



STUDIES ON THE PROPERTIES OF SUSPENSIVE POLYVINYL CHLORIDE GRAINS SEPARATED BY BLOWING AWAY FROM FLUID BED

Andrzej WASICKI

University of Technology and Agriculture
Faculty of Chemical Technology and Engineering
Seminaryjna 3, 85-326 Bydgoszcz, Poland

ABSTRACT

The studies on properties of polyvinyl chloride grains separated by blowing them away from a fluid bed at three air flow rates have been carried out. Seven trade batches of PVC obtained by suspensive method have been tested. Fikentscher number, thermal stability, plasticizer absorptivity, swelling in plasticizer as well as mixing with plasticizer have been determined. The differences in grain structure in the individual fractions were found in all the batches under study. These differences affect polyvinyl chloride properties (mainly swelling), plasticizer absorptivity and thermal stability.

Keywords: suspensive polyvinyl chloride, grain size, plasticizer absorptivity, thermal stability.

INTRODUCTION

Polyvinyl chloride (PVC) is a mass-produced polymer obtained by emulsion, suspension or mass method. The largest quantities of PVC are produced by suspensive method (in suspension). The polymerization products are powders with different structure and various distribution of grain sizes. Most of suspensive PVC (PVC-S) brands (even with high content of plasticizers) form, in suitable temperature, so called "dry blends" [1]. Ability to form dry mixtures is a significant advantage in processing of plastified PVC-S. Application of dry blends enhances the mechanization of processing and cuts down the time of polymer exposure to high

temperatures and sometimes it allows to omit some operations such as rolling or granulation.

Depending on technological requirements and the expected functional properties of final products, the mixture consists of PVC, plasticizers, stabilizers, fillers and other auxiliaries used in suitable ratios. However, the basic component of all the mixtures is PVC and therefore, its features decide about processing properties of prepared mixtures. As it was proved by numerous studies, the absorptivity of plasticizers and rate of gelation depend on PVC-S grain morphology [2–5]. Grain porosity and very extended surface facilitate penetration of large quantities of plasticizer to PVC and allow to preserve dry and loose form of obtained mixture. It was found that PVC-S brands with better plasticizer absorptivity are characterized also by shorter time of gelation under conditions of processing. Absorptivity of plasticizer and the course of grain gelation depend on their homogeneity [6–8]. Therefore, the manufactures of PVC-S try to deliver the polymer characterized by homogeneous, repeatable morphology of grains. However, even in the case when identical apparatus and technological parameters are applied in processing plants, some differences in properties of PVC-S products are often observed [9, 10]. It results in differences of quality in the individual deliveries of PVC-S denoted even by the same symbol.

The following factors related to polymerization conditions influence the size and morphology of PVC-S grains: stabilizers of suspension, modifiers (auxiliary stabilizers of suspension), inhibitors of polymerization, ratio of water phase - monomer, degree of monomer conversion, temperature of polymerization, heat conductivity of reacting mixture, geometry of apparatus, stirring rate, purity of raw materials and autoclave inside, drying - mainly in the final stage and others [10–16]. Apart from the factors mentioned above, the number of polymerization apparatus in one technological line have also affect the quality of grains in respective production batch. In practice, it is difficult to keep identical polymerization conditions in the individual autoclaves or in the total volume of one big autoclave. Therefore, the polymeric suspensions from various autoclaves are mixed together before drying in order to standardize the produced PVC-S. These operations guarantee the sufficient repeatability of properties in successive PVC-S deliveries, however, they do not ensure the grain homogeneity in respective batches. The respective batch can contain the grains characterized by various morphology what can influence the processing and occurrence of defective products [9, 10]. Homogeneity of grain-size distribution in the respective PVC-S batch was determined by the following methods: sieve analysis, sedimentation analysis, fractionation of grains by density method and by blowing away from fluid bed as well as microscopic and electronmicroscopic methods [2–5, 14–16]. Homogeneity of grain-size distribution can be evaluated more precisely after fractioning the respective PVC-S batch, and then the determination of swelling,

plasticizer absorptivity, and rate of gelating in the individual grain fractions [8, 16].

It was found previously that the most advantageous method of PVC-S grains separation was blowing them away from a fluid bed [17]. The present investigations is aimed at the determination of the properties of PVC-S grains separated by the method mentioned above.

METHODS

Samples from seven trade batches of PVC-S produced by "Anwil" SA in Włocławek (Poland) were investigated. They were denoted by numbers from 1 to 7. Grain separation was carried out by blowing them away from a fluid bed. Separation was carried out periodically at three rates of air flow trough a fluidization column (Fig. 1).

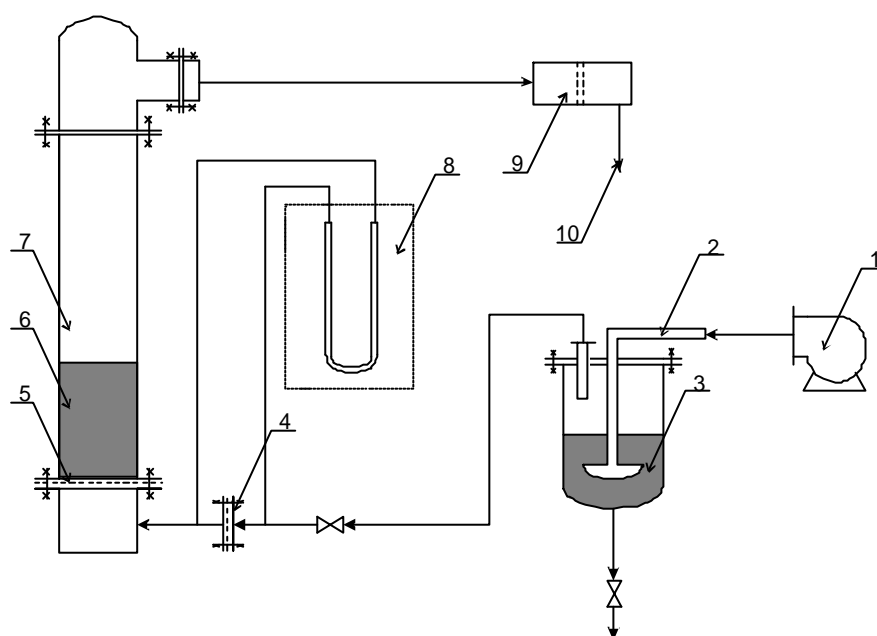


Fig. 1. Diagram of apparatus for PVC-S separation to grain fractions:
 1 – fan, 2 – sparger, 3 – water, 4 – reducing pipe, 5 – porous bottom,
 6 – fluid bed, 7 – fluidization column, 8 – board with manometer,
 9 – sack filter, 10 – collection of grain fractions.

Polyvinyl chloride in the amount of 0.7 kg was introduced into a column. Fractions 1 and 2 were blown away during 2 hours at blowing rates of: 0.05 m/s and 0.1 m/s. Fraction 3 was blown away during 3 hours at blowing rate of: 0.2 m/s. The residue on a sieve, being the column bottom, was accepted as the fourth fraction with largest grain sizes.

Fikentscher number, thermal stability, and plasticizer absorptivity have been determined in the initial PVC-S batches and in separated grain

fractions; the swelling in plasticizer, and operation of mixing with plasticizer have also been studied. Moreover, the grains were observed by a microscope at magnification of approximately 60 times.

Fikentscher number was determined on the basis of the relative density of diluted solutions and fractions in cyclohexanone measured by Ubbelohd's viscometer.

The measure of thermal stability was time (expressed in minutes and seconds) from the moment when the probe with material was immersed in oil bath (180°C) to the moment when Kongo paper changed colour from red to blue.

Determination of plasticizer swelling consisted in measurements of PVC-S linear dimension increments during heating the polymer in primary plasticizer on Boetius' table placed under a microscope equipped with a scaled eyepiece. The grain swelling in plasticizer was observed after plasticizer drop was spread on microscopic slide and the PVC grains were introduced into it. The slide was placed on Boetius' table and preparation image sharpness was adjusted in such a manner that the shapes of several grains could be sharply outlined in transmitting light. The heating rate of Boetius' table was 2°C per minute so that temperature reached 130 – 140 °C in the final phase of measurements. As the temperature increased, the selected grains were measured to the moment of their complete dissolution. Results are presented in the form of dependences between increment of linear dimensions and temperature.

Absorptivity of plasticizer was expressed as an amount (in g) of plasticizer required for moistening the PVC grains. Its determination consisted in introducing of the plasticizer excessive amount into the sample, centrifuging the mixture and then calculating the quantity of plasticizer absorbed by the sample. The value of plasticizer absorptivity determines PVC usability for dry blends preparation.

Studies on grain mixing with plasticizer were carried out in Brabender's plastograph equipped with closed crusher. Investigations consisted in measurements of torque changes during mixing of blend in which swelling of PVC-S grains occurred under the action of plasticizer and the raised temperature. Swelling of grains caused the rapid increase of torque. In the aim to prepare the blends, the following quantities of components were weighted: 28 g of PVC, 20.5 g of plasticizer (dioctyl phtalate) and stabilizers in amounts of: 1 g of tribasic lead sulphate and 0.5 g of dibasic lead stearate. After temperature had been stabilized, 2/3 of PVC and stabilizers were poured into a crusher chamber. Then, plasticizer was proportioned by syringe. By using the key with piston, the rest of PVC was introduced into crusher while the stirrers were rotating. Mixing operation was observed for 20–40 min.

RESULTS AND DISCUSSION

Three or four fractions with various grain sizes were obtained as a result of operations carried out (Tab. 1). The fourth fraction was characterized by the grains of the largest grain sizes and the first fraction by the smallest ones. Percentages of fractions and losses are presented in Table 1. In three separated batches, we did not obtain the grains which separation would be possible at the lowest blowing away rate.

Tab. 1. Percentage by weight of PVC-s grain fractions.

No. of batch	1 PVC-S67	2 PVC-S67	3 PVC-S70	4 PVC-S67	5 PVC-S67	6 PVC-S58	7 PVC-S61
F R A C T I O N	1	0,14	0,00	0,00	1,19	0,68	1,63
	2	0,40	0,27	2,04	0,54	3,84	5,31
	3	8,16	8,70	49,00	14,00	44,82	43,54
	4	87,34	85,98	46,25	80,80	45,45	46,67
loss	3,96	5,05	2,71	4,66	4,70	4,62	2,85

On the basis of microscopic observations in the transmitting and reflected light, it was found that all the studied PVC-S batches showed the significant heterogeneity of the grain shapes and sizes (Fig. 2). The differences in the surface appearance of the individual grains were also observed. The appearance of the larger grains was similar to "snow balls", however, that of the smaller ones (e.g. fraction 1. and 2.) was as "glassy beads". All the PVC-S batches were characterized by the significant scattering of grain sizes ranging from 5 to 200 μm .

Fikentscher number (so called *K* number) characterizes PVC molecular weight and gives information about the average length of macromolecular chains. Its value is of the basic importance for the later processing. The values of *K* number were only slightly various for 2, 3 and 4 fractions for the most of PVC batches studied (Table 2). It was found that it was impossible to determine only one PCV fraction deciding about *K* number of the complete batch which was not blowing away.

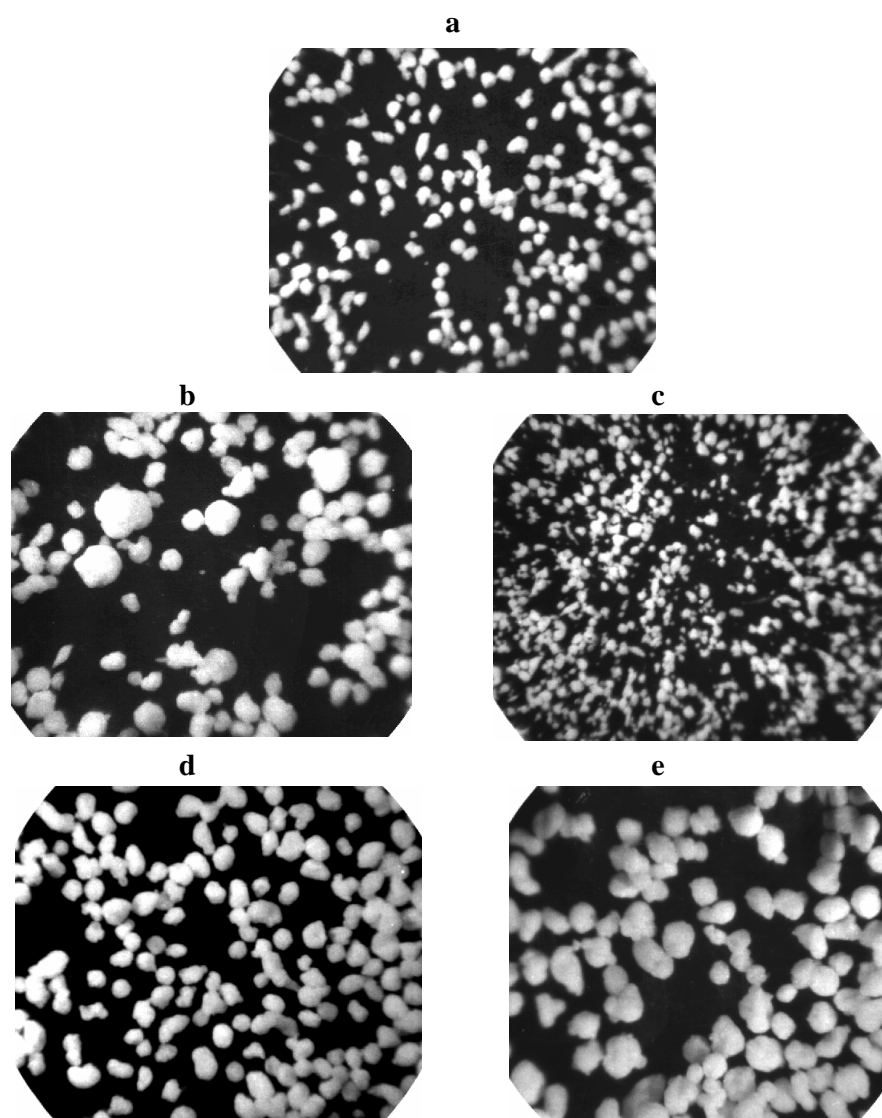


Fig. 2. Microscopic images of non-separated batch 6 (a) and of four fractions obtained (b-e).

Determination of plasticizer absorptivity with the application of dioctyl phthalate did not give the expected results; the results were random. Therefore, this test was repeated using silicon oil (Polsil OM 300) which did not induce swelling of PVC grains. The increase of oil absorptivity was in direct proportion with the increase of grain sizes for each batch studied (Tab. 3).

Tab. 2. Fikentscher numbers of the complete unblown away batch and separated grain fractions.

No. of batch	1 PVC- S67	2 PVC- S67	3 PVC- S70	4 PVC- S67	5 PVC- S67	6 PVC- S58	7 PVC- S61	
0	66,3	65,2	68,1	67,0	67,7	57,0	60,5	
F R A C T I O N	1	69,0	-	-	-	67,8	55,8	60,0
	2	66,0	67,5	69,2	66,0	67,5	58,0	60,5
	3	65,5	69,2	68,0	66,8	67,5	55,5	60,0
	4	66,3	64,8	68,2	67,2	68,0	55,8	61,2

Tab. 3. Silicon oil absorption.

No. of batch	1 PVC S-67	2 PVC S-67	3 PVC S-70	4 PVC S-67	5 PVC S-67	6 PVC S-58	7 PVC S-61	
0	0,1964	0,2368	0,2175	0,2351	0,1775	0,1496	0,1853	
F R A C T I O N	1	0,183	-	-	-	0,166	0,142	0,134
	2	0,189	0,2334	0,2163	0,219	0,202	0,126	0,182
	3	0,193	0,236	0,219	0,230	0,177	0,158	0,185
	4	0,202	0,240	0,214	0,238	0,176	0,131	0,201

Determination of the heat distortion point of suspensive polyvinyl chloride consisted in measurement of time required for liberation of detectable quantities of hydrogen chloride from polymer subjected to the action of high temperature. Generally, we can state that thermal stability was higher for the finest fractions (1 and 2) and lower one for fractions with larger grains (3 and 4) (Fig. 3).

It was found that the preliminary softening temperature of the PVC batches under the study was within the range from 95 to 105 °C and inhibition of grain growth occurred at 110 °C or 120 °C. Fluidity of grains occurred after reaching 140 °C or 150 °C. For all the PVC-S batches studied, the increment of the linear dimension of grains in fraction 1. was higher than that in fraction 4. The value of grain swelling was inversely proportional to grain sizes (Fig. 4).

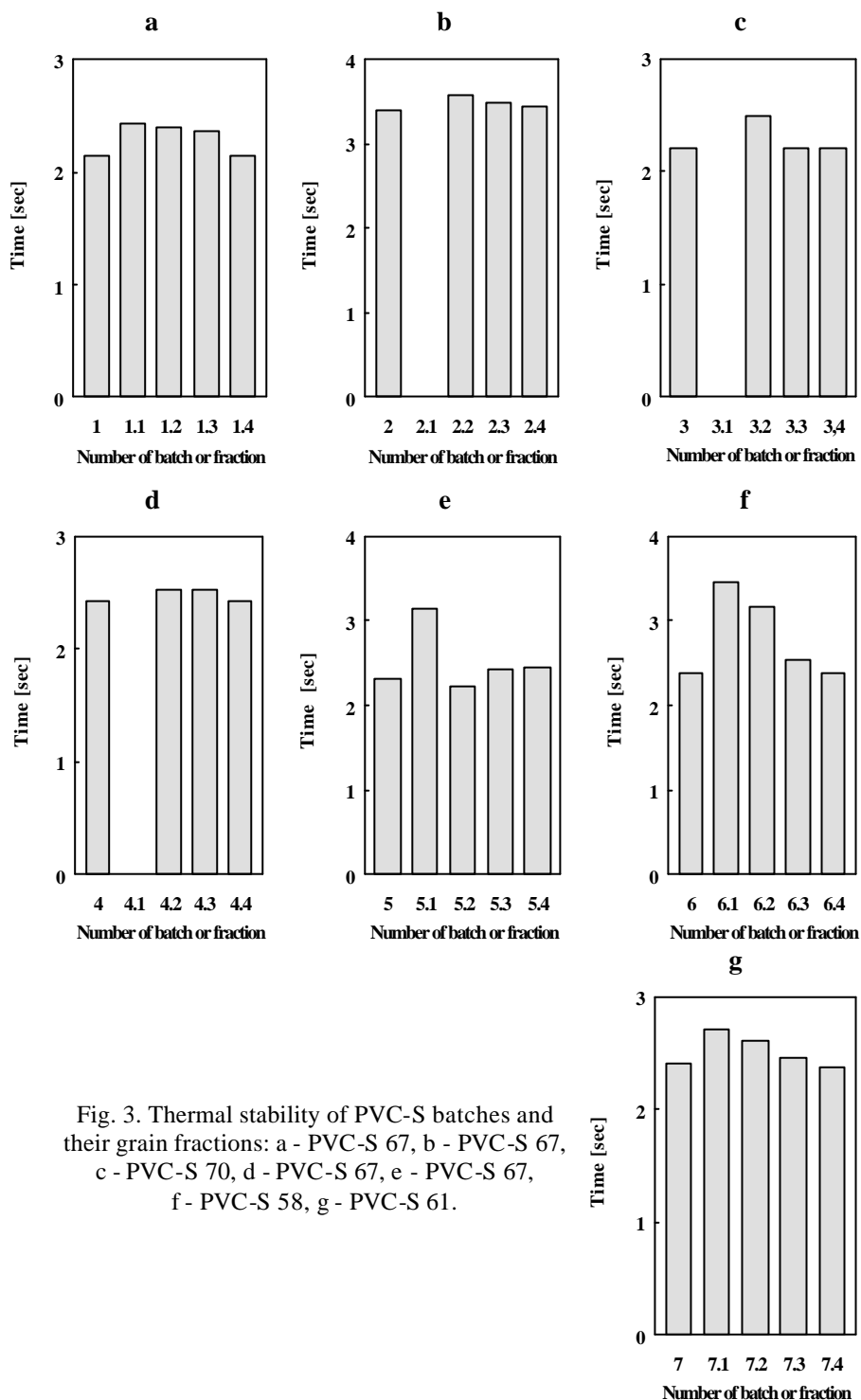


Fig. 3. Thermal stability of PVC-S batches and their grain fractions: a - PVC-S 67, b - PVC-S 67, c - PVC-S 70, d - PVC-S 67, e - PVC-S 67, f - PVC-S 58, g - PVC-S 61.

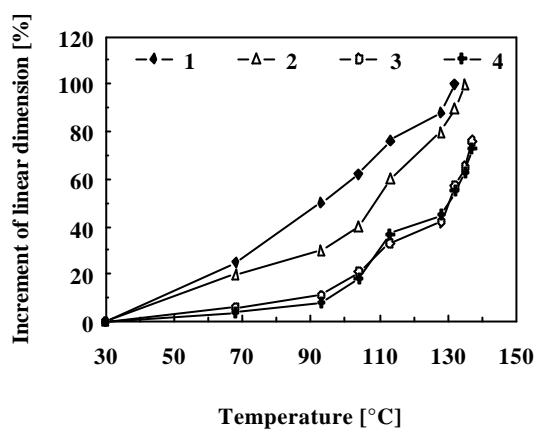


Fig. 4. Changes of average linear dimension of grains (from four fractions of batch) immersed in plasticizer at rising temperature to the moment of grain dissolution: 1 – fraction 1, 2 – fraction 2, 3 – fraction 3, 4 – fraction 4.

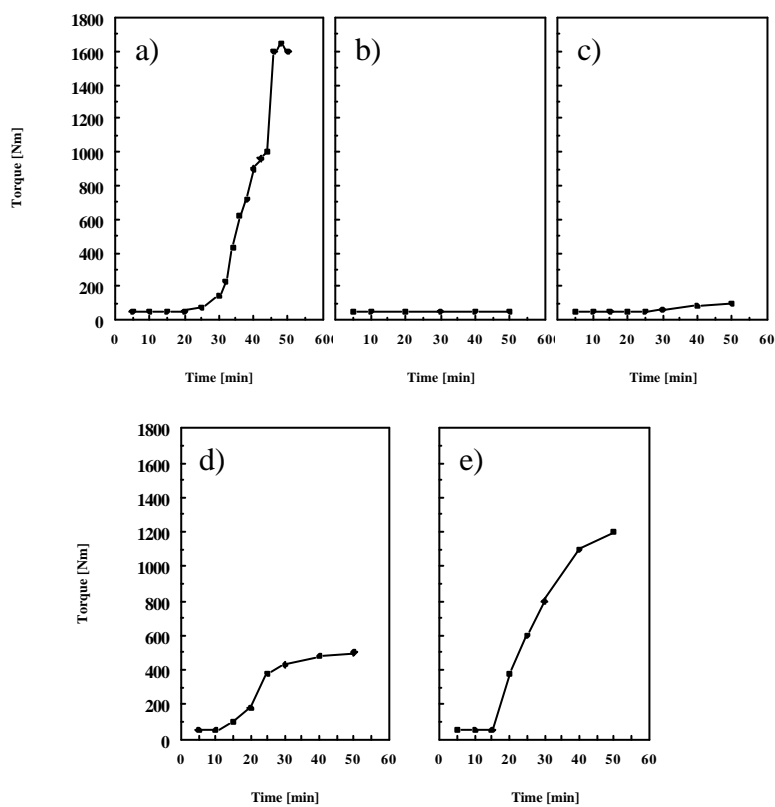


Fig. 5. Mixing plastograms at rising (a) and constant (b-e) temperature a - 80°C - 110°C, b - 82°C, c - 84°C, d - 88°C, e - 95°C.

The investigations of dry blend formation were carried out for all the fractions and unblowed sample of batch 7 (PVC-S 61) (Fig. 5).

The attempts to establish one - common for all the fractions - temperature at which the blend got the form of dry blend i.e. it reached "dry point" (T_s) were made during the investigations. This temperature was approximately $84\text{ }^{\circ}\text{C} \pm 0.5$ for unblowed sample and fraction 4, but, for the other fractions it was $86\text{ }^{\circ}\text{C} \pm 0.5$.

CONCLUSIONS REMARKS

1. It was found that the grain sizes were heterogeneous in the individual batches. The highest percentage participation of fraction 4 (i.e. fraction with the largest grains and the longest time of polymerization) was observed in each batch. The lowest percentage participation was obtained in the case of fraction 1 i.e. with the finest grain sizes.
2. Analysis of the thermal stability of PVC-S batches studied (the first fractions neglected) allowed us to conclude about the lack or only slight effect of the structure on the thermal stability. The thermal stability of the first fraction was various; it was lower or higher depending on the type of sample.
3. Observations of PVC-S grains swelling allowed us to conclude that their structure was various and affects the course of curves. The increment of the grain linear dimensions was inversely proportional to the grain size for each PVC-S batch under the studies. However, time of swelling in the given batch was similar but different for various batches of PVC-S.
4. Our studies confirmed the significant effect of PVC grain structure on their susceptibility to the action of plasticizer. It results from the analysis of curve course for mixing and plasticizer absorptivity that T_s parameter (time when dry point is reached) increased as the grain size was increased. The results point out the general dependence between T_s time and the absorbtivity of silicon oil. Time when dry blend was obtained was longer as the absorbtivity was decreased.

Generally, the differences of the grain structure in the individual fractions were observed for all the batches under the study. These differences have an effect on properties of polyvinyl chloride, mainly on swelling, plasticiser absorptivity and thermal resistance. It was observed the most distinctly in the fifth (PVC-S 67) and the seventh (PVC-S 61) batch.

REFERENCES

- [1] M. Oblój-Muzaj, B. Swierz-Motysia, B. Szablowska, *Polichlorek winylu*, WNT, Warszawa, 1997 (in Polish).
- [2] V. L. Balakirskaya, O. A. Piekaryeva, B. P. Shtarkman, *Vysokomol. Soed.* 1968, A10, 883.
- [3] G. Buchman, K. Grill, *Kunststoffe* 1961, 51, 21.
- [4] V.N. Cvietkov, V.S. Gorshkov, M.P. Voronina, *Plast. Massy* 1970, no. 10, 50.
- [5] K. Bischof, K. Lorenz, *Plaste und Kautschuk* 1963, 10, 201.
- [6] L.N. Malyshev, B.P. Shtarkman: *Plast. Massy* 1971, no. 12, 19.
- [7] J. Skraga, S. Zajchowski, K. Piszczek, K. Szymanski, *Polimery (Warsaw)* 1979, 24, 229.
- [8] S. Zajchowski, J. Skraga, K. Piszczek, *Polimery (Warsaw)* 1980, 25, 94.
- [9] J. Skraga, A. Wasicki, J. Kania, *Sci. Papers UT-A Bydgoszcz* 1975, no. 15, 73 (in Polish).
- [10] O. Leuchs, *Kunststoffe* 1960, 50, 227.
- [11] J. Skraga, S. Zajchowski, K. Piszczek, I. Zubek, *Sci. Papers UT-A Bydgoszcz* 1975, no. 15, 87 (in Polish).
- [12] P.N. Bort, E.E. Rylov, N.A. Okladov, *Vysokomol. Soed.* 1965, 7, 50.
- [13] N.L. Sirotkina, V.S. Gorshkov, *Plast. Massy* 1969, no. 10, 65.
- [14] J. Lunkiewicz, W. Dahlig, *Polimery (Warsaw)* 1971, 15, 1.
- [15] W. Dahlig, W. Kocimowski, J. Lunkiewicz, *Polimery (Warsaw)* 1974, 19, 154.
- [16] H. Luther, F.O. Glander, E. Schleese: *Kunststoffe* 1962, 7, 52.
- [17] K. Piszczek, A. Wasicki, S. Zajchowski, *Study of Properties PVC-S Grains Separate Dissagregation by Different Methods*, proc. XIIIth Int. Symp. ARS SEPARATORIA, Gniew, Poland, 1998.