

"Fish-eyes" in Poly(vinyl Chloride)

"Fish-eyes" in suspension-polymerized poly(vinyl chloride) (PVC) are particles which gel much slower than the bulk of the resin. They show up in transparent films as ungelled spots which in pigmented compositions remain colorless.¹ They are a serious defect in certain applications of PVC resin such as wrapping material and bottles. The prevailing contention about the origin of "fish-eyes" is still that of Rector,² namely, that they are due to either foreign material such as dust or fibers or to admixtures of PVC of different molecular weight or different polymerization history such as crust from the reactor wall. In the present communication, an observation is reported which shows that "fish-eyes" are also caused by factors besides the above-mentioned ones.

A series of suspension polymerization of vinyl chloride was carried out in this laboratory in a 2-liter S.F.S. glass reactor. Practically the same formulation (amount of water, monomer, initiator, and suspending agent) was used throughout, and the reactions were run at the same temperature to about the same degree of conversion. The only variable was the rate of rotation (rpm) of the agitator. The reactors were meticulously cleaned with tetrahydrofuran after each run so that both foreign PVC and dust were definitely excluded. From the resulting resins, sheets were milled together with stearic acid, calcium stearate, and carbon black for 6 and 8 min. The "fish-eyes" in these sheets show up as translucent points. The results are summarized in Table I. For most rpm, two to three runs were carried out; all counts are tabulated to indicate the degree of reproducibility.

TABLE I

rpm	Number of "fish-eyes" per 25 sq cm	
	6 min milling	8 min milling
500	>1000; >1000	>1000; 400
650	>1000; >1000	125; 100
750	>1000; >1000	375; 200
850	300; 25; 150	60; 1; 3
1000	15; 75; 70; 2; 0	4; 0; 3; 1; 0
1200	7; 0	0; 0
1500	0	0

The reproducibility is far from perfect, yet there is a definite tendency of decreasing "fish-eyes" content with increasing rpm. While runs made with 500 rpm have a high "fish-eyes" content, those made with 1200 rpm are practically free of "fish-eyes."

It is thus evident that "fish-eyes" can be caused not only by dirt and foreign PVC, but also by insufficient and improper agitation. This finding may be of little importance in large commercial production reactors in which the *linear* velocity of agitation exceeds the ones used in the present work; it is of significance in small experimental reactors.

No explanation about the nature of the "fish-eyes" caused by imperfect agitation can be given. Most likely our observation is connected with the change from unicellular grains at low agitation to pluricellular grains at high agitation observed by electron microscopy.³

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References

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