particle Size of PVC Resin

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Through the study of three grades of low polymerization degree poly(vinyl chloride) resins, the molecular weight distribution of low polymerization degree PVC resins was influenced by the particle size. The number of sub micro particles in low polymerization degree poly(vinyl chloride) resin is related to the molecular weight distribution. The higher the number of sub micro particles are, the higher the molecular weight and molecular weight distribution. It is presented a detailed study on the relationship of the molecular weight distribution and inner morphology.

Key Words: Poly(vinyl chloride), Morphology, Molecular weight distribution.

INTRODUCTION

Low polymerized degree of poly(vinyl chloride) is referred to PVC resin with a degree of polymerization of 600 or below. The low polymerization degree of poly(vinyl chloride) resin has the property of low molecular weight and good fluidity. It finds application mainly in the production of transparent films, sheets and bottles. The molecular weight or more precisely the molecular weight distribution (MWD) as characterized by the number average molecular weight (\bar{M}_N) or the weight average molecular weight (\bar{M}_W) is a fundamental property of every polymer. It is common practice to determine the molecular weight of polymer by gel permeation chromatograph¹. The processing ability of the PVC resins mainly depend on particle size, particle size distribution and the morphology of the resins². Nakajima and Harrell³ synthesized PVCs with particle size ranging from 15 to 0.2 μm and smaller. Percec *et al.*⁴ reported the metal-catalyzed living radical graft copolymerization experiments initiated from the structural defects of PVC with narrow molecular weight distribution. Nakajima and Daniels⁵ reported that the large particles are agglomerates consisting of primary particles. Mahmud *et al.*⁶ measured the shape and size distributions of PVC resin particles by scanning electron microscopy. Xu *et al.*⁷ studied the influence of molecular weight on the thermal stability of PVC. The molecular weight also influenced by the particle size. There are a few reports studied on the relationship between molecular weight and the particle size. In fact the particles with the highest

molecular weight distribution play a main role during the processing. The inner morphology can reflect the structure of the sub micro particles.

Therefore, in this paper relationship between molecular weight distribution and morphology was studied with different grade low polymerization degree of PVC resins.

EXPERIMENTAL

Three different grades of low polymerization degree of PVC resins (S-1, S-2 and J-1) were used in this study. S-1 and S-2 were with the degree of polymerization of 500 and 600 and purchased from Qilu Petrochemical Corp., Shandong Province, China. J-1 was with the degree of polymerization of 600 (use Polyvinyl Alcohol as dispersant) and purchased from Tianjin Chemical Corp., Tianjin, China.

Detection Method: Morphologies of the low polymerization degree poly(vinyl chloride) resins were determined by mounting the specimens and observing their features on a scanning electron microscope (Cambridge S250). Specimens were cut into thin films (50 μm) and surfaces were coated with a thin layer (10-20 nm) of gold. The coating was carried out by placing the specimen in a high-vacuum evaporator and vaporizing the metal held in a heated tungsten basket. Molecular weight and molecular weight distribution of these resins were analyzed by using gel permeation chromatograph (GPC, Waters 150 C). In general, \bar{M}_W/\bar{M}_N and $(\bar{M}_W \cdot \bar{M}_N)^{1/2}$ are using to express molecular weight distribution of low polymerization degree PVC resins. However, $(\bar{M}_W \cdot \bar{M}_N)^{1/2}$ is the

more effective expression due to more sensitive in particle size change.

RESULTS AND DISCUSSION

It is reported that the molecular weight distribution of PVC resins change as changing the particle size⁸. Table-1 shows the molecular distribution of S-1 resin with respect to particle size.

From the Table-1, molecular weight (\overline{M}_N and \overline{M}_W) of S-1 resin decreased and molecular weight distribution ($\overline{M}_W/\overline{M}_N$) was widened as decreasing the particle size. Suspension polymerization of vinyl chloride is a typical precipitation polymerization⁹. It is difficult for chain transfer and termination in precipitated phase. So it is easy to form high molecular weight chains. Which means, during the precipitation polymerization, free radicals are more likely to stay in larger particles and resulted in larger molecular weight.

Fig.1 shows the SEM images of S-1 resin at different particle sizes.

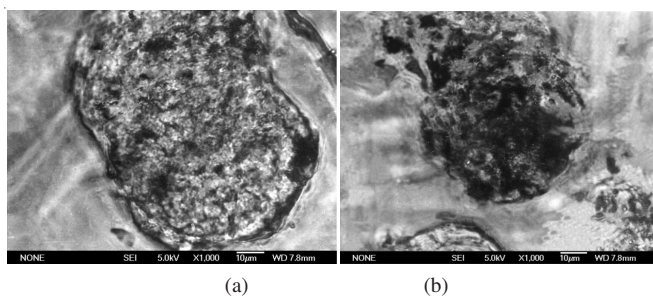


Fig.1. SEM images of S-1 resin at (a) 100-120 and (b) 180-200 mesh

Several reports¹⁰⁻¹³ on the mechanism of particle formation and the morphology of the PVC suspension polymerization has been appeared. From these studies, the highly stable primary particles formed in the early stages of suspension polymerization. These primary particles further agglomerate to form the final sub micro particles. The structure of the sub micro particles has closely relationship with the automatic acceleration phenomenon in the polymerization process. The

automatic acceleration in the polymerization process resulted in the sub micro particles with compact structure. In general, the black areas and the white areas reflect the sub micro particles with compact structure and porous structure, respectively. Fig.1 shows the inner morphology of S-1 resin at 100-120 and 180-200 mesh. The black areas are less and well-distributed in Fig.1a than in Fig.1b, so the molecular weight distribution is smaller. There are a lot of black areas with higher molecular weight in Fig.1b, the molecular weight distribution of S-1 resin with 180-200 mesh is much larger than 100-120 mesh.

From Table 2, \overline{M}_N and \overline{M}_W of S-2 resin increased and the molecular weight distribution widened with decreasing the particle size. In the synthesis of high-molecular-weight PVC, the individual free radicals in the vinyl chloride monomers polymerize quickly, making the molecular weight increase fast and the polymer precipitate quickly from the system. Therefore, higher molecular weight and molecular weight distribution can be obtained from smaller particle size. Fig. 2 shows the SEM images of S-2 resin.

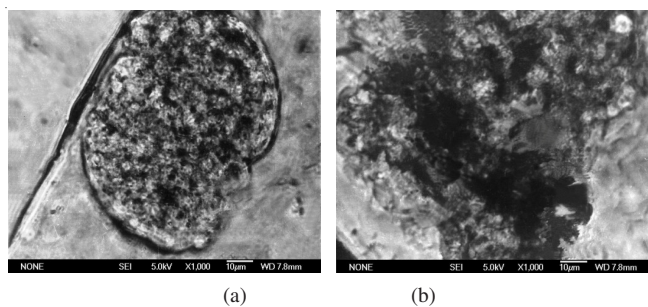


Fig. 2. SEM images of S-2 resin at (a) 100-120 and (b) 180-200 mesh.

Similar to the S-1, there are a few black areas and they are well dispersed in Fig. 2a. There are a large number of black areas in Fig. 2b and the distribution of the black areas is uneven, so the molecular weight distribution of S-2 resin with 180-200 mesh is much larger than 100-120 mesh.

Table-3 showed that the average molecular weight of J-1 is higher than that of S-1 or S-2. Because the polymerization process has been taken over by a new type of initiator and

TABLE-1
MOLECULAR WEIGHT DISTRIBUTION OF S-1 RESIN AT DIFFERENT MESH RANGES

Mesh range	$\overline{M}_N \times 10^{-4}$	$\overline{M}_W \times 10^{-4}$	$\overline{M}_W/\overline{M}_N$	$(\overline{M}_W/\overline{M}_N)^{1/2} \times 10^{-4}$
100-120	2.35	5.57	2.37	3.62
120-140	2.08	5.34	2.57	3.33
140-160	1.61	4.28	2.65	2.63
160-180	1.41	4.34	3.08	2.47
180-200	0.71	2.22	3.13	1.26

TABLE-2
MOLECULAR WEIGHT DISTRIBUTION OF S-2 RESIN AT DIFFERENT MESH RANGES

Mesh range	$\overline{M}_N \times 10^{-4}$	$\overline{M}_W \times 10^{-4}$	$\overline{M}_W/\overline{M}_N$	$(\overline{M}_W/\overline{M}_N)^{1/2} \times 10^{-4}$
100-120	2.23	4.66	2.09	3.22
120-140	2.38	5.90	2.48	3.75
140-160	2.93	6.69	2.28	4.43
160-180	2.89	6.55	2.26	4.35
180-200	2.29	8.36	3.65	4.37

TABLE-3
MOLECULAR WEIGHT DISTRIBUTION OF J-1 RESIN AT DIFFERENT MESH RANGES

Mesh range	$\overline{M}_N \times 10^{-4}$	$\overline{M}_w \times 10^{-4}$	$\overline{M}_w / \overline{M}_N$	$(\overline{M}_w / \overline{M}_N)^{1/2} \times 10^{-4}$
100-120	4.05	8.23	2.03	5.77
120-140	4.55	9.10	2.00	6.43
140-160	4.38	9.19	2.10	6.34
160-180	3.93	7.80	1.98	5.54
180-200	5.12	9.37	1.83	6.93

dispersion system, $\overline{M}_N \cdot \overline{M}_w$ and $\overline{M}_w / \overline{M}_N$ does not change obvious with the change of particle size. This can also be seen from the SEM images shown in Fig. 3.

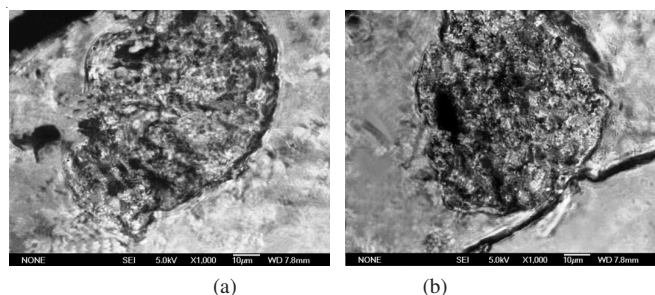


Fig. 3. SEM images of J-1 resin at (a) 100-120 mesh and (b) 180-200 mesh

There are a few black areas in Fig. 3. The automatic acceleration phenomenon in the polymerization process is not obvious due to using PVA as dispersant. The molecular weight distribution does not change with the change of particle size and it is close to 2. Therefore, PVC resins like J-1 are easy to break during processing due to the loosely porous structure.

Conclusion

The molecular weight distribution of 30 grades of low polymerization degree PVC resins was studied. The structure

of the sub micro particles has close relationship with the automatic acceleration phenomenon in the polymerization process. The automatic acceleration in the polymerization process resulted in the sub micro particles with compact structure. In general, the black areas in the picture of the inner morphology of PVC reflect the sub micro particles with compact structure. From present study, we can concluded that the more the number of black areas, the wider the molecular weight distribution.

REFERENCES

1. K. Weisskopf and G. Meyerhoff, *Polymer*, **24**, 72 (1983).
2. D. Cheng, A. Kruszewski, J. Senior and T.A. Roberts, *J. Math. Sci.*, **25**, 353 (1990).
3. N. Nakajima and E.R. Harrell, *J. Colloid Interf. Sci.*, **238**, 105 (2001).
4. V. Percec, A. Cappotto and B. Barboiu, *Macromol. Chem. Phys.*, **203**, 1674 (2002).
5. N. Nakajima and C.A. Daniels, *J. Appl. Polym. Sci.*, **25**, 2019 (1980).
6. F. Mahmud, M. Atiqullah, N. Jarrah and I. Hussain, *Eur. Polym. J.*, **28**, 1039 (1992).
7. P. Xu, D. Zhou and D. Zhao, *Eur. Polym. J.*, **25**, 581 (1989).
8. R. Jing and Y. Chen, *Polyvinyl Chloride*, **2**, 17 (1985) (in Chinese).
9. J. Ugelstad, P.C. Mork, F.K. Hansen, K.H. Kaggerud and T. Ellingsen, *Pure Appl. Chem.*, **53**, 323 (1981).
10. J. Wilson and E. Zichy, *Polymer*, **20**, 264 (1979).
11. W. Cooper, R. Speirrs, J. Wilson and E. Zichy, *Polymer*, **20**, 265 (1979).
12. W. Starnes Jr., *Procedia Chem.*, **4**, 1 (2012).
13. J.F.J. Coelho, A.C. Fonseca, P.M.F.O. Gonçalves, A.V. Popov and M.H. Gil, *Polymer*, **52**, 2998 (2011).