

FRAUNHOFER DIFFRACTION LASER MULTICHANNEL PHOTOPASTEGRAPHIC
(FDLMP) MEASUREMENT OF CROSSLINKING IN CHEMICALLY
MODIFIED WAXY CORN STARCH

by

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TABLE OF CONTENTS

	Page
INTRODUCTION	1
REVIEW OF LITERATURE	3
What Starch Is	3
Crosslinked Starches	4
Effects of pH.	5
Starch Gelatinization	6
Characterization of Starch Pasting	6
Gelatinization Temperature	8
Viscometry	8
Viscosity of Starch Pastes	10
Photopasteography.	10
Fraunhofer Diffraction Laser Multichannel Photopasteography (FDLMP)	12
MATERIALS AND METHODS.	14
Materials.	14
Methods.	14
A. Microscopy.	14
B. Viscometry.	14
C. Fraunhofer Diffraction Laser Multichannel Photopaste- ography (FDLMP).	15
D. Refractive Index.	19
E. Mechanical Degradation Kinetics Study	19
DISCUSSION	21
Microscopy	21
Viscometry and Effect of Acidification	21
Conventional FDLMP	24
FDLMP with Gravity Flow	30

	Page
FDLMP with the Peristaltic Pump.	38
Refractive Index as a Factor	44
Mechanical Degradation Kinetics Study.	46
Off-line FDLMP Parameters.	61
Determination of the Degree of Crosslinking by off-line FDLMP.	63
Recommendations.	66
Conclusions.	67
LITERATURE CITED	69
APPENDICES	75

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1. Optical system of the Leeds and Northrup Microtrac Particle Size Analyzer.	16
2. Schematic view of recirculating sample system.	16
3. Brabender amylograms on corn starches.	22
4. FDLMP (relative PHV) on waxy corn starch and its crosslinked modifications.	25
5. Maximum relative PHV and amount of crosslinking reagent, conventional FDLMP	26
6. Temperature of maximum RPHV and amount of crosslinking reagent.	26
7. FDLMP (median diameter) on waxy corn starch and its cross-linked modifications	27
8. Gravity flow FDLMP (relative PHV) on waxy corn starch and its crosslinked modifications.	31
9. Gravity flow FDLMP (median diameter) on waxy corn starch and its crosslinked modifications.	32
10. Conventional and gravity flow FDLMP particle size distributions of WM-0.	34
11. Conventional and gravity flow FDLMP particle size distributions of WM-.05.	35
12. Conventional and gravity flow FDLMP particle size distributions of WM-.08.	36
13. Conventional and gravity flow FDLMP particle size distributions of WM-.13.	37
14. WM-0 relative PHV photopasteograms compared.	39
15. WM-.13 relative PHV photopasteograms compared.	40
16. WM-0 photopasteograms of median diameter compared.	41
17. WM-.13 photopasteograms of median diameter compared.	42
18. Comparison of particle size distributions of WM-.13.	43
19. Effect of impeller pump shearing on waxy corn starch	47

	<u>Page</u>
20. Effect of impeller pump shearing on WM-.05.	48
21a. Effect of impeller pump shearing on WM-.08.	49
21b. Effect of impeller pump shearing on WM-.08.	50
22a. Effect of impeller pump shearing on Wm-.13.	51
22b. Effect of impeller pump shearing on WM-.13.	52
23. Off-line FDLMP on WM-0.	56
24. Off-line FDLMP on WM-.05.	57
25. Off-line FDLMP on Wm-.08.	58
26. Off-line FDLMP on WM-.13.	59
27. How maximum relative PHV varies with crosslinking at various time exposures to shear	66
28. How relative PHV at 77°C and 209 seconds of shear exposure varies with crosslinking.	67

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1. Gelatinization temperature ranges of modified waxy corn starches.	21
2. Selected conventional FDLMP parameters.	28
3. Selected parameters of FDLMP with gravity flow.	28
4. Off-line FDLMP parameters.	63

INTRODUCTION

The starch granule has been called elusive (1); starch chemistry, anomalous (2, 3). Starch has had a broad spectrum of uses; from the most trivial like powdering hair (4), to the most fundamental - food. It is with this two-fold charm, elusiveness and usefulness, that starch has attracted much study.

The gelatinization behavior of starch has been one of its more elusive aspects. Although, basically, one chemical formula covers starch of all botanical origins (5), starch pasting behavior varies. It is characteristic of its botanical source, preparation procedure, and other elements of its historical background (6).

Understanding and characterization of starch pasting however, is important. Major uses of starch in one way or the other involve this phenomenon (7). It occurs in many food processing operations - the baking of bread and cakes, the extrusion of cereal-based products, the production of soups and many others (8). In food product formulations it is utilized to achieve the right rheological property, certain degrees of transparency, a desired mouthfeel that might spell acceptability or otherwise for the food product.

In all these, wise choices will have to be based on collections of laboratory data. This is most especially true for developing countries, where research facilities, equipment and technical knowhow are not readily available.

Quite a number of methods have been devised to generate data at one or more stages, on one or more manifestations of starch pasting. One of

these is photopasteography. The method was not considered sensitive enough for determining initial gelatinization (9). Kainuma et al. (10), however, were able to increase sensitivity of the measurement such that evidence of pasting could be found at much lower temperatures than before.

Here in Kansas State University, D. L. Wetzel and M. S. Gilmore (5) modified a commercial particle measuring instrument introducing Fraunhofer diffraction laser multichannel photopasteography (FDLMP) to catalog the pasting parameters of a broad variety of starches.

FDLMP data gave rise to a paradox. The quantitative and linear nature of the FDLMP response to crosslinking makes the technique useful and the results difficult to ignore but the relative granule sizes reported upon pasting and the magnitude of the optical responses to pasting were not in the order one would expect from perusal of starch literature.

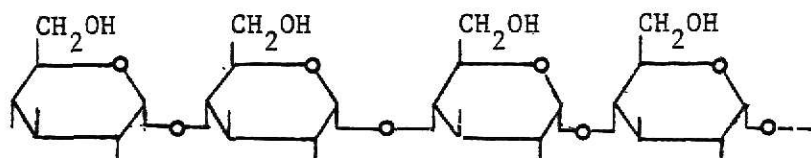
It was the purpose of this study to find out what caused the unrealistic data. It was also its purpose to inquire deeper into what kind of pasting measure the FDLMP could offer. To do so, the pasting behavior of a family of starches differing only in the degree of crosslinking and previously studied with the FDLMP was differentially characterized using modifications of the FDLMP method coupled with other parallel starch pasting measures.

REVIEW OF LITERATURE

What Starch Is

Starch is the chief source of dietary carbohydrates for man and makes up the reserve food supply of all plant life (11). Microscopic examination has shown that starch is organized into tiny granules, the physical appearance of which is characteristic of the plant origin (11). Size of the granules varies from 5 to 100 μm in diameter (7).

Starch granules are made up of a mixture of polymers of D-glucose. Details of their structure had to await the fractionation work done by T. J. Schoch (12, 13). Models of these polymers, amylose and amylopectin, had been proposed by Nikuni (14). Amylose is a linear polymer containing only glycosidic bonds; the molecular weight of which varies from a few thousand to 150,000 (15).

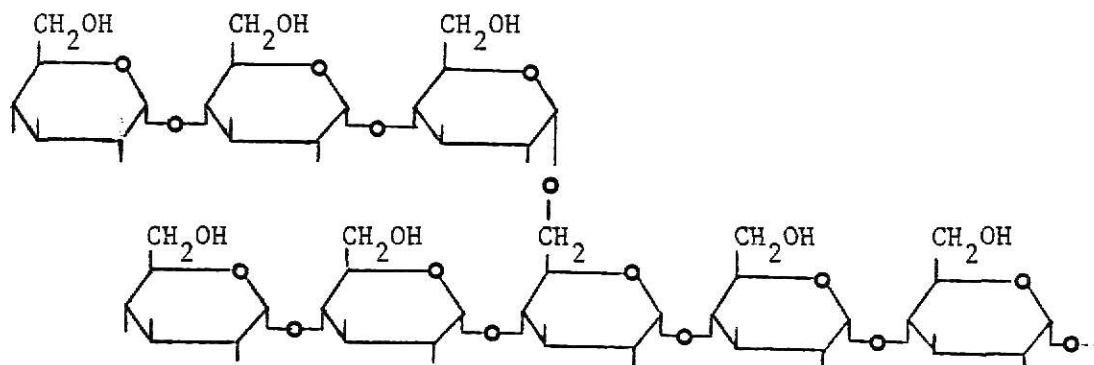


Amylose

Amylopectin is a highly branched polymer primarily containing α -(1 $\rightarrow$ 4) glycosidic linkages with periodic α -(1 $\rightarrow$ 6) linkages (15). The molecular weight of amylopectin is generally believed to be over a million.

Normally, starches contain about 25% amylose and 75% amylopectin, but some varieties of cereal grains produce waxy starches which are about 99% amylopectin (7).

Whenever the linear portions of starch molecules are arranged in



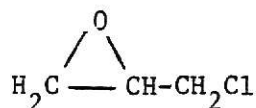
Amylopectin

parallel fashion, because they can form hydrogen bonds, crystalline or micellar regions appear (11). About two-thirds of the molecules are not arranged in such fashion. They are also associated by hydrogen bonding but more loosely. The regions occupied by these are called amorphous regions (16). The crystalline structure gives rise to the birefringence observed under the polarizing microscope (17). A recent study by Sarko and Wu (18) on crystal structures of amylose and starch revealed the similarities and differences between the A-starch of cereals and the B-starch of tubers and roots.

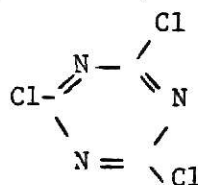
Crosslinked Starches

Natural starches are sometimes modified to meet special needs in their specific uses. One type of modification is chemical crosslinking. The term "crosslinked starch" normally implies inter-molecular bridges even though intramolecular links also take place (19).

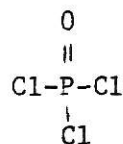
Some of the compounds used in crosslinking starch include epichlorohydrin, phosphorus oxychloride, (20) cyanuric chloride, and succinic anhydride (21).



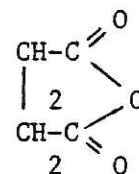
epichlorohydrin



cyanuric chloride

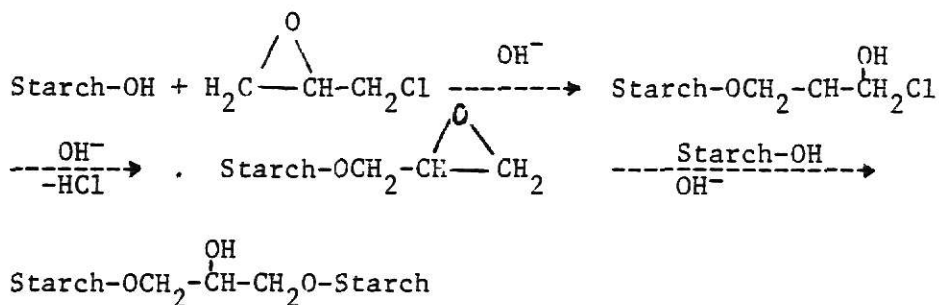


phosphorus oxychloride



succinic anhydride

These compounds are capable of reacting simultaneously with two or more hydroxyl groups of the starch to form the crosslinks. As with epichlorohydrin, the reaction as given by Roberts (19) is:



Chabot et al (22) found no substantial differences in the structure of the granules related to the type of crosslinking agent used but they found substantial differences between the unmodified starches versus their crosslinked counterparts. They found that crosslinking starch increased stability during cooking especially under shear or acid conditions.

Effects of pH

The pH values of most foods are in the range of 4-7 (21); though some bakery goods like crackers have a pH of 7.0- 8.5 and devils food cake, 7.5-8.4 (23). Variations in the 4-7 pH range have negligible effect on granule expansion and viscosity, though in strongly alkaline solutions

(pH=10) increased rate of swelling had been observed. Acid conditions can cause hydrolytic cleavage hastening gelatinization and increasing granule fragility (21).

Starch Gelatinization

In proportion to the relative humidity of the atmosphere, the hydrophilic groups of the starch molecule cause it to take water; 12-14% for cereal starches under normal conditions (21). Placed in cold water, the starch granule can reach 30% moisture content (21) without noticeable swelling, except under careful observation under the microscope. When the water is heated to a temperature high enough to furnish energy to break hydrogen bonds in the amorphous regions, the swelling becomes noticeable and birefringence is lost. Further heating causes more loosening of the granule meshwork and allows more water to enter forming an expanded network of micelles. Either due to temperature, agitation or both, there is a release of exudate identified as amylose (24).

Characterization of Starch Pasting

The pasting of starch has been observed in many ways. El Saadany et al (25) found that irradiation decreased the viscosity and the swelling power, but increased the solubility of rice starch. Hizukuri and Takeda (6) explored the effect of alcohol on pasting of cereal starches. Watson and Johnson (26) showed that gelatinization could be inhibited by protein and various cellulose derivatives especially at moisture levels below 80%. Medcalfe et al. working on wheat starches (27) theorized that polar lipid fractions prevent hydration of amorphous regions while non-polar lipid fractions prevent hydration of the crystalline regions. This was to explain the observed lowering of viscosity with polar lipid frac-

tions and greater maximum viscosities with nonpolar lipid fractions.

Various methods have been used to measure starch pasting. On the molecular level, pulsed NMR was used by Lelievre and Mitchell (28) to detect mobility and hydration of the polymer chains. Also with proton magnetic resonance, Jaska (29) determined gelatinization temperature range and solubility. Water-binding capacity and the influence of starch type and modification on endothermic changes associated with gelatinization was investigated by Wooton and Bamunuarachchi (30, 31) with differential scanning calorimetry. The dependence of loss of birefringence on the temperature jump was studied by Marchant and Blanshard (8) using a small angle light scattering system on granules mounted on microscope glass coverslips.

The scanning electron microscope, in spite of its limitation to a very small sample and an incapability for a continuous observation of pasting, has proved a useful tool in revealing ultrastructure of starch granules before, at selected stages during, and after pasting (22, 32, 33, 34).

The more common and perhaps more practical methods used to observe and measure starch pasting are light microscopy, viscometry, photopastography, and measurements of swelling power and solubility.

Measurements of swelling power and solubility (35, 36) consists essentially of heating a starch suspension to the desired temperature in a constant temperature bath for 30 minutes, centrifuging the mixture, drawing off the supernate and drying it to get the % solubles. The weight of the sedimented paste gives a measure of the swelling power. The procedure is very time consuming (36), laborious and requires much skill, care and patience especially if the characterization is to be

done over the whole pasting process, even if determinations are to be made at the suggested 5° intervals from 60 - 95°C.

Gelatinization Temperature

The determination of the gelatinization temperature, a temperature range at which the granules of a starch sample lose birefringence is a widely used method. It is usually determined with an electrically heated microscope hot stage and a polarizing microscope. The starch granules are watched for disappearance of polarization crosses (37). Gough and Pybus (38) say that the gelatinization temperature of starch is independent of heating and is regarded as a function of the crystalline structure of the granule. Marchant and Blanshard (8) wrote that it reflects the reduction in the intra-intermolecular ordering in the granule. Hill and Dronzek (34) finding exudate coming from the granules at low temperature associated this with the loss of birefringence.

Determination of the gelatinization temperature by watching the polarization crosses disappear deceptively appears simple, but it is not. It requires much practice and is quite subjective. The sample being too small, it is virtually impossible to make a large enough number of observations to give good statistical validity (5).

Viscometry

Viscosity measurement seems to be the most widely used starch pasting measure method. It is perhaps because important changes in viscosity and other rheological properties of a starch paste indicate utility of products in specific applications and because they reflect properties encountered by the user during the preparation of products (39).

The Brabender amylograph, which in studies seems to be the most pre-

ferred viscometric equipment, is described as a rotational device which permits continuous determination of viscosity while cooking the starch paste. There is a rotating sample cup or bowl which contains a number of fixed vertical pins and is driven at a constant speed by a synchronous motor. A circular disc with metal pins projecting vertically downward into the sample, dynamically balanced by a torsion spring serves as a sensing element. An angular deflection of the sensing element shaft accompanies the application of the restoring force and this is continuously recorded on a strip chart recorder (39).

The maximum viscosity that may be encountered during cooking of the starch, the ease in cooking it, the stability of the paste, and the set-back on cooling are some of the information that the Brabender curves can furnish (39).

In spite of the apparent practicality of viscometric measure, Myers and Knauss (40) wondered if viscometry of starch pastes is worth the effort saying that all reported starch viscosities were of limited value because of the arbitrary nature of the conditions under which they were determined. They wrote that most viscosity measures involve breakdown of structure by shear when the relationship between viscosity and shear had not been demonstrated as cause-and-effect.

Sandstedt and Abbott (41) comparing various starch pasting measure methods indicated how viscometric measures fail to show early stages of pasting and how with change in starch concentration, the apparent temperature of pasting also changed. A 35% wheat starch gave an apparent pasting temperature of 58°C while a 6.2 slurry of the same starch, a pasting temperature of 87°C .

There are many viscometric procedures based on rotational devices

and flowthrough orifices. For control testing of thin-boiling starches during manufacturing, Poyser and Wright (42) had come up with an automatic viscometer.

Viscosity of Starch Pastes

What makes for the viscosity of a starch paste is still not very clear. Schoch (17) wrote that a cooked starch paste develops viscosity when the granules become sufficiently swollen to crowd one another. Leach (9) assigned a major role in viscosity to the expanded network of micelles giving the granules elastic properties. Miller et al (32) in their study on wheat starches concluded that it is the exudate, not the swollen granules that cause viscosity. Hill and Dronzek (34) and Allen et al.(33) also noted appearance of extragranular material before an increase of viscosity could be observed. Hood (43) in his discussion on corn starches wrote that both the exudate and the swollen granules contribute to viscosity development as peak viscosity is approached.

Loney et al.(44) working on wheat starch said it is the high amylose in solution that increases the pasting strength. Though not in exact contradiction, Juliano and Perdon (45) felt it is the amylopectin rather than amylose that is the major contributor to viscosity of rice starch pastes.

Photopasteography

Photopasteography has traditionally consisted of recording the relative turbidity of a starch suspension through the various stages of the pasting process (5). Early work done by Cook and Axtmayer (46) on tropical starches revealed that photopasteograms can be used for identifying starches. Morgan (47) showed that the light transmission patterns of

tapioca starch modified by oxidative treatment can indicate the extent of modification since the modification can make the starch to paste at a lower temperature. Both of these studies made use of unfiltered light for measuring transmittance changes. Beckord and Sandstedt (48), on the other hand, adapted the spectrophotometer for observing the pasting properties of various starches.

Sandstedt and Abbott (41) showed that light transmission curves are essentially similar to viscosity, swelling, and solubility curves. Leach (9), however, pointed out the lack in sensitivity of photopasteography saying that the granules in a 1% aqueous dispersion must have absorbed 15 times their own weight of water to increase the transmittance by only 3%.

With a modified automatic titration equipment, Kainuma et al. (10) studied the pasting of corn starch at varying filter-selected incident radiation. The significance of the method was in the use of radiation of shorter wavelength ($372\mu\text{m}$) with which minor changes in transmittance caused by initial changes in the starch granules could be detected. Pasting changes at temperatures from 5 to 10°C lower than the conventional methods were observed.

Kainuma et al. (10) measured transmitted radiation at filter-selected wavelengths. Measurements were taken with continuous stirring through an optical cell of 3.7 cm. I.D. with starch concentration of 50-100 mg. (D.B.) in 50 ml. of water and a temperature ramp of $2^{\circ}\text{C}/\text{min.}$ from 30°C to 98°C . He reported photopasteograms of corn starch, potato starch and sweet potato starch. He plotted Transmittance as a function of temperature using a linear temperature program. The corn starch which he studied showed a decrease in Transmittance from an initial setting of ca. 17% to

a low of ca. 10% occurring at ca. 68°C. Initial changes were noted at ca. 62°C. Kainuma continued to measure the Transmittance which returns to the initial level at ca. 72°C and continued to rise to virtual transparency with an 88% T reading at 98°C. The shapes of such Transmittance curves were reportedly characteristic of different starches.

Fraunhofer Diffraction Laser Multichannel Photopasteography (FDLMP)

Since it is the FDLMP that is of particular interest in this study, a more detailed description of equipment and procedure is found under Materials and Methods.

Briefly it involves obtaining a measure of the total particulate hard volume (PHV) and the median diameter of the starch particles as a suspension of the starch sample is heated and undergoes pasting. Measurement is done with a particle size analyzer equipped to determine among other information, the size distribution by volume of small (1.9-176 μ m diameter) particles from their laser light scattering. The theory and mathematical considerations behind the particle analyzer is given by Wertheimer and Wilcock (49) and the principle of operation, by Weiss and Frock (50). Additional design and functional details as well as their limitations will be found under the discussion section.

Wetzel and Gilmore (5) listed the advantages of the multichannel photopasteography as follows:

1. As the aqueous starch slurry is cycled through the cell, the particle size analyzer rapidly collects data on it and gives a 13-channel histogram showing the distribution of the starch particles re size throughout the pasting process.

2. Unlike turbidimetric measurements where light scattering varies as a function of particle size, the calculated size measurement obtained

with the instrument takes into account the population of each size channel and the differences in light scattering characteristics for particles of different sizes are compensated for in the summative equation.

3. Unlike in microscopy, with FDLMP, a large number of particles is measured.

4. The system operates effectively at what can be called as infinite dilution, hence each particle is able to act independently.

Wetzel and Gilmore (5) enumerated the limitations of the FDLMP as:

1. The wavelength used sets the lower limit of the size that can be monitored.

2. The optical system does not provide for indication of the point of loss of birefringence.

3. It does not necessarily reflect the behavior in a limited water system.

4. A practical temperature of ca. 85°C is imposed by bubble formation and thermal limitations of the optical cell.

Wetzel and Rooney (51) using two different lines of field-selected 0-3 non-waxy dose grain sorghum crosses reported that FDLMP data was indicative of the genetic trait of non-waxiness. Linear correlation was observed both with magnitude and temperature of occurrence of pasting.

Unpublished data of Wetzel and Stalnaker (52) indicated that a linear measure of the extent of crosslinking of chemically modified corn starch may be effected by FDLMP. They also noted that combination of starches with different levels of crosslinking would not result in pasting properties predicted by direct interpolation.

MATERIALS AND METHODS

Materials:

Four corn starches: WM-0, WM-.05, WM-.08 and WM-.13 were studied. WM-0 is normal waxy corn starch with zero modification. WM-.05, WM-.08, and WM-.13 are corn starches of .05, .08 and .13 relative degrees of non-waxiness achieved by modification of WM-0 through chemical crosslinking with phosphorous oxychloride as crosslinking reagent. The parent waxy starch and the chemical modifications thereof were provided by American Maize (Hammond, Indiana). Common commercial corn starch with the Monarch brand to use for comparison was obtained at a local food store.

Local tap water of pH 9.35, debubbled and degassed as described later, was used.

Methods:

A. Microscopy

The gelatinization temperature range was determined with a Kofler microscope hot stage and a polarizing microscope. The method used was by Watson (37) except that instead of the suggested 100 to 200 granules, only 25 were continuously watched. The granule sizes were observed before and after loss of birefringence. The same samples were sent to another laboratory for the same measure.

B. Viscometry

Viscosity was measured with a visco-amylo-graph, Model no. 736 of C. W. Brabender (North Hackensack, N. J.) and according to a modified method here described.

Sufficient distilled water was added to 25.3 g (D.B.) starch sample to bring the total weight to 460 g. Using the 700 g cm cartridge, the

amylograph was started at 65°C and the slurry was heated till it reached 95°C, after which it was held at that temperature for 15 minutes. Amylograms of the same samples were also obtained using exactly the same procedure except for the addition of 8 ml of glacial acetic acid.

C. Fraunhofer Diffraction Laser Multichannel Photopasteography (FDLMP)

The equipment for the FDLMP as described by Wetzel and Gilmore (5) consisted of a Leeds and Northrup Microtrac Particle Size Analyzer as the basic instrument. The instrument is equipped with a 2 mW helium-neon laser, the light of which strikes the particles of the sample as they pass through an optical cell (see Fig. 1). As the light from the laser strikes the particle, it is diffracted at a small angle in a forward direction and this diffracted light is sorted out in space by a special mask and shutter system. It is then focused onto a detector, and the photocurrent at different periods of time on the detector are digitized and fed to a microprocessor built into the instrument. The microprocessor solves the necessary equations to generate the 13-channel histogram. A digital printer makes a printout of individual channels as well as the summative data.

The sample slurry is recirculated from the mixing bowl to the sample cell (Fig. 2) by means of a pump. The pump, later suspected of shearing the pasted granules, is a P-6 model from Eastern Pumps Products Division Hamden, Conn.). It has a 4-vaned impeller with a 0.025/0.035 inch clearance from the adjacent wall of the adapter and an rpm of 3200. From the supply line, water for the sample slurry is first passed through a filter, then through a needle valve and into an expansion chamber in the instrument to debubble and degass it before it enters the mixing bowl.

For FDLMP purposes, the Microtrac Analyzer was modified by insulating the mixing bowl and by applying silicon rubber sealant (DOW) at the glass/

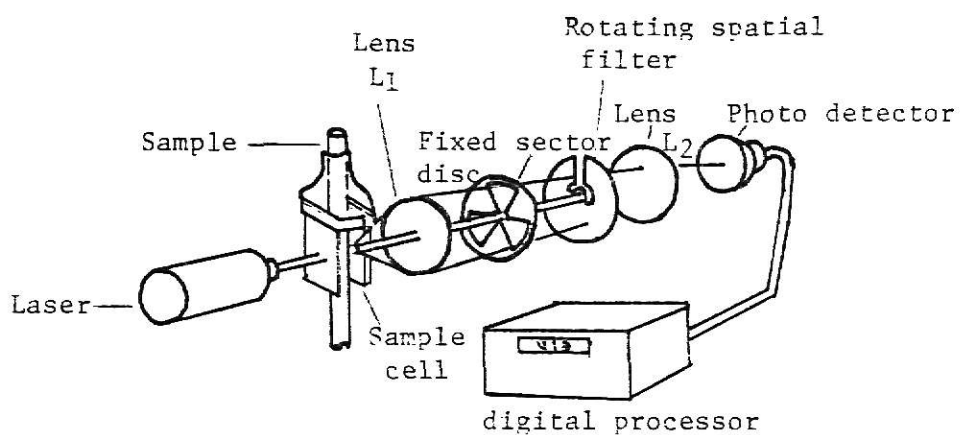


Fig. 1 Exploded view of the optical system of the microtrac particle size analyzer (50)

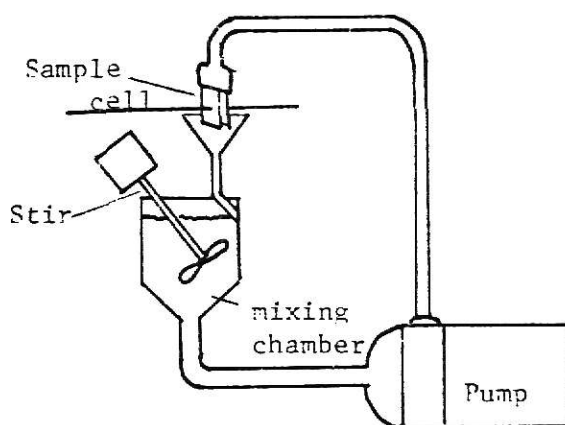


Fig. 2 Schematic view of the recirculating sample system (50)

molded epoxy interfaces of the sample cell. The latter was done to prevent any leakage which could occur upon thermal expansion of the cell. Heating of the starch slurry was accomplished with a YSI Model 71-A Thermoregulator and heating element. The temperature was manually programmed by adjusting the thermoregulator settings to provide a linear ramp of 1°C per 4 minutes. The heater lag to manual programming was determined and corrected with the use of a mercury bulb thermometer.

A 0.5 g starch sample was introduced and allowed to disperse within 20 seconds into the water heated to 40°C in the mixing bowl of the analyzer. From 40°C to 80°C data was automatically accumulated continuously in 100 second segments, with alternate data representing each whole degree rise to construct the pasteogram.

FDLMP Modified to Substitute Gravity Flow for the Impeller Pump

FDLMP parameters were obtained without the use of the built-in Microtrac Analyzer sample impeller pump. The sample was transported to the cell by gravity flow from an elevated reservoir of 21 cm I. D. Polyvinyl chloride and polyethylene tubings summing up to about $1\frac{1}{2}$ m in length, connected with suitable fittings and provided with a coarse needle valve to shut off flow when necessary conducted the starch slurry from the reservoir to the sample cell. The limiting orifice was the $\frac{1}{8}$ in I. D. of the tubing and the set-up provided a cell flow rate of 12.8 ml/second at 31.5°C .

The same thermoregulator and heating element of the conventional FDLMP was used but augmented with a TekPro Heatstir 36 from Scientific Products, Model H2397-1 placed under the reservoir. The rate of heating of the system was measured with the mercury bulb thermometer. The temperature ramp of $1^{\circ}\text{C}/4$ min was kept as smooth as possible and the pressure

head fairly constant (42.2 ± 1.45 cm of water) by using 500 ml insulated Erlenmeyer flasks as receptacles and pouring back the contents into the reservoir about every 40 seconds.

To simulate water conditions provided by the debubbler and filter of the Microtrac Analyzer, tap water used was first boiled, carefully siphoned while hot (about 75°C) into bottles and this was again carefully siphoned into the reservoir when to be used. A constant but gentle stirring with a micromotor-driven stirrer kept the suspension homogeneous.

The sample size was reduced from 0.5 to 0.25 g for WM-.05, WM-.08, and WM.13 because the detector and microprocessor got overloaded with the 0.5 g samples at 72°C or higher. The change in sample size affected only the raw PHV data since these values were normalized by dividing by the PHV at 40°C to obtain the relative PHV's (RPHV) which were plotted.

FDLMP Using a Peristaltic Pump for Circulation of Sample

With the 115-volt Standard Model of the Manostat Varistaltic pump (New York) to transport the starch slurry to the cell, FDLMP data were obtained on samples WM-0 and WM-.13. A pump setting of 7; polyvinyl chloride tubing of $\frac{1}{2}$ in I. D. and wall thickness of $\frac{1}{16}$ in at the pump and connected to a polyethylene tubing $\frac{1}{8}$ in I. D. provided a flow rate of 22.3 ml/second at 31.5°C . Clearance between the rollers and its housing was $\frac{3}{16}$ in. Tubings of slightly larger than $\frac{3}{8}$ in O. D. used in an attempt to increase the flow rate at a low pump setting were destroyed by the pump.

Temperature programming and water conditioning were the same as with the gravity flow procedure. Stirring at the slowest rate possible was accomplished with the TekPro Heatstir 36. Spattering on the lenses and on the cell due to the pulsating flow of the slurry from the cell onto

the collecting funnel was prevented by partly covering the funnel with aluminum foil layered on top with polyvinyl chloride electrical tape. Starch slurry concentrations approximated that of gravity flow.

The flow rate for each method was measured by collecting water flowing through the cell for 60-second periods and measuring the volume with a graduated cylinder. The flow rate with the impeller pump was 23 ml/second which was closely approached by the flow rate of the peristaltic pump. Difficulty of pouring back the sample slurry into the reservoir at a height greater than was used (about 1.74 m from the floor) limited the flow rate with gravity flow to 12.8 ml/second. The possible effect of the flow rate differences on the investigation was examined and considered negligible.

D. Refractive Index

Preliminary investigation was made on the possibility of the unrealistic data being due to the pasted granules matching the refractive index of the water and thus failing to give Fraunhofer diffraction patterns. These consisted mainly of heating starch slurry off-line and pipetting it into a suspension medium with a refractive index different from water at 80°C.

E. Mechanical Degradation Kinetics Study

A kinetics study on the fragility of the pasted starch granules to shear by the impeller pump was made on all samples. A suitable slurry of the starch sample, (WM-0, 15 g in 3 li of water; WM-.05, WM-.08, and WM-.13; 7.5 g in 3 li) was heated off-line but still employing the same temperature ramp of 1°C/4 min. An aliquot of 100 ml was pipetted and allowed to disperse for 20 seconds in the Microtrac mixing bowl after which 18 successive readings were taken at 13-second intervals.

On sample WM-0, determinations were made at 40°C and at every degree from 61 to 80. On WM-.05, WM-.08, and WM-.13, measurements were made at 40°C and at every degree from 61 to either 87 or 89.

DISCUSSION

Microscopy

The gelatinization temperature ranges of the samples shown in Table 1, both for Laboratory 1 and Laboratory 2 determinations were close and overlapping. No clear trend with regard to the amount of crosslinking is apparent. What is apparent is the difference in values from the two determinations indicating the subjectivity of the method.

There was a doubling or more in size of the granule after the loss of birefringence.

Table 1

Gelatinization Temperature Ranges of Modified Waxy Corn Starches

Starch Sample	Gelatinization Temperature Range °C			
	Laboratory 1	Laboratory 2		
	Range	Initial	50%	Endpoint
WM-0	62-72	66	73	78
WM-.05	65-75	64	72	78
WM-.08	66-74	67	74	78
WM-.13	62-75	65	72	78

Viscometry and Effect of Acidification

The amylograph results (Fig. 3) with and without acetic acid showed that within the given temperature and time ranges the starch samples were

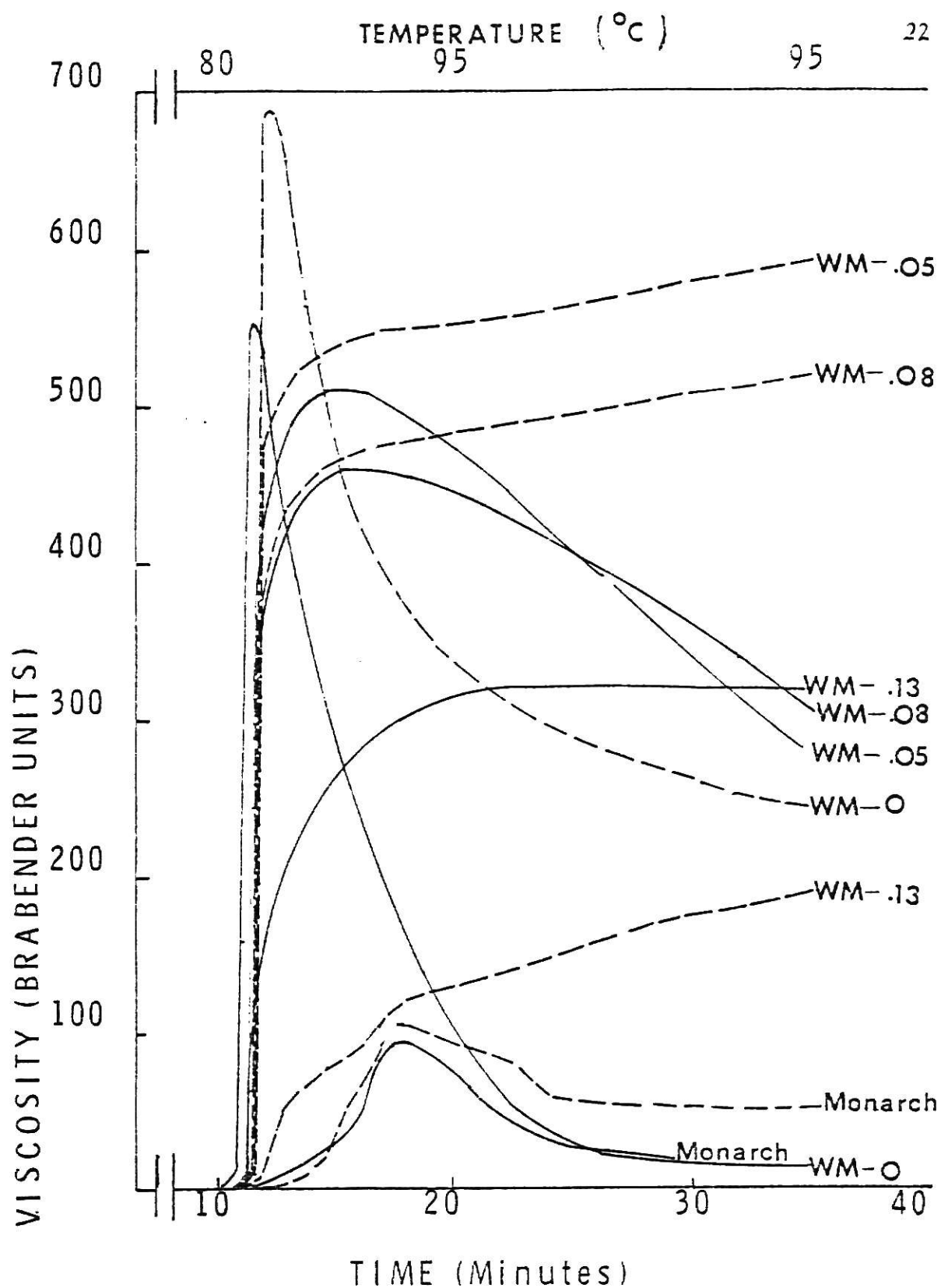


Fig. 3. Brabender amylograms on corn starches. — with acetic acid; ---- without acetic acid.

cooked in the amylograph, the peak viscosity attained was in the order WM-0 > WM-.05 > WM-.08 > WM-.13. Peak viscosity decreased with increased crosslinking, but the least viscous was the common non-waxy corn starch measured for comparison.

Without the acetic acid treatment, the retention of viscosity by the crosslinked starches was noticeable as opposed to the behavior of the parent starch WM-0. Chabot et al (22) wrote that maintenance of a high viscosity was directly correlated with the retention of intact granules. Since the fragile granules of WM-0 after pasting did not remain intact, viscosity went down fast while the viscosity of each of the crosslinked samples was retained. This then meant that crosslinking decreased the fragility of the pasted granules.

Acidification of WM-0 resulted in an earlier rise and peaking of viscosity, marked reduction in peak viscosity, and an even more drastic lowering of final viscosity. This could mean hastened granule swelling overtaken by an increased rate and more extensive granule fragmentation.

With WM-.05 and WM-.08 acidification resulted in reduced final viscosity and with WM-.08 ending up as more viscous than WM-.05. A greater swelling and/or greater amount of exudate released could have given WM-.05 the edge in viscosity over WM-.08 without the acid treatment and even with the acid from the beginning of rise in viscosity up to the point before their curves crossed over; but the more crosslinked and, therefore, stronger granules of WM-.08 caused the paste to retain its viscosity better than WM-.05.

The acid treatment made the viscosity of WM-.13 rise earlier and higher. The viscosity was maintained such that where without the acid, its final viscosity was lowest of the four samples, now it was highest.

This can be rationalized as due to earlier and much greater swelling than that without the acid with the least fragmentation because of the greatest extent of crosslinking.

Additional amylograph data found in the appendix is indicative of the reproducibility obtained.

Conventional FDLMP

With conventional FDLMP, i.e. with the use of the impeller pump, the order in maximum relative particulate hard volume (PHV) reached was WM-0 < WM-.05 < WM-.08 < WM-.13 (Fig. 4). The same order was observed with the temperature at which these maximum relative PHV's were attained. This meant that crosslinking increased the maximum relative PHV as well as the tolerance of PHV to temperature rise. Figs. 5 and 6 indicate the linear measure of the extent of crosslinking.

Fig. 7 illustrates how the median diameter behaved with temperature. Table 2 shows that initial rise in PHV was preceded by rise in median diameter. It also shows that the temperature of maximum median diameter practically coincided with the temperature of maximum relative PHV. One is led to conclude that the magnitude of the PHV was dictated by granule swelling though the exudate was expected to have added to it.

Examining the data from microscopy, viscometry and conventional FDLMP, it can be seen that:

1. The gelatinization temperature range was not very far from the temperature range of initial rise to maximum PHV.
2. The reported median diameter changes (Table 2) did not correspond to the observed doubling or more of individual granule diameters on pasting, specifically for WM-0.

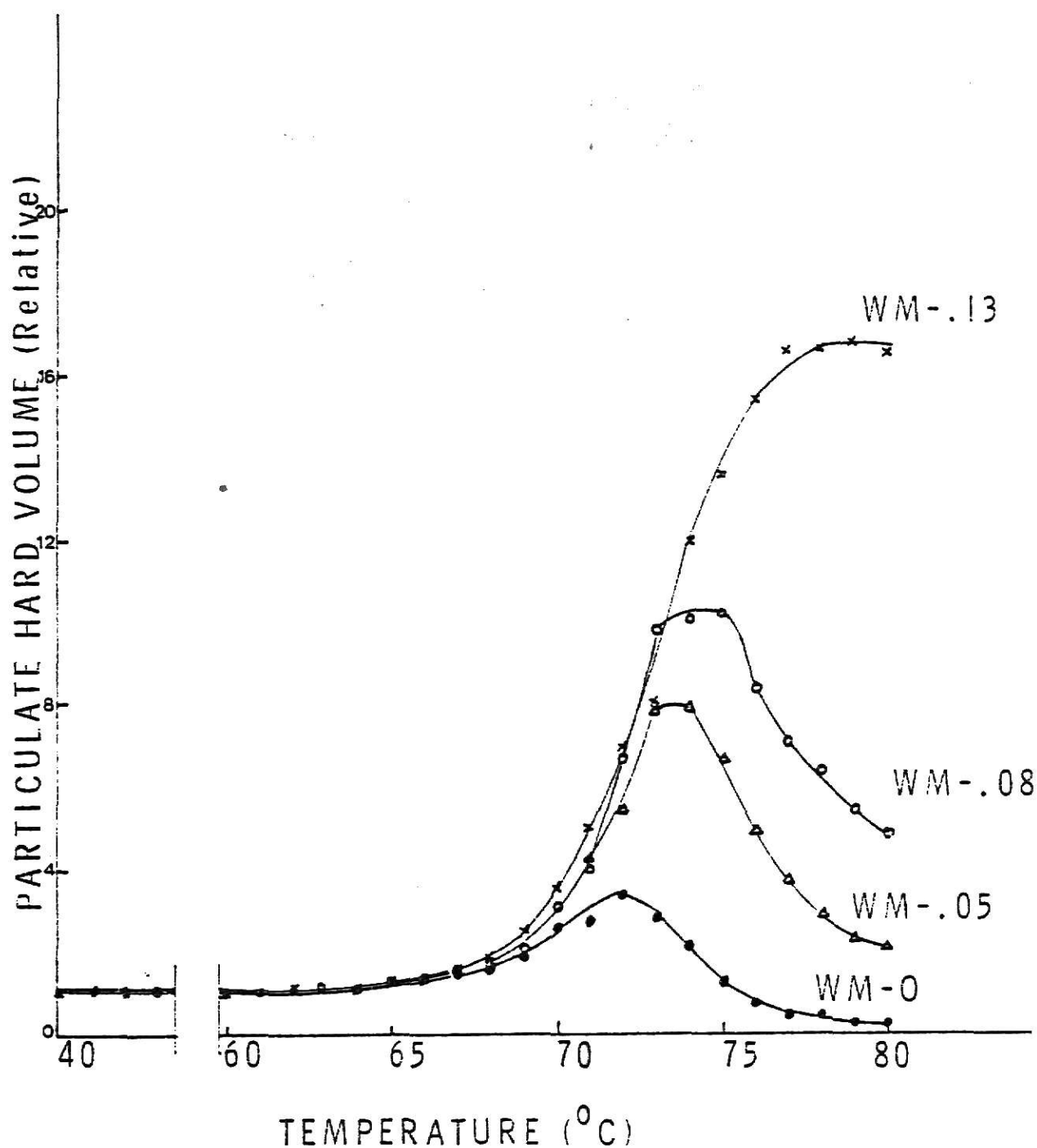


Fig. 4. FDLMP on waxy corn starch and its crosslinked modifications. Relative particulate hard volume (RPHV) vs. temperature.

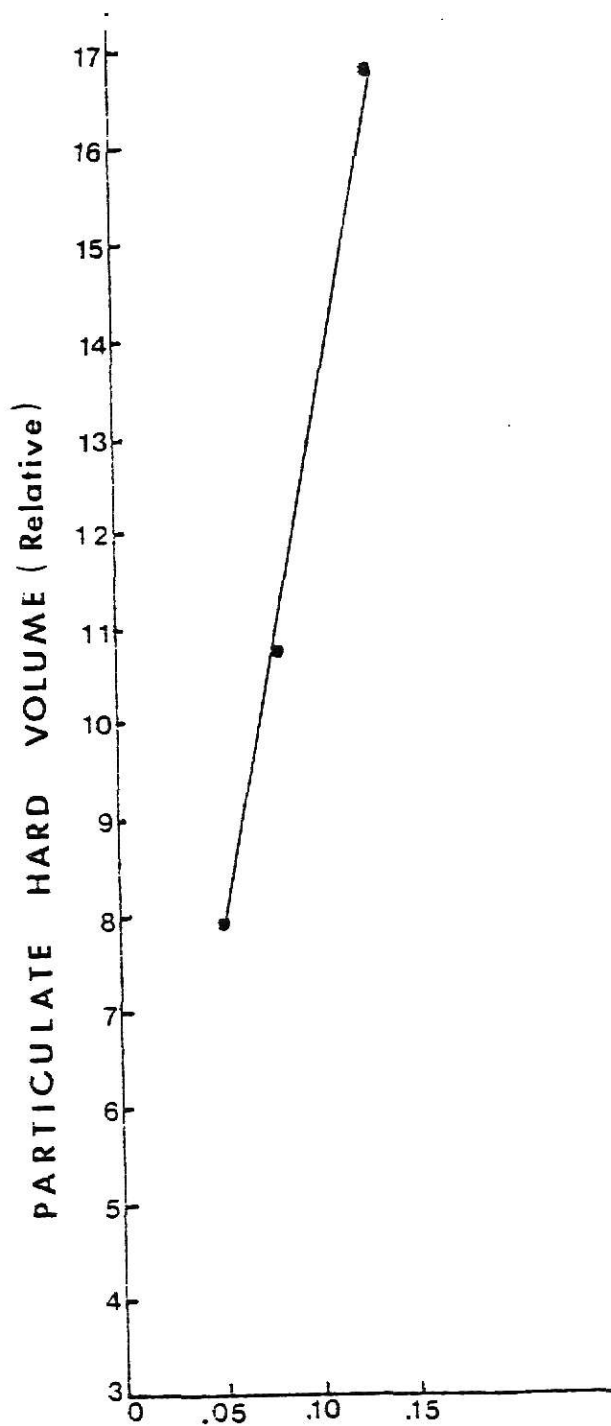


Fig. 5. Relation between relative particulate hard volume (PHV) of crosslinked waxy corn starch and amount of crosslinking reagent.

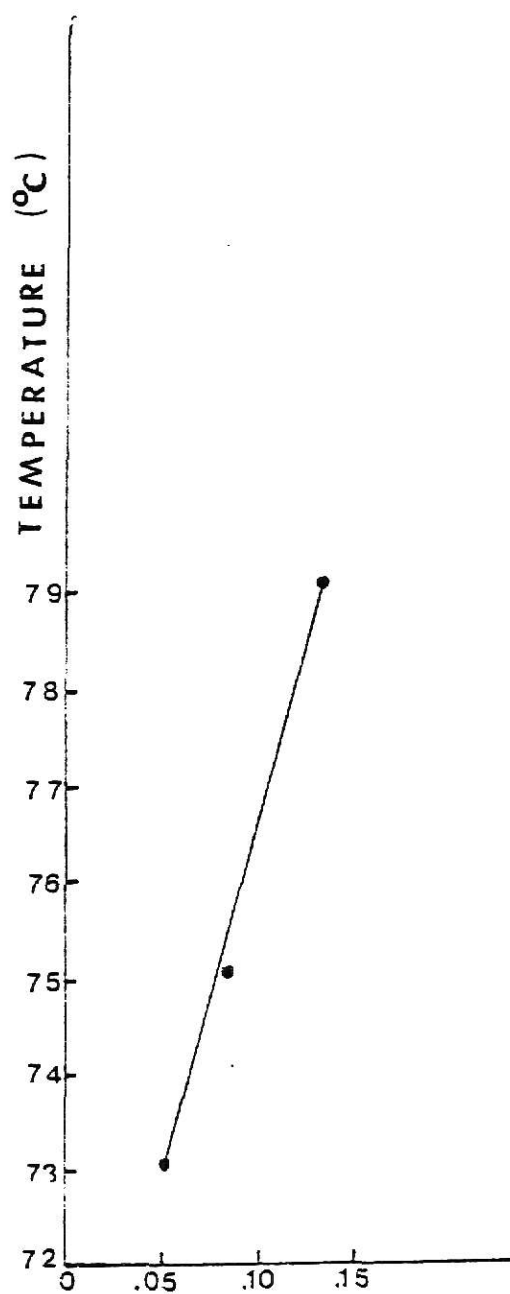


Fig. 6. Relation between temperature of maximum relative PHV of crosslinked waxy corn starch and amount of crosslinking reagent.

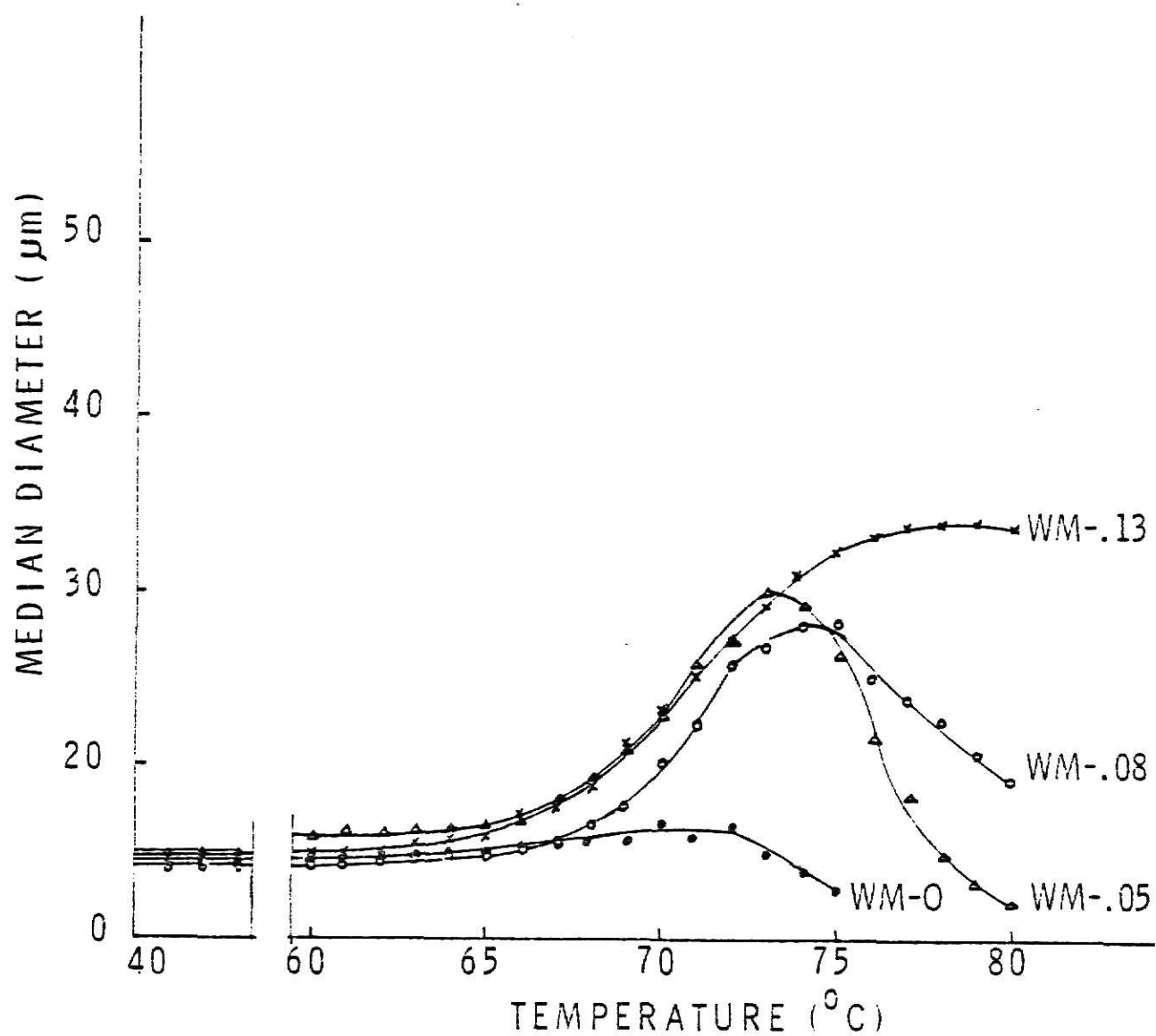


Fig. 7. FDLMP on waxy corn starch and its crosslinked modifications. Median diameter vs. temperature.

Table 2

Selected Conventional FDLMP Parameters

Starch Sample	Diameter			Temperature °C					
	Ini. $\mu\text{m.}$	Max. $\mu\text{m.}$	Change $\mu\text{m.}$	Ini. Rise Diam.	Max. Diam.	Ini. Rise PHV	Max. PHV	Max. PHV (cm^3g^{-1})	Max. RPHV
WM-0	14.8	16.5	1.7	64	72	66	72	.236	3.42
WM-.05	15.0	29.9	14.9	66	73	67	73	.362	7.87
WM-.08	14.0	28.3	14.3	67	75	67	75	.574	10.63
WM-.13	14.6	33.9	19.3	66	79	67	79	.680	16.59

Table 3

Selected Parameters of FDLMP with Gravity Flow

Starch Sample	Diameter			Temperature °C					
	Ini. $\mu\text{m.}$	Max. $\mu\text{m.}$	Change $\mu\text{m.}$	Ini. Rise Diam.	Max. Diam.	Ini. Rise PHV	Max. PHV	Max. PHV (cm^3g^{-1})	Max. RPHV
WM-0	17.1	35.0	17.9	66	73	66	73	.651*	.930
WM-.05	15.7	66.7	51.0	61	76	66	**	.610	19.06
WM-.08	16.5	64.6	47.1	62	**	63	**	.702	27.00
WM-.13	14.8	63.2	48.4	***	**	63	**	.587	20.96

*The sample used for WM-0 was .5 g; the rest, .25 g.

**The PHV seemed to still be on the increase at 80°C.

***The median diameter was too fluctuating to tell.

3. Viscosity rose at temperatures above 80°C for all samples when FDLMP values of relative PHV and median diameter except with WM-.13 had fallen appreciably low. WM-0 which had registered the highest peak viscosity at about 83° and had its relative PHV below baseline at 80°C .

4. The order of maximum relative PHV is the same as the order of final viscosity with acidification.

The foregoing comparative observations suggest that:

1. FDLMP can give information on early gelatinization that is less subjective and more reliable than that from microscopy.

2. With the FDLMP something was happening to the pasted granules causing a fall in median diameter and relative PHV premature to what was expected.

3. Shear and/or heating conditions in the amylograph could be milder for the pasted granules than those in the Microtrac Analyzer.

4. If final viscosity is a measure of intact granules or the lack of it, then FDLMP could be measuring the fragility of the granules as they underwent pasting, not so much their increase in size and the amount of extragranular material.

Two possible explanations of the puzzling FDLMP data were put forward. One was that the pasted granules were being sheared by the Microtrac Analyzer. The most probable place of shearing was narrowed down to the sample impeller pump. The other explanation was that the refractive index of the pasted granules matched that of the water in which they were suspended thereby becoming invisible to the Microtrac Analyzer. The WM-0 pasted slurry being clearest to the eye, the refractive index matching of the sample and suspending medium was assumed greatest hence the already lower than baseline relative PHV at 80°C though it had the highest

peak viscosity at 83°C with the amylograph.

FDLMP with Gravity Flow

In Figs. 8 and 9 are photopasteograms obtained when gravity flow was used in place of the impeller pump to avoid the suspected shearing effect if there was any. Table 3 gives the corresponding parameters. The relative PHV photopasteograms (Fig. 8) are more indicative of the extent of crosslinking than the ones for median diameter (Fig. 9).

The increase in size of the granules with gravity flow was more realistic; but the difficulty of simulating conditions provided by the Microtrac water conditioning system with a completely manual operation made quantitation less certain. Despite the factor of uncertainty, repeated determinations made it conclusive that the impeller pump was indeed the cause of premature fall in PHV and median diameter especially for the crosslinked samples.

There was a shift in the order of maximum relative PHV (see Figs. 4 and 8). With gravity flow, WM-.08 > WM-.13. This, however, can be understood by considering two opposing processes taking place; fragmentation lowering relative PHV and granule expansion raising it. The lesser degree of crosslinking in WM-.08 allowed it to expand yet resist fragmentation. The greater extent of crosslinking in WM-.13 while it prevented fragmentation inhibited expansion.

The relative PHV of WM-0 at 80°C though it increased to .160 with gravity flow from .036 with the impeller pump, was still comparatively low. It also started to fall after peaking at 73°C, just 1° higher than that with the impeller pump while all the others appeared to still be on the rise at 80°C. This suggested then that though the shearing by the

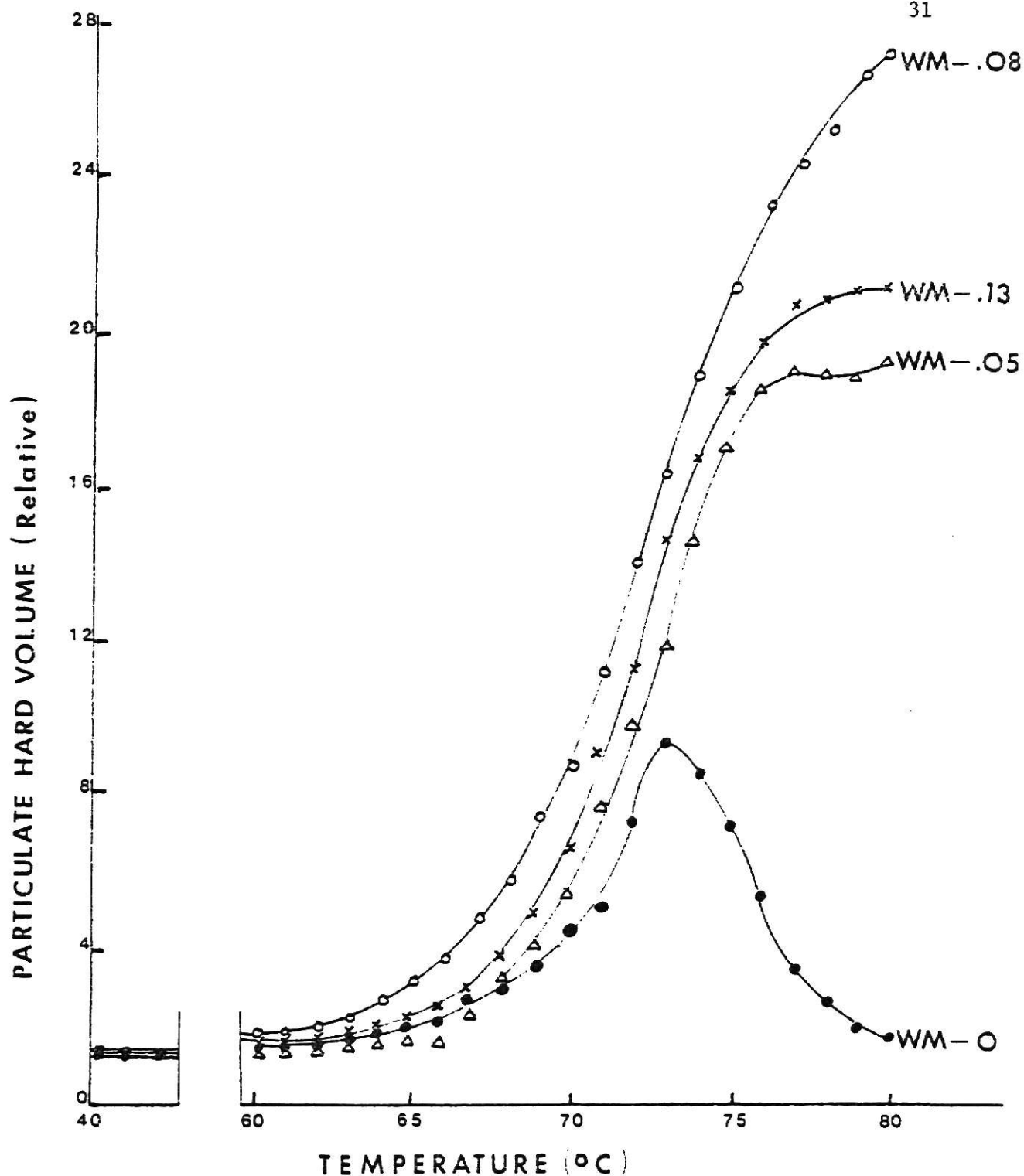


Fig. 8. Gravity flow FDLMP on waxy corn starch and its crosslinked modifications. Relative particulate hard volume vs. temperature.

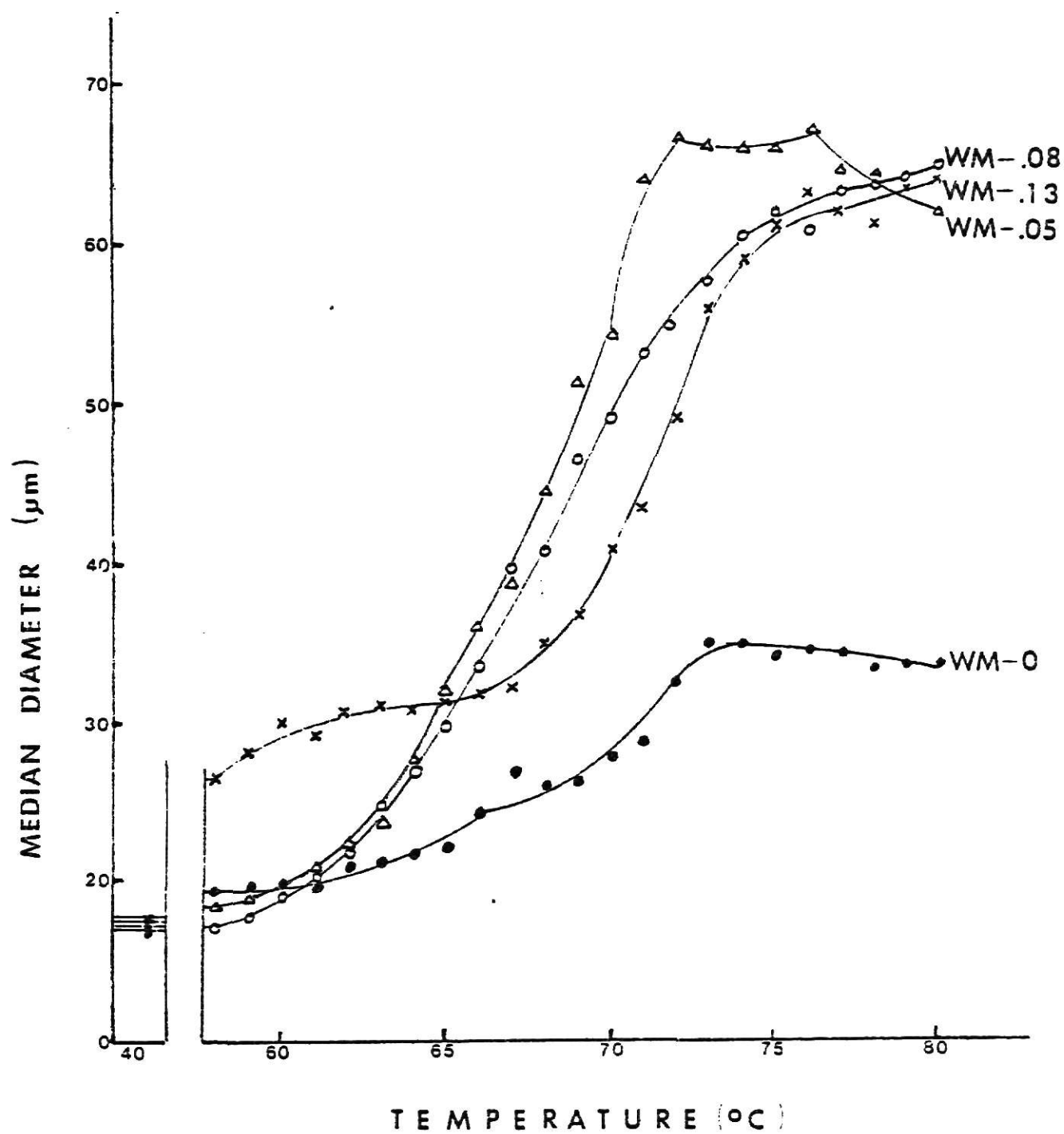


Fig. 9. Gravity flow FDLMP on waxy corn starch and its crosslinked modifications. Median diameter vs. temperature

impeller pump was the major cause of the low FDLMP parameters for the crosslinked starches, it was not so with WM-0.

The changes in particle size distribution of the starch granules as they underwent pasting using the impeller pump and with gravity flow are illustrated by Figs. 10-13. An overview of all the figures reveal almost normal distributions at the pasting temperatures for all samples with the impeller pump, and distributions very skewed to the right with gravity flow. This must be due to the absence of shearing with gravity flow.

Fig. 10 (left) shows that at 40°C with the impeller pump, the greatest number of particles for WM-0 were in the 16 μ m channel. At 60°C to 73°C there was a shift of population to the 22 μ m channel, and a broadening of the peak. Above 73°C, there was again a shift back toward the lower channels culminating in the erratic distribution at 79°C which suggests an earlier and more extensive fragmentation compared with that of gravity flow (Fig. 10, right) though at 79°C the particle size distribution of the latter also indicates fragmentation even without the shearing of the impeller pump.

Examination of the particle size distributions with the impeller pump of WM-.05 (Fig. 11, left), WM-.08 (Fig. 12, left), and WM-.13 (Fig. 13, left) show that as in WM-0, the 16 μ m channel was of highest population at 40°C but there was a shift to 31 μ m at 70° and to 44 μ m at higher temperatures indicating that the crosslinked starches were able to swell more than WM-0 before fragmentation. The same distributions also show how at 77°C the channel of highest population for WM-.05 was the 16 μ m channel while it was the 31 μ m for WM-.08 and with WM-.13 it was the 44 m up to 79°. Again this observation points toward the decrease in fragility in crosslinking.

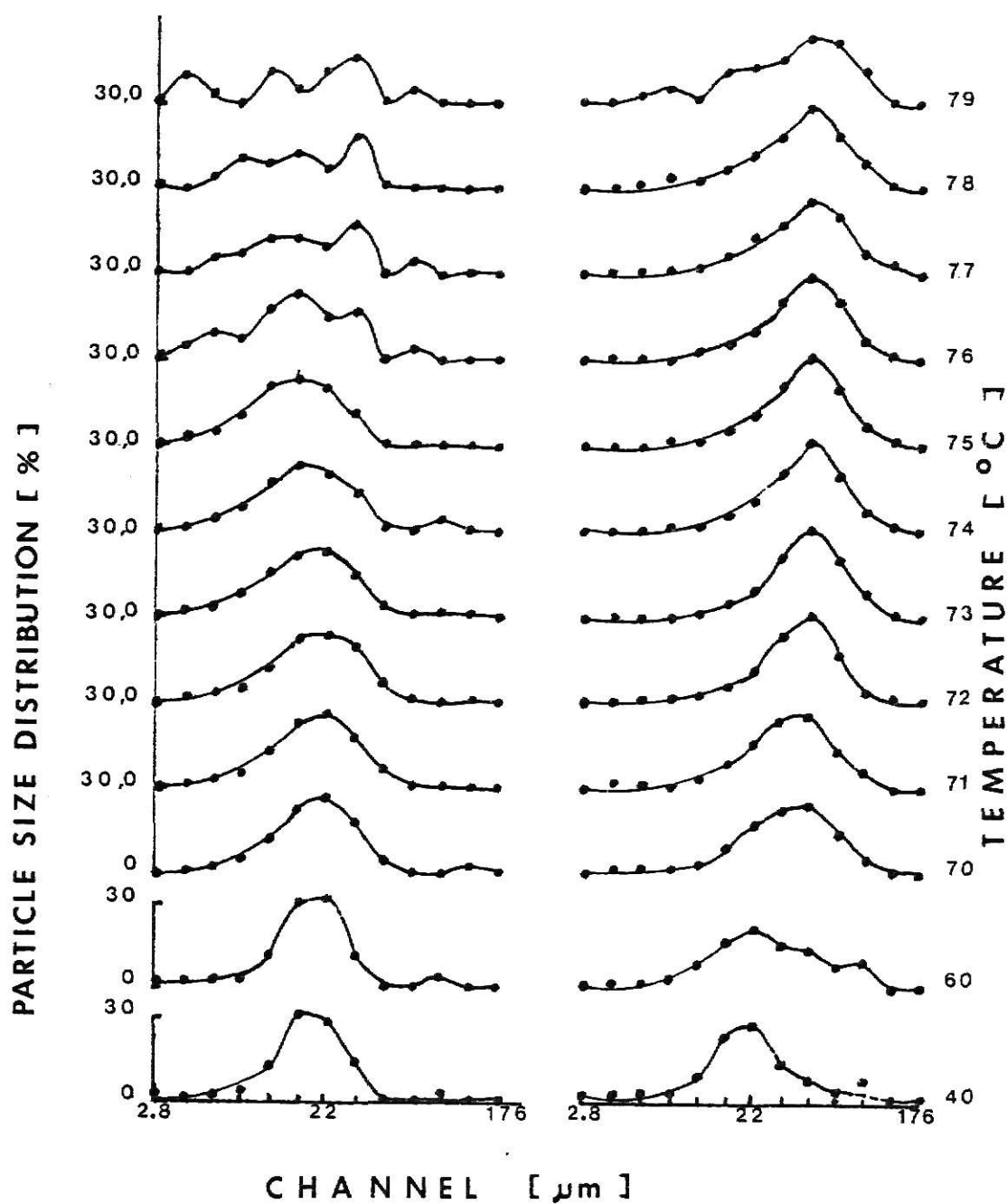


Fig. 10. FDLMP particle size distribution of WM-0 at 40, 60, 70-79°C (left) with impeller pump; (right) gravity flow.

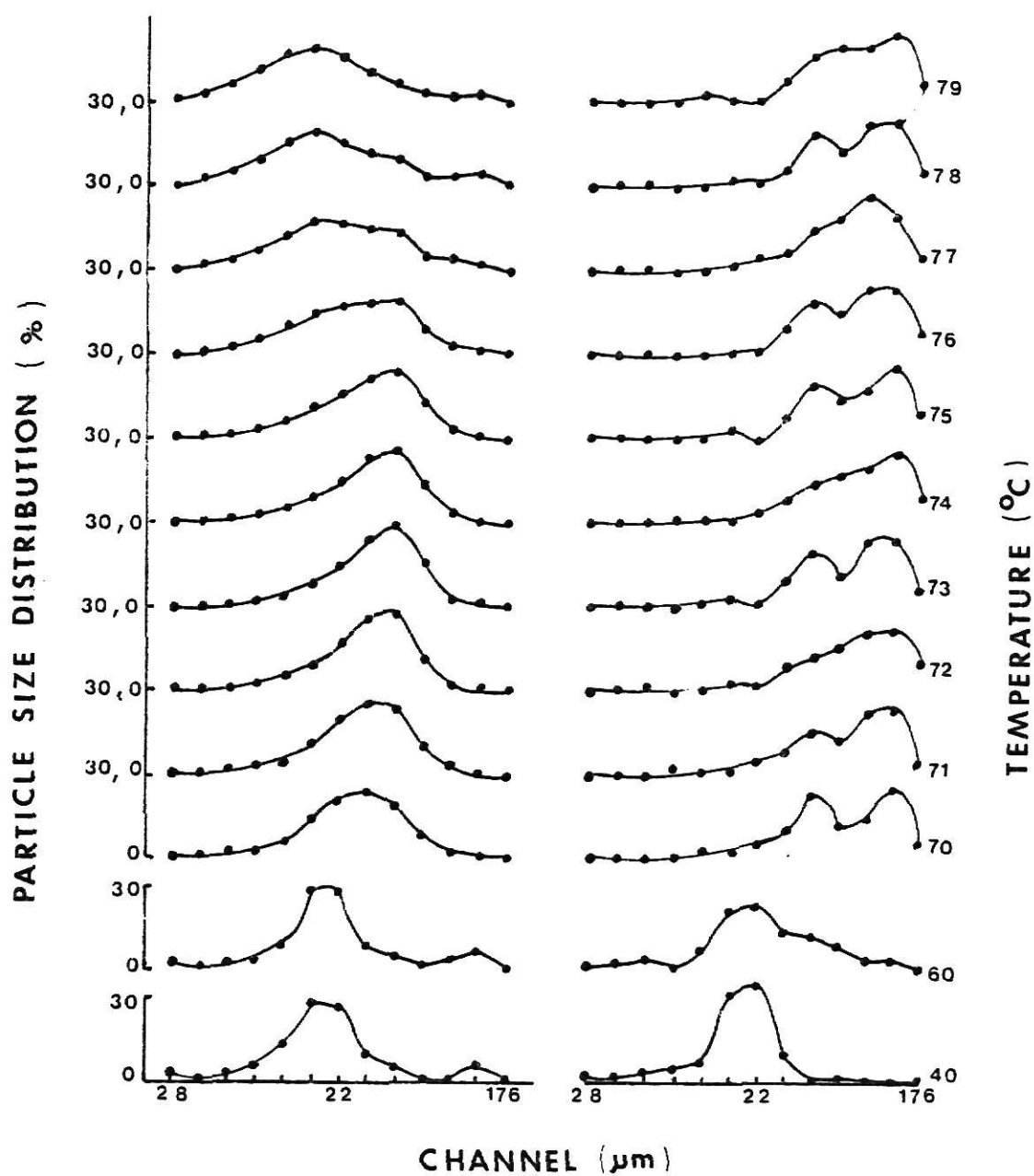


Fig. 11. FDLMP particle size distribution of WM-.05 at 40, 60, 70-79°C (left) with impeller pump; (right) gravity flow.

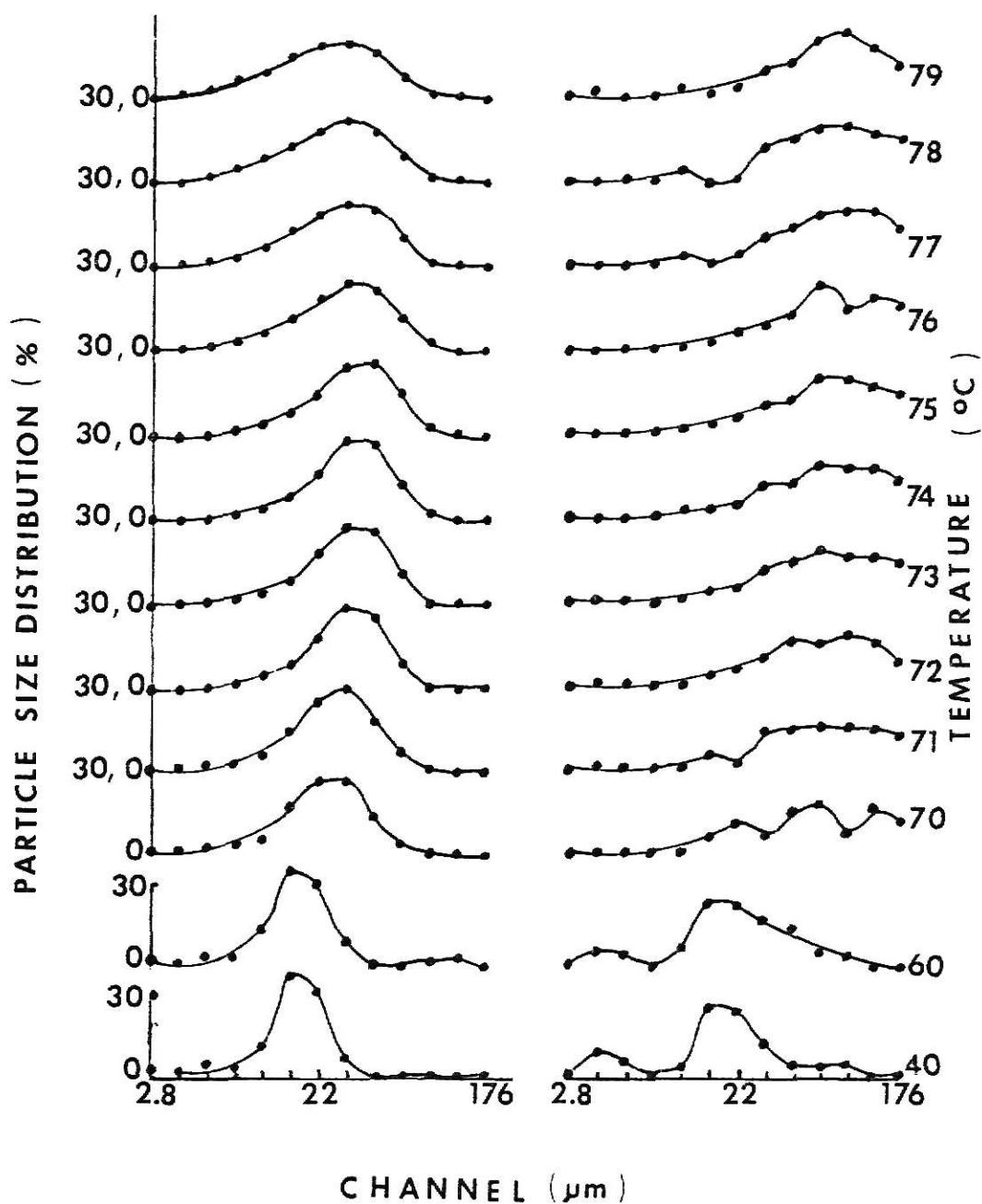


Fig. 12. FDLMP particle size distribution of WM-.08 at 40, 60, 70-79°C (left) with impeller pump; (right) with gravity flow.

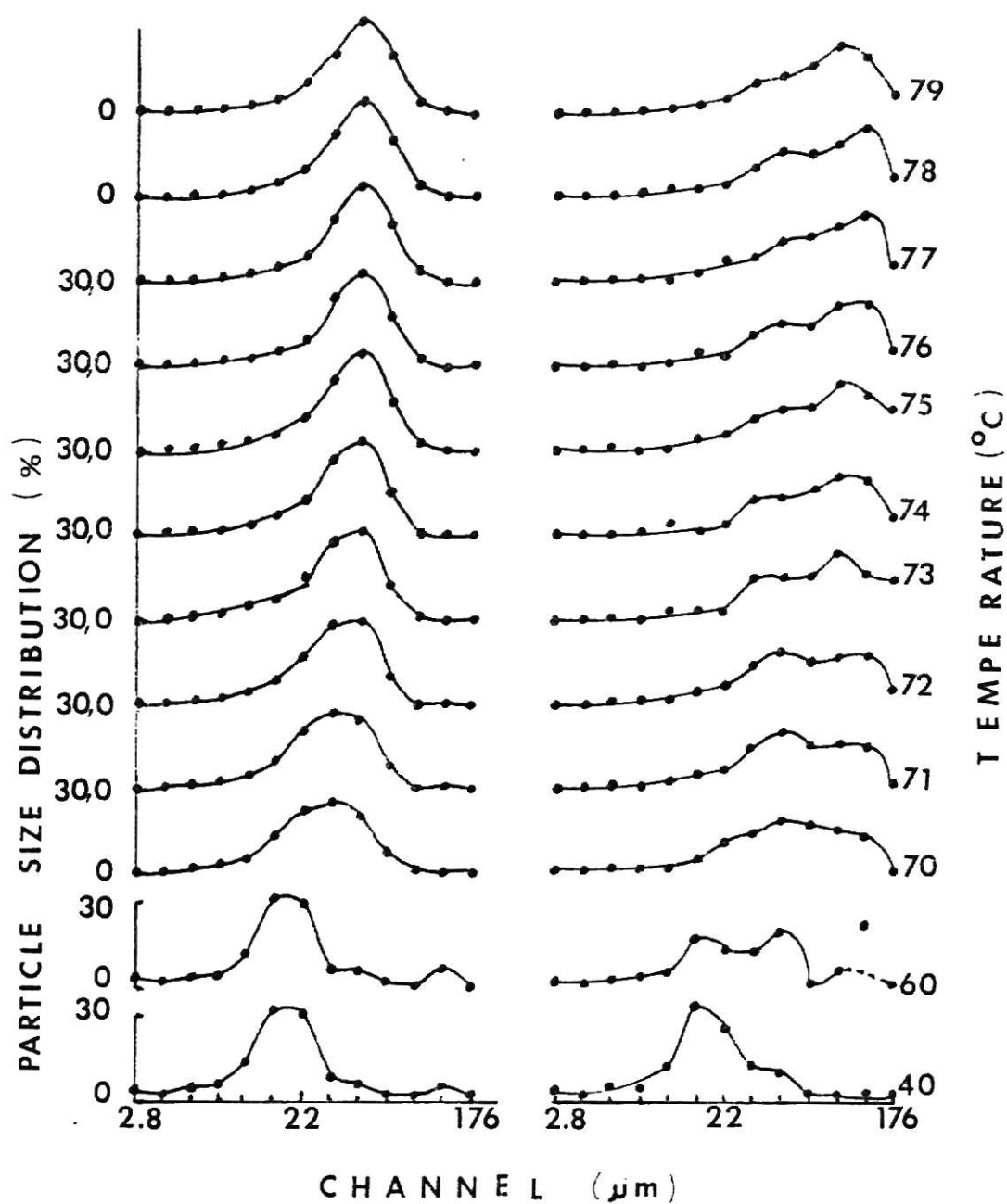


Fig. 13. FDLMP particle size distribution of WM-.13 at 40, 60, 70-79°C (left) with impeller pump; (right) with gravity flow.

Though the distributions for the crosslinked starches with gravity flow (Figs. 11b, 12b, and 13b, right) present more fluctuating patterns from one centigrade degree to the other, still they are consistent in their message that the pasted starch granules were, collectively speaking, bigger when the impeller pump was not used for transporting the sample slurry.

FDLMP with the Peristaltic Pump

To ease the difficulty of sample slurry circulation by the gravity flow method, and reduce the shear by an impeller, a peristaltic pump was used. A comparison of the relative PHV curves with the a) impeller pump, b) gravity flow, and c) peristaltic pump for WM-0 and WM-.13 is given by Figs. 14 and 15 respectively. The corresponding curves for median diameter are in Figs. 16 and 17.

With WM-0, the peristaltic pump gave a maximum relative PHV about $\frac{1}{2}$ (0.51) that of gravity flow and 1.37 times that of the impeller pump. It would appear then that the peristaltic pump though with negligible shear was also causing much granule break-up.

The behavior of WM-.13 was puzzlingly interesting. Though the peristaltic pump gave a maximum relative PHV still about $\frac{1}{2}$ (0.61) that of gravity flow, this time, it was not higher than that with the impeller pump, but just about $\frac{1}{2}$ (0.76) of the latter. Another puzzle was its early rise. The histograms (Fig. 18) revealed practically the same particle size distribution for both the impeller pump and peristaltic pump at 40°C and at 80°C. Could the rollers of the peristaltic pump have a crushing action on the granules? Could such action have at first just flattened and elongated the granules and favorable orientation in the laser beam caused the early rise in relative PHV as well as in median diameter?

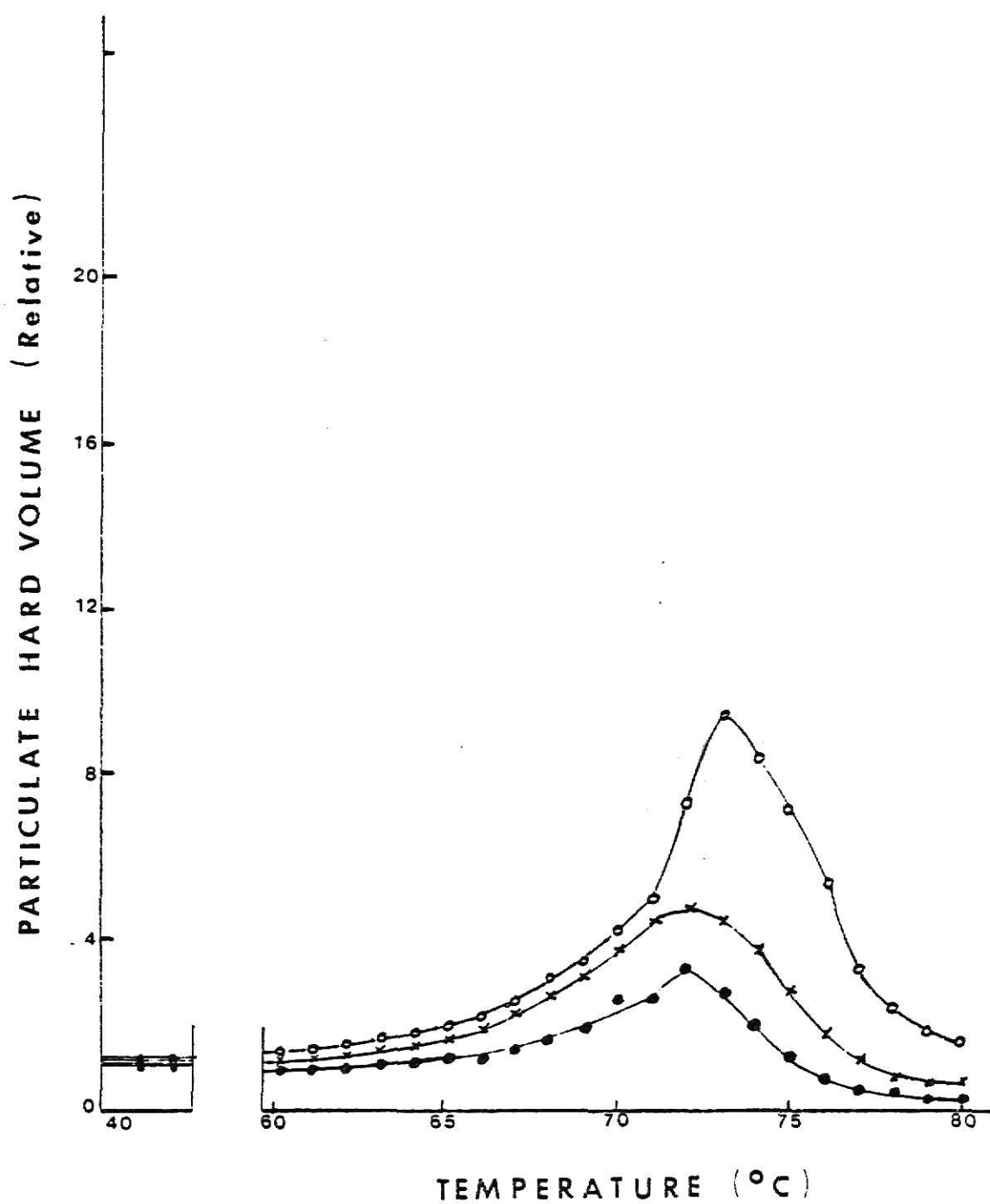


Fig. 14. WM-O RPHV photopasteograms compared. ●●● for impeller pump; ○○○ for gravity flow; ××× for peristaltic pump.

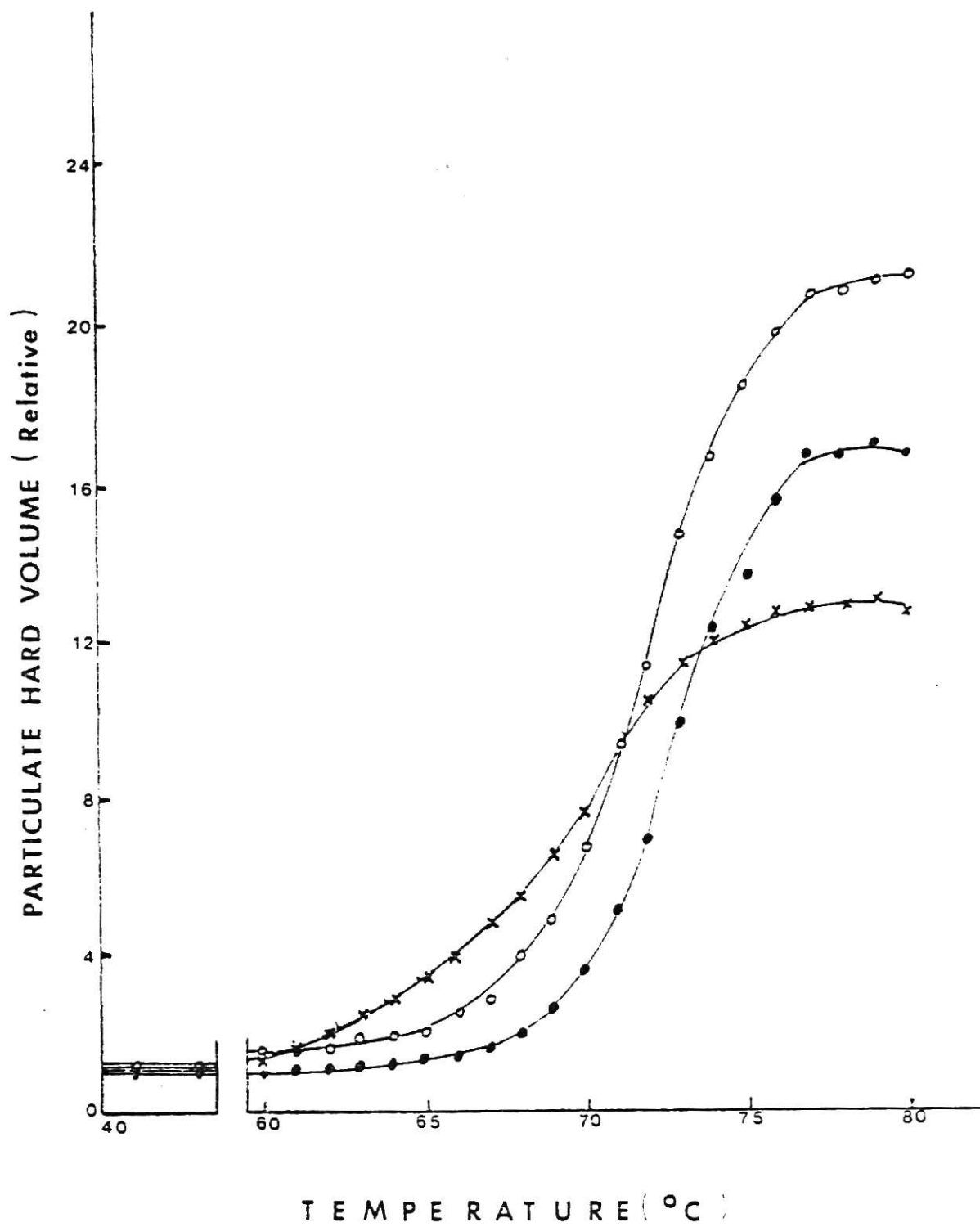


Fig. 15. WM-.13 RPHV photopasteograms compared. ●●● for impeller pump; ooo for gravity flow; xxx for peristaltic pump.

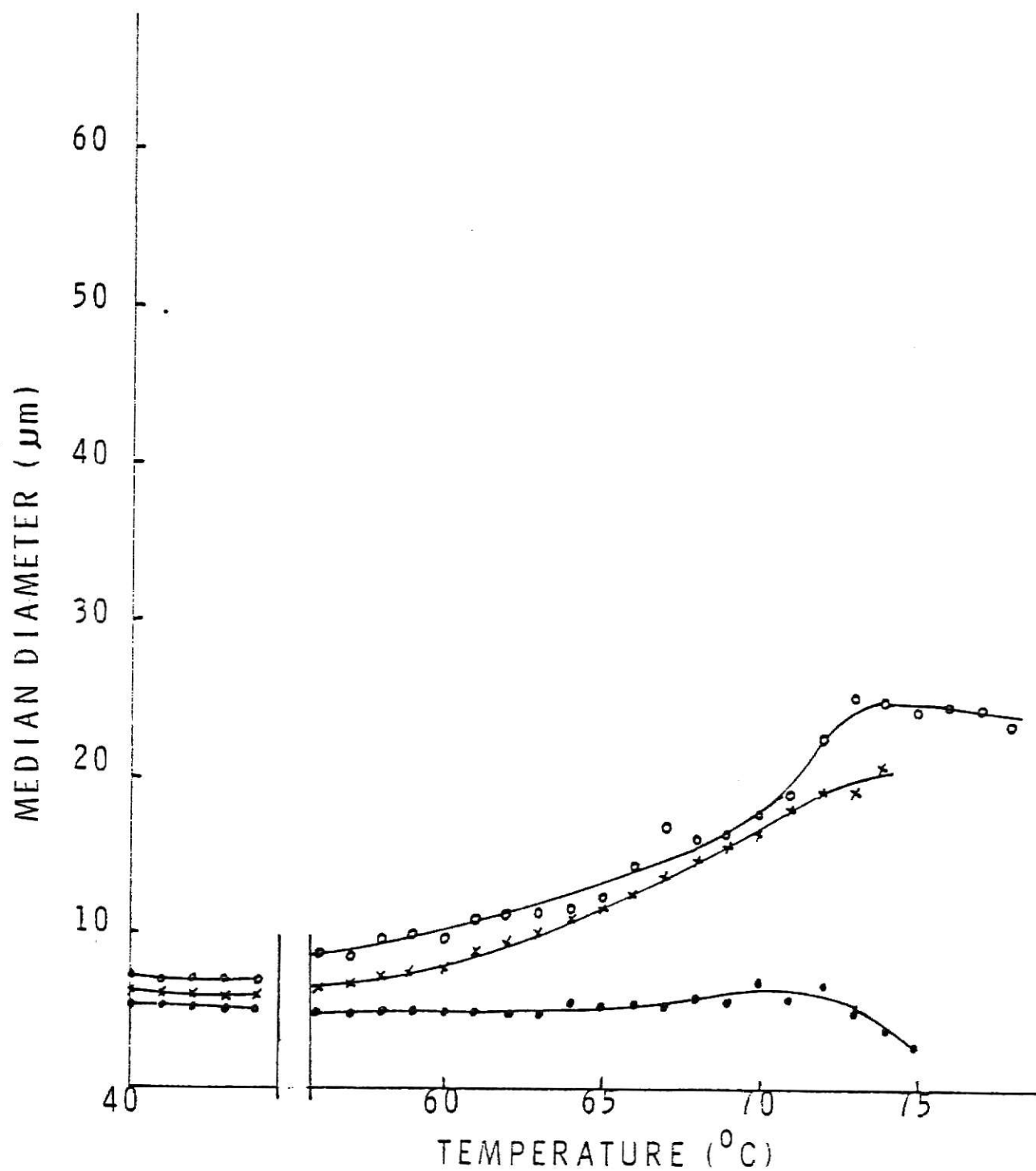


Fig. 16. WM-O photopasteograms of median diameter compared. ●●● for impeller pump; ○○○ for gravity flow; ××× for peristaltic pump.

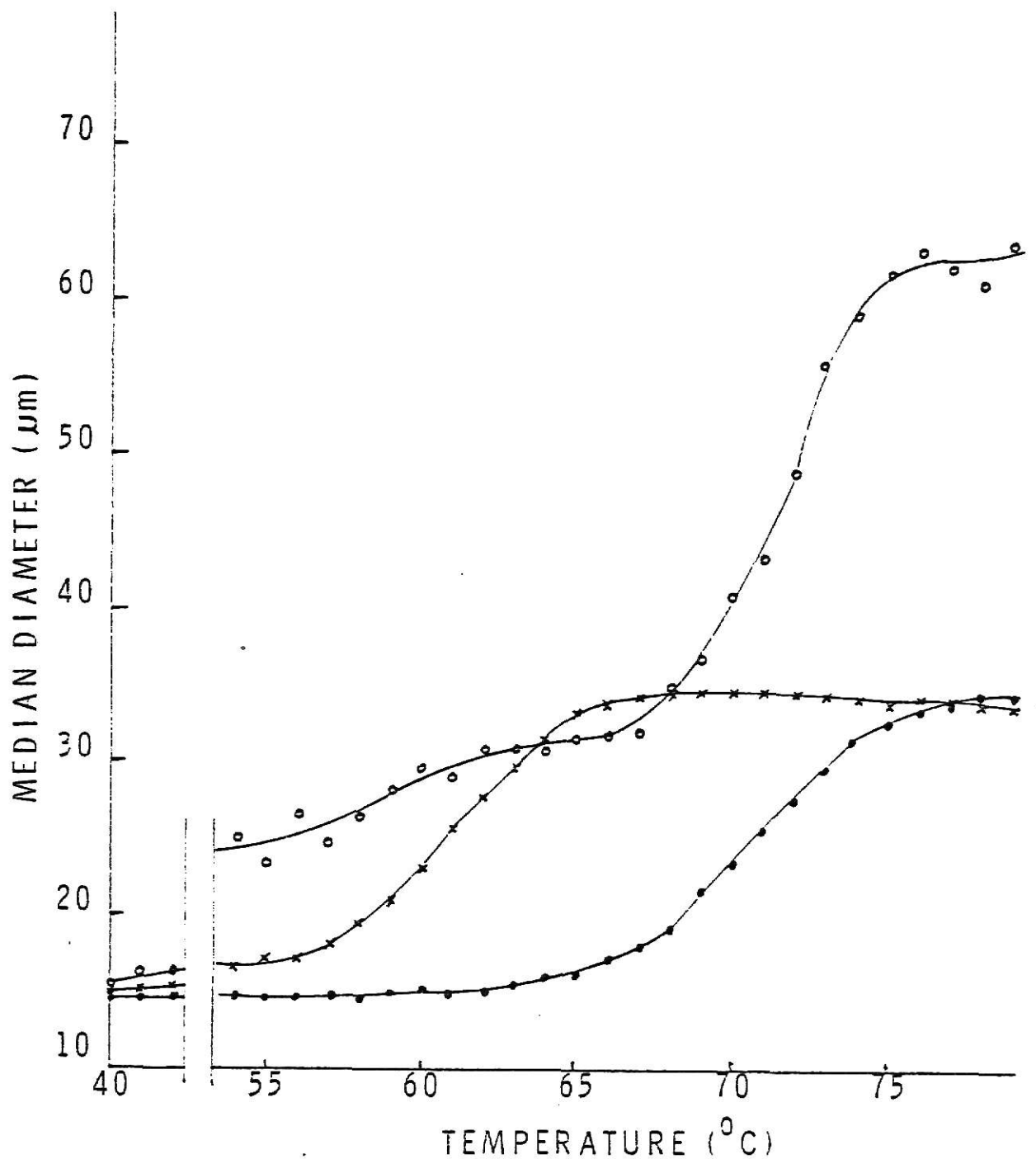


Fig. 17. WM-.13 photopastecgrams of median diameter compared.
 ●●● for impeller pump; ○○○ for gravity flow; ××× for peristaltic pump.

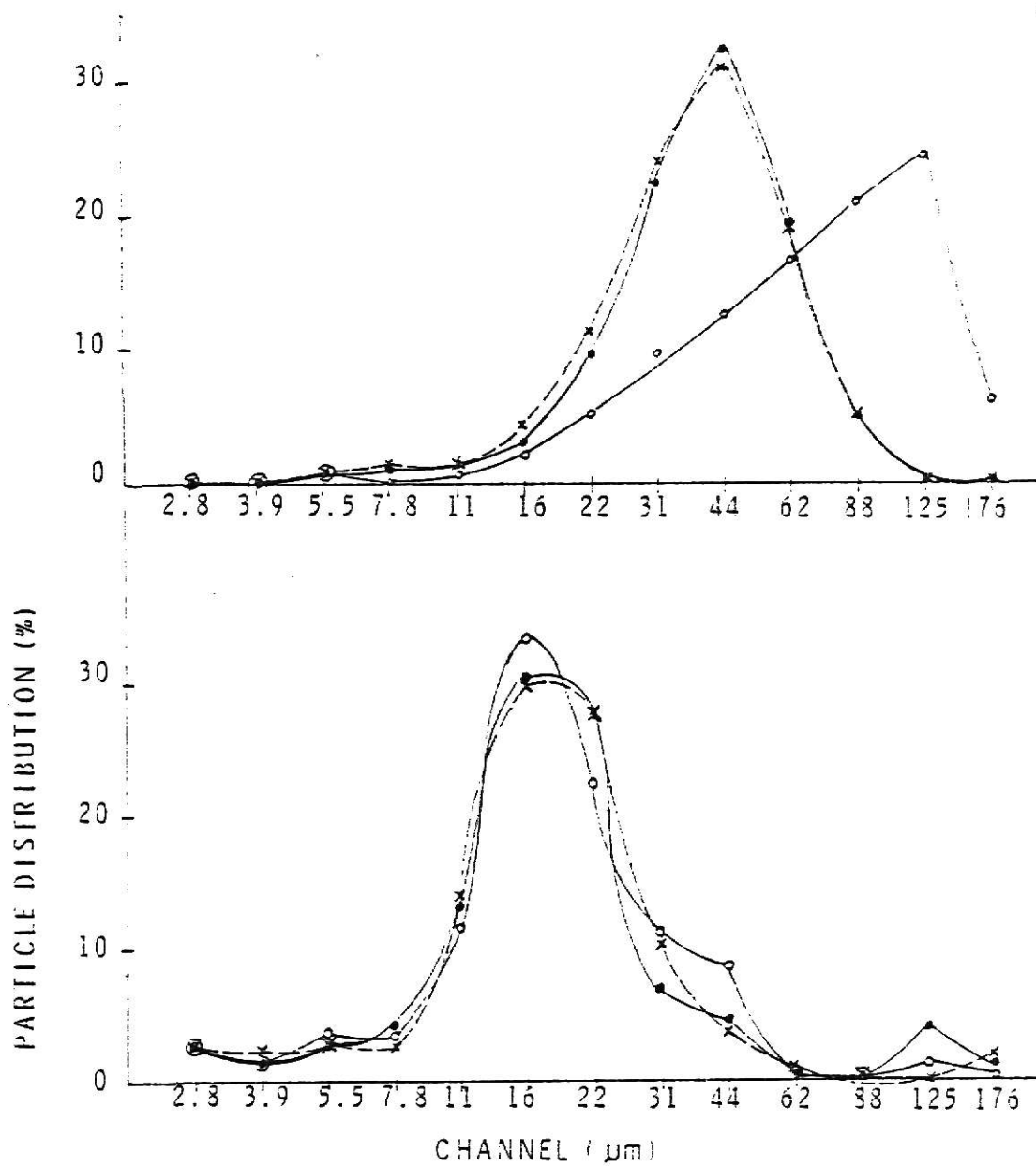


Fig. 18. Comparison of particle size distributions of WM-.13 (above) at 80°C; (below) at 40°C. ●●● for impeller pump; ○○○ for gravity flow; and ××× for peristaltic pump.

Could the crushing action, at higher temperatures have resulted in fragmentation greater than the stretching-shearing effect of the impeller pump as observed later in the work? Since the peristaltic pump could not take the place of gravity flow without considerable granule breakup, it was abandoned and the mechanism of apparent breakup not sought further.

Refractive Index as a Factor

Preliminary investigations were made on whether the matching of the refractive index of water by the starch granules especially WM-0 caused them to disappear from the sight of the Microtrac Analyzer resulting in low relative PHV and median diameter. The refractive index of the suspension medium was changed first by the addition of sucrose then by temperature variation. The results, though reproducible, were inconclusive. The sucrose seemed to compete with the granules for water to give smaller diameter at corresponding temperatures. Attempts to match the index of refraction by temperature variation failed to explain low changes in PHV because the variable introduced (temperature) was probably a greater factor than the small refractive index adjustment afforded.

The aforementioned investigations, however, revealed how the relative PHV of a starch sample heated to pasting temperature off-line then pipetted into the Microtrac mixing bowl changed considerably with time exposure to shear by the impeller pump. It was realized that with such data, conditions of maximum and minimum pasting, paste strength to shear at any desired temperature could be obtained easily and quickly. It could also possibly yield the more realistic granule size and optical response sought previously with gravity flow by extrapolation to zero time.

Work on the refractive index thus led into the mechanical degradation kinetics study.

In the meantime, an inquiry by Fry (53) into the principle and mathematics of the Microtrac Analyzer ruled out further work on the refractive index. An important advantage of the near forward Fraunhofer diffraction approach when $\theta < 11^\circ$ and $D > \frac{10}{\pi} \lambda$ is that the particle size distribution so determined is independent of the optical properties of the sample (e.g. transparency and refractive index). For the Microtrac Analyzer operating at scattering angles $\theta < 11^\circ$ and particle diameter, $D > \frac{10}{\pi} \lambda$, Fraunhofer diffraction predominates over reflection and refraction phenomena. For visible incident laser light (e.g. $\lambda = 0.6328 \mu\text{m}$) Fraunhofer diffraction in the angular region 11° may be used to determine particle size distributions in the diameter range from 2-200 μm (49, 50). Reflection and refraction may be neglected with these conditions. The smaller particles in the diameter range (2-200 μm) produce a relatively low intensity diffraction signal at the larger diffraction angles within the near forward zone up to 11° . As the particle size increases in the diameter range 2-200 μm , a more intense Fraunhofer diffraction signal results, however, this occurs at smaller and smaller diffraction angles. For this reason, the upper limit of the particle size that can be measured in this way is determined by the difficulty in measuring diffracted light at small near forward angles approaching the remaining bright undiffracted laser beam.

The intact starch granules fall within the 2-200 μm range. Part of the amylose units leached out during pasting would probably fall below the 2-200 μm range but it is believed that the Microtrac Analyzer is capable of measuring particles as low as 0.5 μm in diameter (49, 50) these registering in the 2.8 μm channel. There is the possibility of these smaller than 2 μm particles being lost to measurement by refractive

index matching, but compared to the much bigger granules and exudate within the 2-200 μ m range, such loss could not be the cause of the comparatively much lower magnitude and temperature of maximum relative PHV of WM-0 (Tables 2 and 3) compared to its crosslinked modifications. This suggests that this observation is not due to matching of refractive index, neither to shearing (as shown by gravity flow) but to another factor, like low temperature tolerance to fragmentation.

Mechanical Degradation Kinetics Study

With the conventional FDLMP and with the Brabender amylograph, shear and temperature are two intertwined variables. The photopasteograms and the amylograms present a measure of their combined effects. In the gelatinization temperature determination by microscopy, shear is eliminated, but as was mentioned, the method is too subjective and statistically limited. With gravity flow FDLMP shear was also eliminated, but quantitation was uncertain.

With the off-line FDLMP, the possibility of measuring the effect of the two variables separately with statistical validity, certainty, and ease became evident. Heating the starch slurry to a given temperature before subjecting it to the constant shear of the impeller pump and making measures at definite time intervals would yield data to generate curves showing how the starch sample at that certain temperature would be changed by shear alone. Extrapolation of the curves to time zero, i.e. before the sample is exposed to shear would yield values showing how the starch sample was changed by temperature alone.

Figs. 19-22 show how the relative PHV for each starch sample at varying temperatures was affected by the impeller pump. As might be expected,

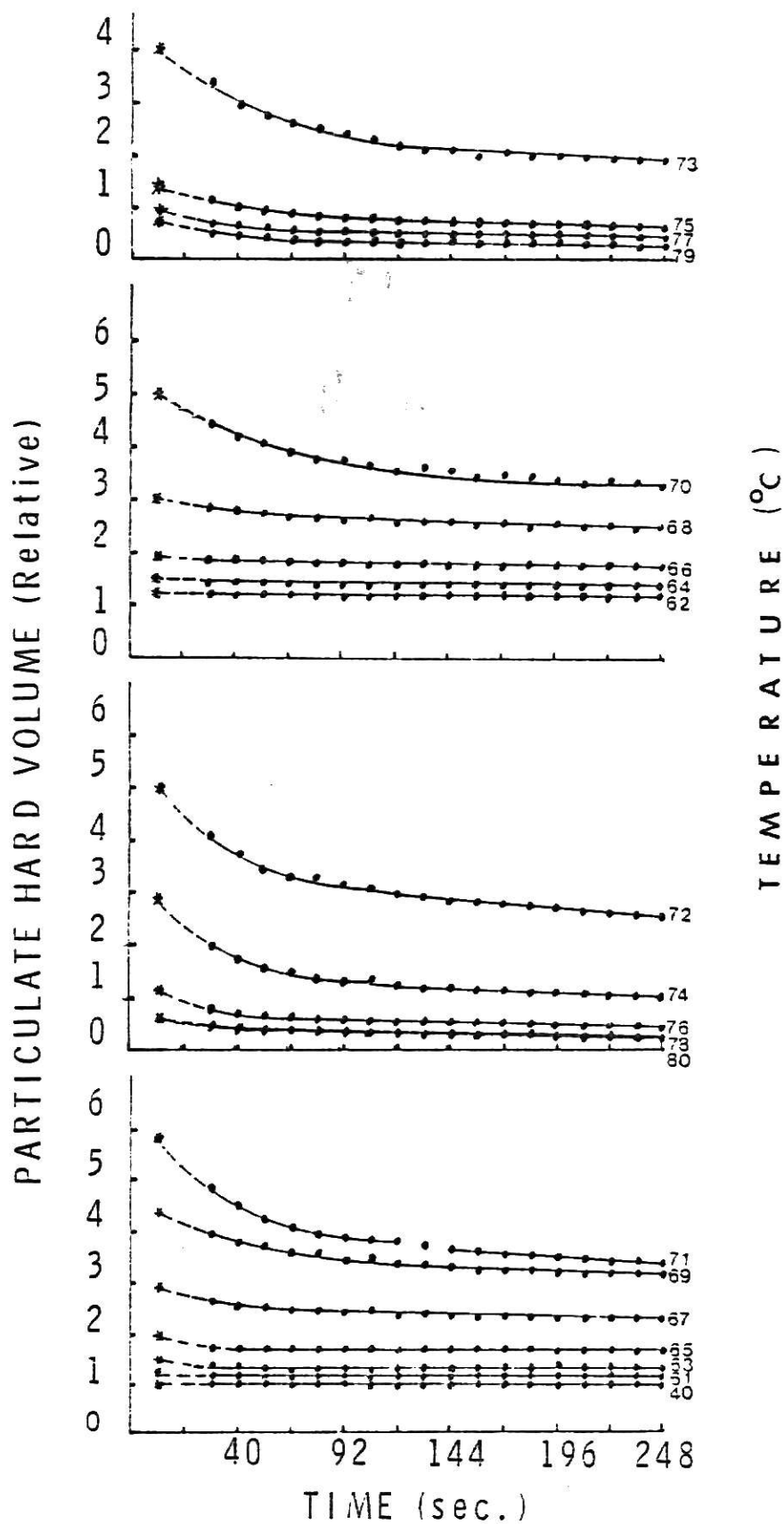


Fig. 19. Effect of impeller pump shearing on waxy corn starch. RPHV vs. time exposure to shear. * represents the point to which the curve was extrapolated to time zero.

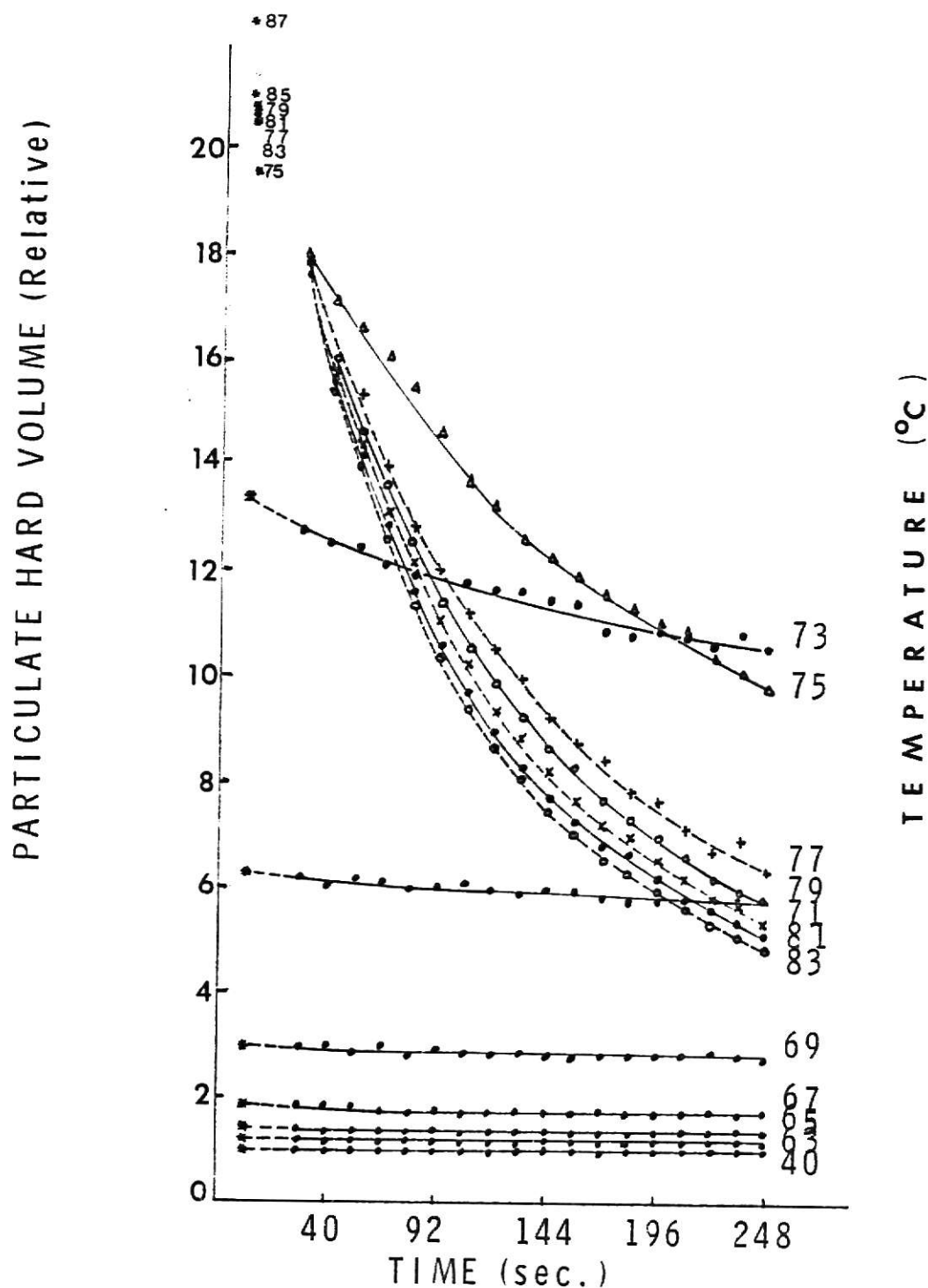


Fig. 20. Effect of impeller pump shearing on WM-.05. RPHV vs. time exposure to shear. * represents the point to which the curve was extrapolated to zero time.

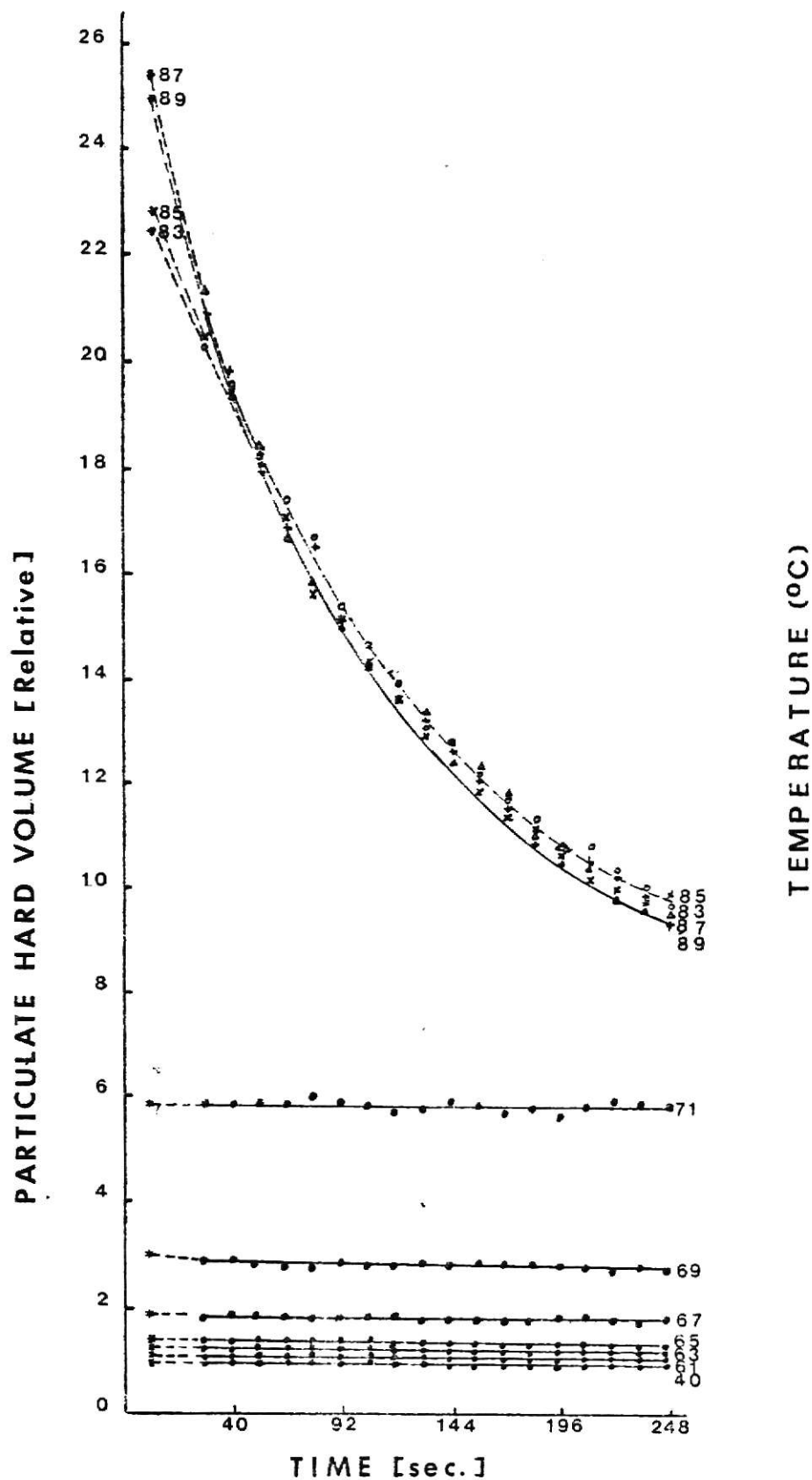


Fig. 21a. Effect of impeller pump shearing on PM-.08. RPHV vs. time exposure to shear. * represents the point to which the curve was extrapolated to zero time.

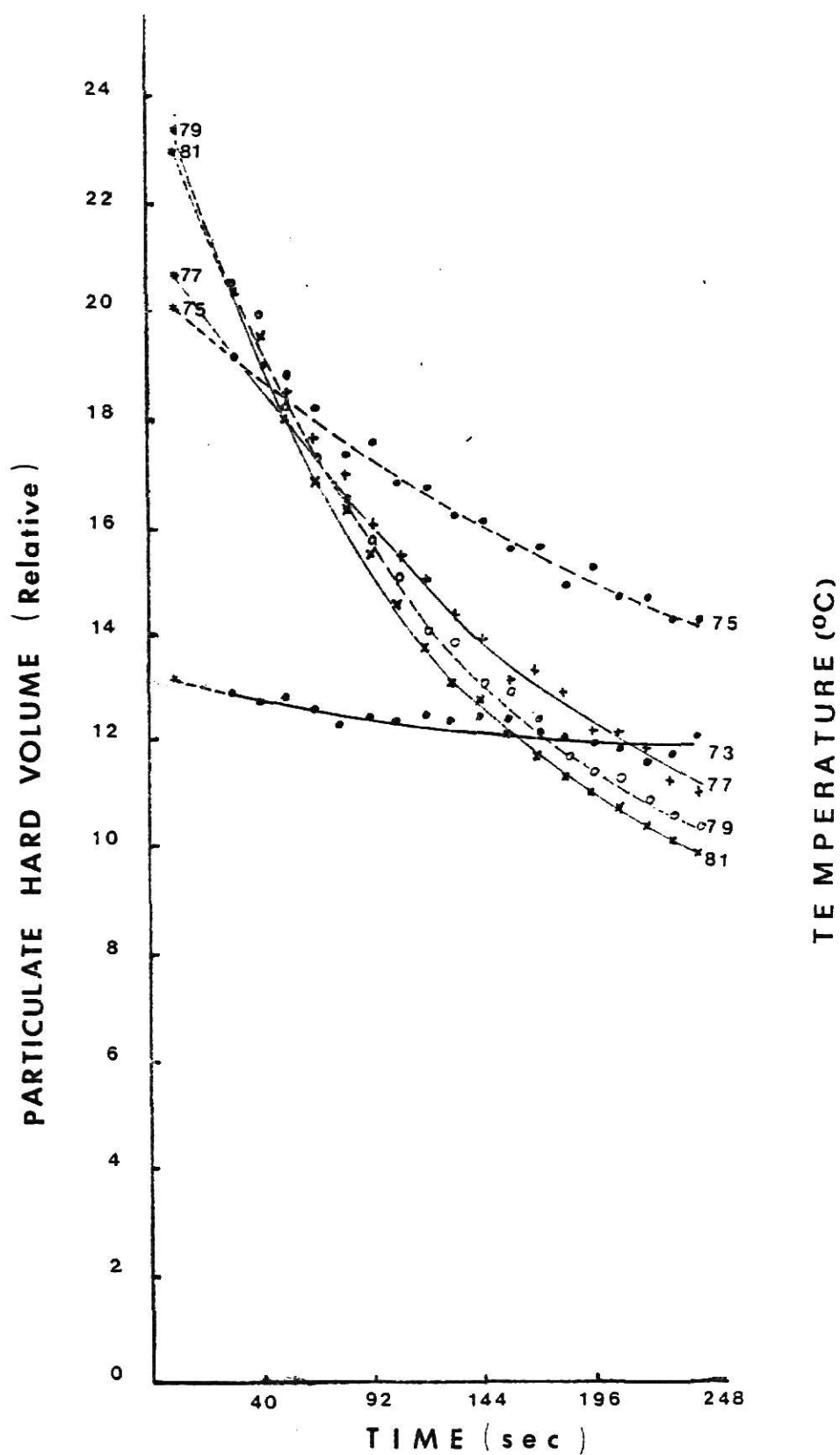


Fig. 21b. Effect of impeller pump shearing on VM-08. RPHV vs. time exposure to shear. * represents the point to which the curve was extrapolated to zero time.

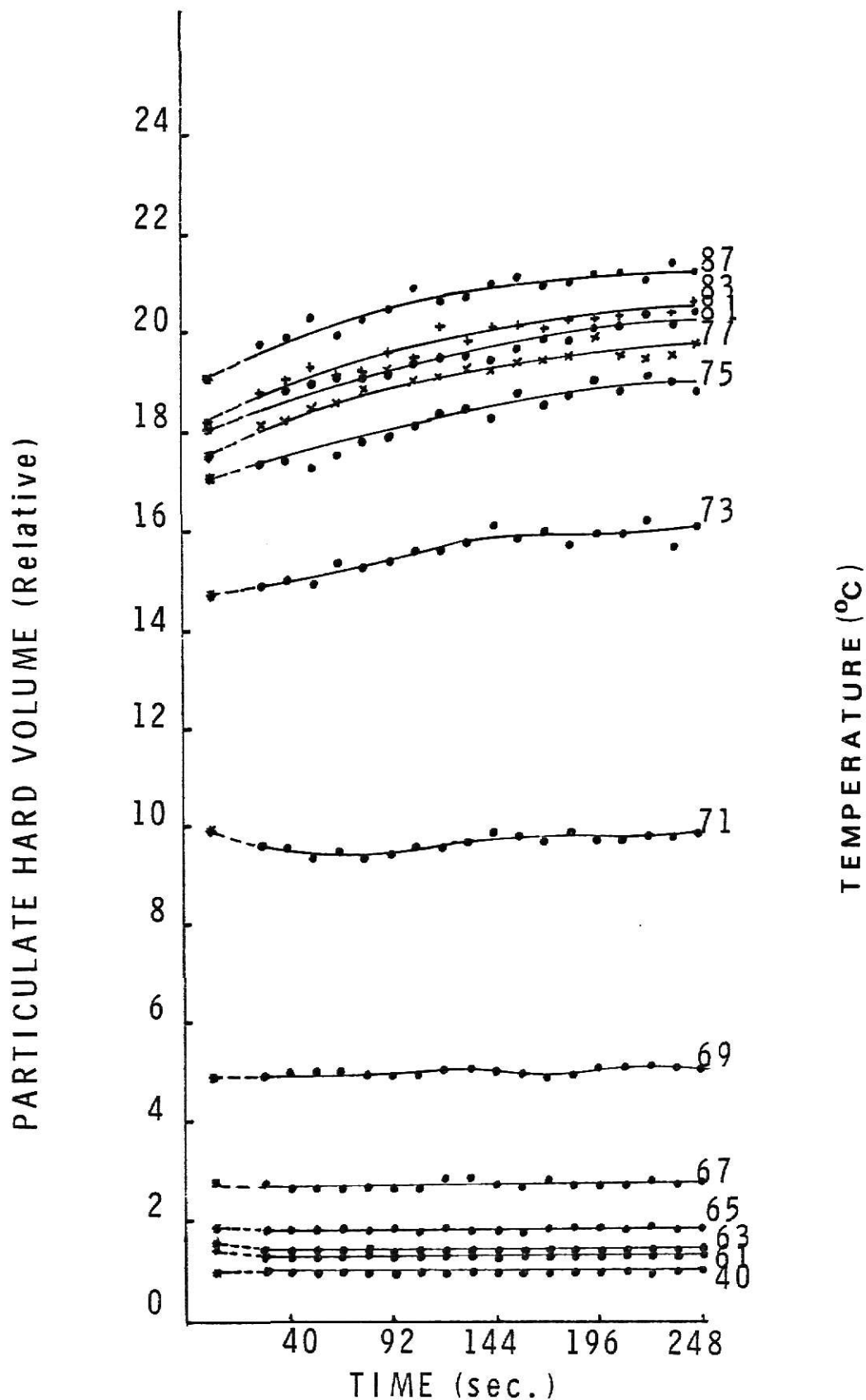


Fig. 22a. Effect of impeller pump shearing on WM-.13 RPHV vs. time exposure to shear. *represents the point to which the curve was extrapolated to zero time.

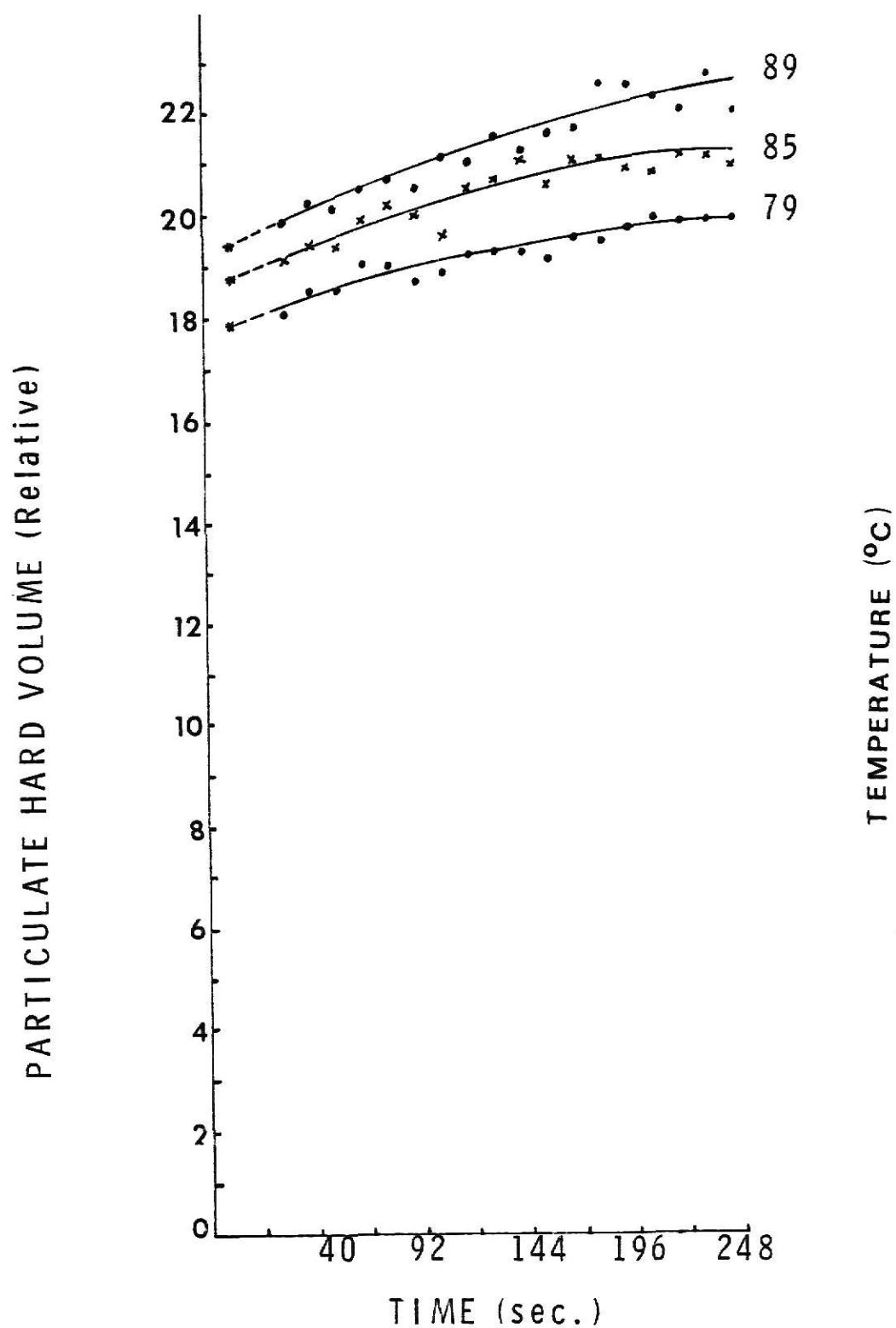


Fig. 22b. Effect of impeller pump shearing on WM-.13.
RPHV vs. time exposure to shear. * represents the
point to which the curve was extrapolated to zero
time.

at temperatures prior to pasting, the degradation curves were just horizontal lines with zero slope meaning the granules before the onset of pasting were invulnerable to shearing by the impeller pump. At higher temperatures (e.g. 75°C and above for WM-.05 and WM-.08), the slope of the curves became higher, meaning that the starch granules on pasting became fragile and vulnerable to shear. After maximum pasting, response to shear went down again. This is illustrated by WM-0 (Fig. 19) and at 80°C, its curve approximated a horizontal line again. This point was not reached for the cross-linked samples; at 87 and 89°C their curves still had the steep slopes meaning their tolerance to fragmentation by temperature was still high.

The absolute slope of the degradation curves in general had this order: WM-.05 > WM-.08 > WM-.0 > WM-.13. Considering the crosslinked starches alone, the results indicated that fragility of the pasted granules decreased with crosslinking.

A quick look at the slopes of the degradation curves for all the samples might lead one to think that WM-0 pasted granules were less fragile than WM-.05 and WM-.08 because of the low slopes of WM-0. A closer study of the curves, however, would reveal that the tolerance of WM-0 to fragmentation was low. Degradation due to pasting must have been going on already in WM-0 to such an extent that the potential of the granules to further degradation by shear was already comparatively low. This leads to the conclusion that the comparatively low magnitude and temperature of maximum relative PHV of WM-0 (Tables 2 and 3) compared to its crosslinked modifications is due to low temperature tolerance to fragmentation.

In contrast, the almost parallel degradation lines at different temperatures most evident in WM-.05 and to a less extent in WM-.08 indicate a tolerance to variation of temperature for pasting as well as nearly the

same rate of mechanical degradation due to shear even at these different temperatures.

It is interesting to note that though the degradation curves of WM-.13 did not depart from the indicated trend of decreased fragility with increased crosslinking (WM-.05 > WM-.08 > WM-.13), unlike those of the others, their slope is positive. This would suggest that added to resistance to shear was another phenomenon contributing to relative PHV and thus opposed to the expected effect of shearing. Scanning electron micrographs of crosslinked waxy corn starch at 85°C showed the granules very convoluted and folded (43). Chabot et al (22) reported that Brabender cooking of modified waxy corn starch resulted in elongation and stretching of the granule. This could account for the phenomenon contributing to relative PHV. What the shearing of the Brabender amylograph did to the modified waxy corn starch, the Microtrac impeller pump shearing could have accomplished with WM-.13, increasing its relative PHV. The same could also have been happening to WM-.05 and WM-.08 but to a lesser extent, and since they were more fragile, decrease in relative PHV was the predominant effect, hence the negative slope of their curves.

Extrapolation of the degradation curves to time zero, i.e., to the time before the granule was exposed to shearing by the impeller pump gave values lower than gravity flow for WM-0, WM-.08, and WM-.13, but higher for WM-.05. For instance, at 75°C, WM-.08 and WM-.13 extrapolated relative PHV values were 6% and 5% lower than those of gravity flow, respectively. The difference progressively increased with temperature. The deviations could be due to the probable greater rate of shearing during the first 23 seconds during which the analyzer was not yet taking readings. Again, the aforementioned experimental difficulty and concomitant uncer-

tainty of the quantitation with gravity flow could be a contributing factor.

Figs. 23-26 each contains a series of photopasteograms constructed from the mechanical degradation curves. They also give an idea as to where in the time range of exposure to shear, the conventional FDLMP parameters, those of gravity flow, and those of the peristaltic pump were measured.

Only the FDLMP of WM-0 fell within the time range of the kinetics study. A longer shearing time would be necessary for the other three. Puzzlingly again, WM-.13 seemed to need less shear exposure to approach conventional FDLMP values (Fig. 26), as if the cumulative shearing during the whole pasting process had produced less effect than the 248 seconds of the kinetics study. But then if it is recalled that though 248 seconds of shearing action could result in elongation and unfolding of the convoluted granules to produce a slight increase in PHV, cumulative shearing through the entire pasting process could go beyond unfolding into fragmenting, then this observation becomes reasonable.

Fig. 23 shows that the relative PHV of the conventional FDLMP and that with the peristaltic pump of WM-0 both peaked at 72°C, that with gravity flow at 73°C, and that of the kinetics study at 71°C. The higher temperature of maximum relative PHV with gravity flow could be attributed to minimal shear. The lower temperature for the kinetics study could be due to the fact that though the temperature ramp was kept as identical as possible, all the other 3 methods had the slurry continuously circulating and being cooled on the line unlike in the kinetics study where the starch slurry was subjected to a more sustained heating.

Of the three temperatures of maximum relative PHV for WM-0, the one from the off-line method, 71°C, must be the real one since it is where

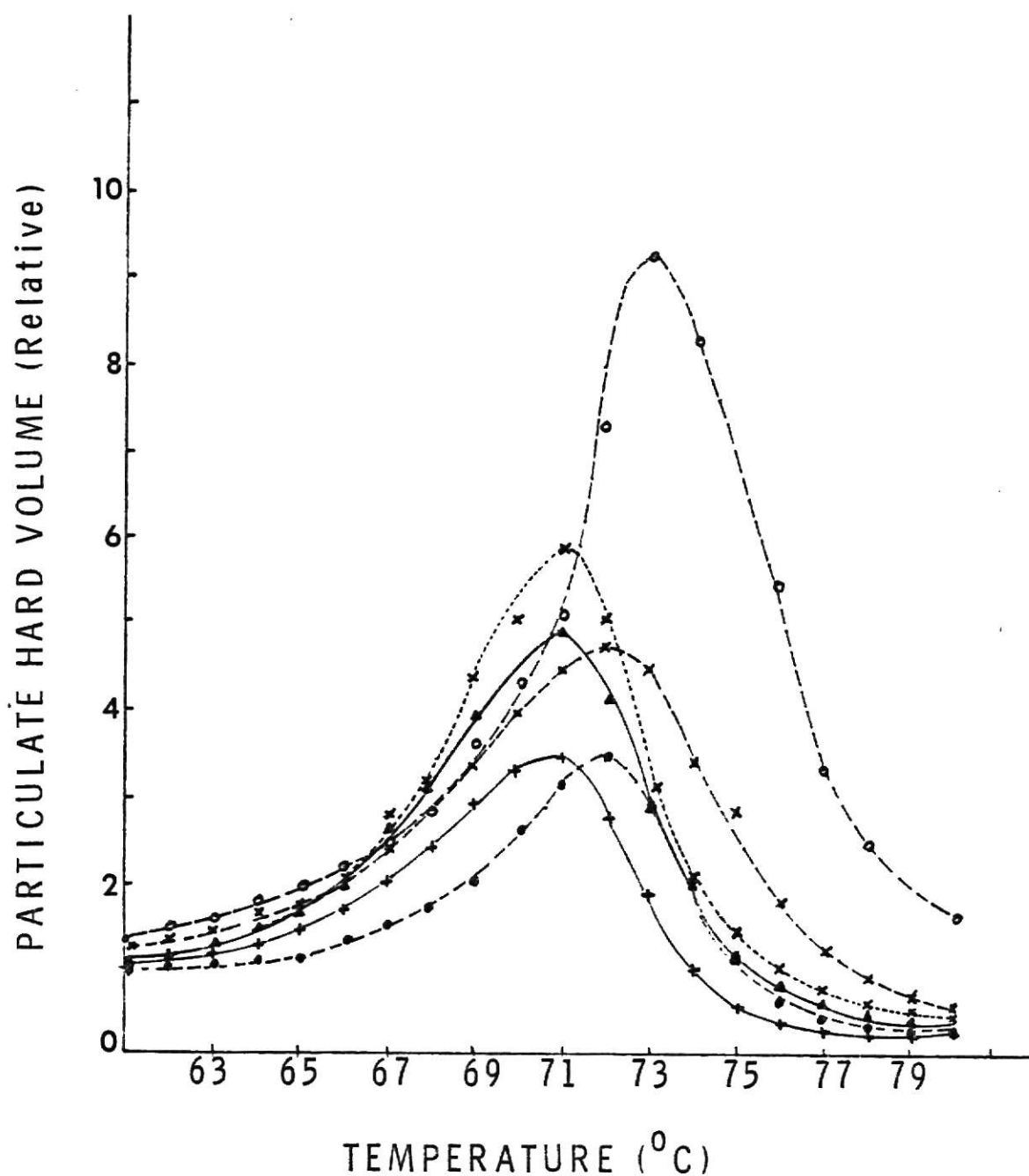


Fig. 23. Off-line FDLMP on WM-0. RPHV vs. temperature. Also indicated are FDLMP by gravity flow, by peristaltic pump, by impeller pump and by extrapolation to zero time. --o-- for gravity flow; x--x-- for peristaltic pump; ●●● by impeller pump; x...x... for extrapolation to zero time.

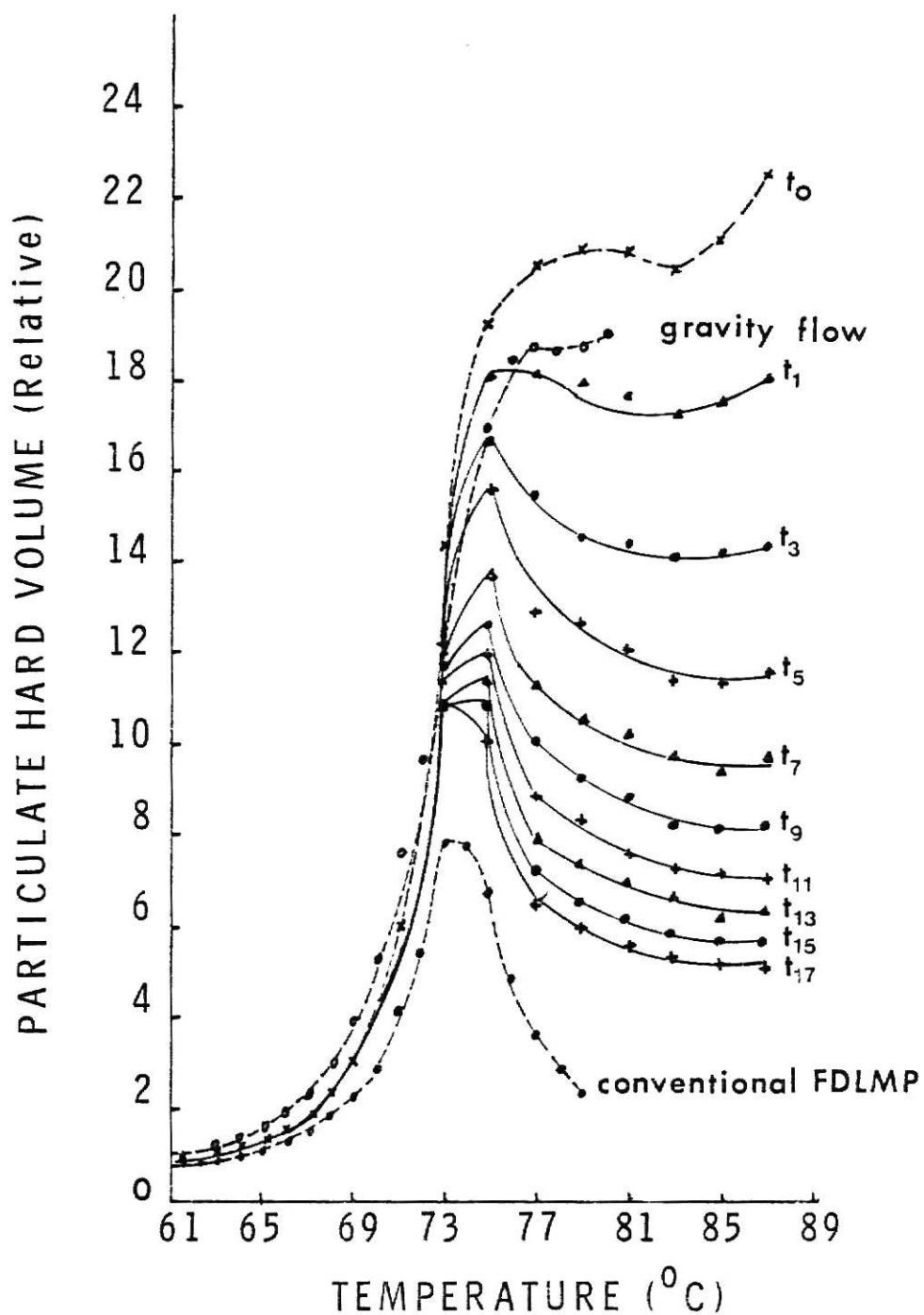


Fig. 24. Off-line FDLMP on WM-.05. RPHV vs. temperature. Also indicated are FDLMP by gravity flow, by impeller pump and by extrapolation to zero time.

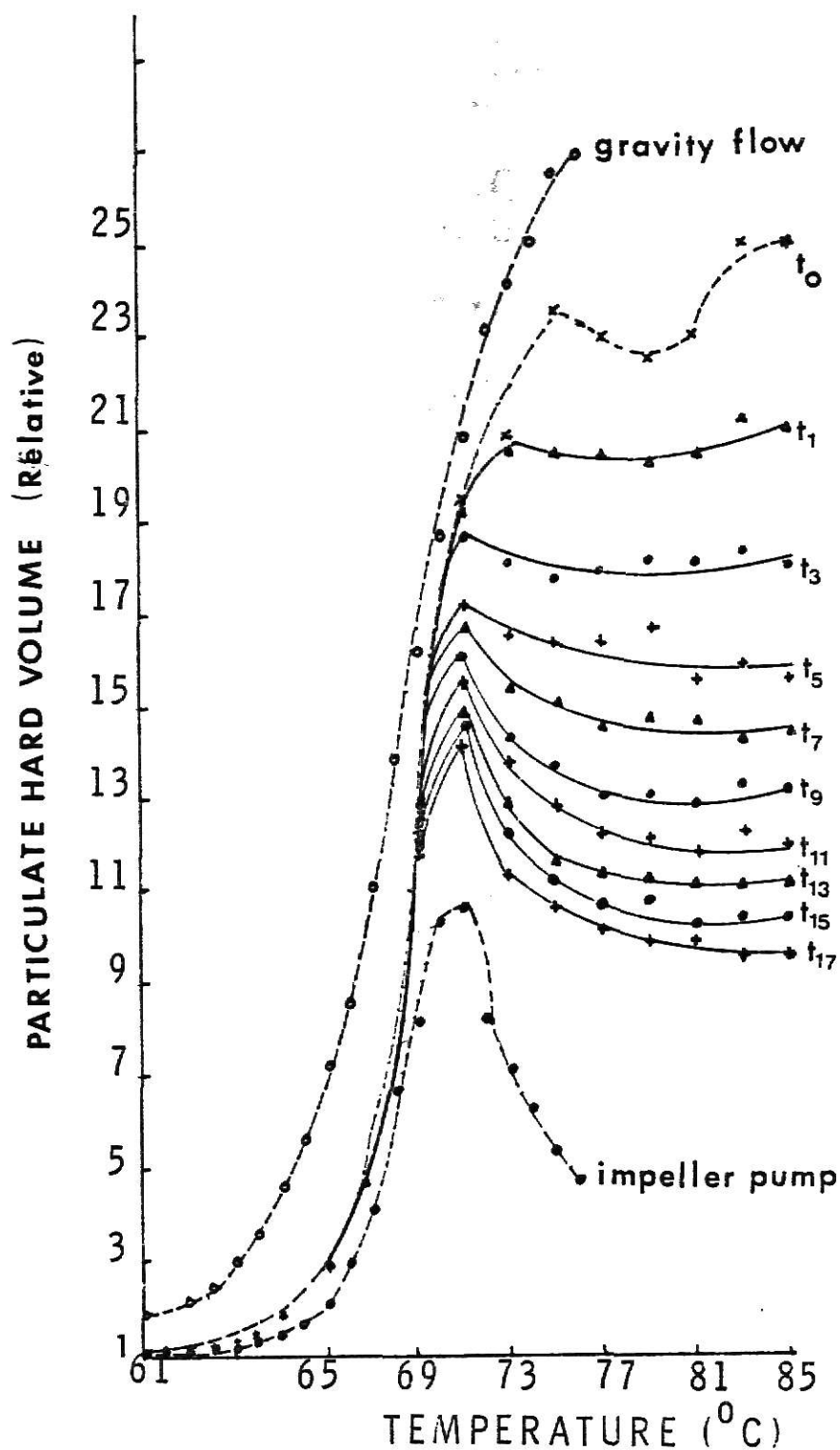


Fig. 25. Off-line FDLMP on WM-.08. RPHV vs. temperature. Also indicated are FDLMP by gravity flow, by impeller pump and by extrapolation to zero time.

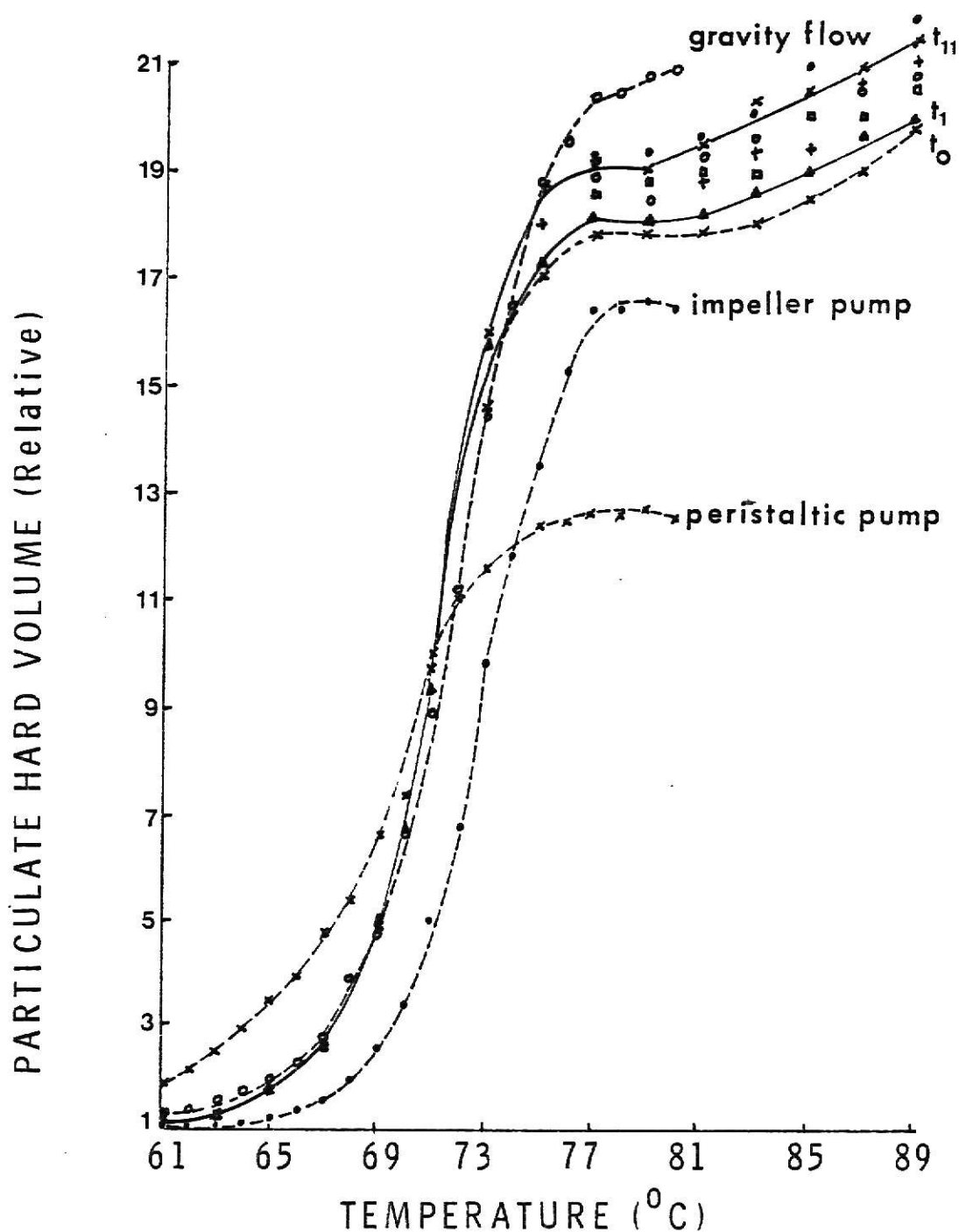


Fig. 26. Off-line FDLMP on WM-.13. RPHV vs. temperature. Also indicated are FDLMP by gravity flow, by impeller pump, by peristaltic pump and by extrapolation to zero time.

the extraneous condition of cooling on the line was not introduced.

Figs. 24 and 25 underline the similarity in behavior between WM-.05 and WM-.08 which was also manifested by the amylograms. Evidence of shearing both began just beyond 73°C and vulnerability to shear was both greatest at 75°C. The photopasteograms also indicate how much more fragile WM-.05 was than WM-.08. Fig. 26 shows the interesting effects on WM-.13 of negligible shear (gravity flow), some amount of shear (kinetics study), cumulative shear (conventional FDLMP) and little shear but crushing action (peristaltic pump).

Of the three FDLMP modifications here employed, namely; that with gravity flow, that with the peristaltic pump, and the off-line method of the kinetics study, the latter holds the most promise for development into an easy, quick, and practical starch pasting measure method. Gravity flow, the writer believes, is not worth the trouble unless as in this work it was done to answer a question that had a more important implication - to find out just what kind of pasting measure the FDLMP data was affording. Except for the easier circulation of sample slurry, the peristaltic pump method had no merits to it. It lacks the only advantage of gravity flow, negligible fragmenting effect. It has all the drawbacks of gravity flow—difficult simulation of water conditioning and time-consuming dismantling and clean-up after running each sample; plus some of its own—spattering, changing flow.

For the study of the overall pasting process continuously and as it occurs, conventional FDLMP has its merits. Perhaps it is even better that the impeller pump shears the pasted granules. Pasting strength and other properties associated with it are more important than actual granule size where functionality is concerned.

Another limitation of the conventional FDLMP, in addition to the list given under Review of Literature, is the inability to observe pasting in the presence of other substances such as acid or salts due to uneconomical amounts necessary and possible harmful effects of the chemicals to the equipment. It must be pointed out, however, that though the lower limit for size may cause some of the finer material leached out to escape detection, still the FDLMP has advantage over traditional turbidimetry even with the improvement by Kainuma in that in the FDLMP, a 13-channel histogram, provides the distribution of the particles re sizes throughout the pasting process. Also, though the point of loss of birefringence, which anyway is not sharp, is not indicated by FDLMP, the temperature range of initial rise to maximum relative PHV approximates it (see Tables 1 and 2). This temperature range is determined with more constancy.

Some other advantages of the conventional FDLMP in addition to those enumerated under Review of Literature are:

1. The simplicity of operation requiring little or no operator skill after acquainting oneself with the equipment.
2. The total lack of subjectivity of the results obtained.
3. It consumes but little sample (.25 g to .5 g) and yet a large number of particles are measured at the same time and continuously.
4. The optical responses are quantitative measures and in the case of crosslinked starches, they are even linearly correlated to the degree of crosslinking (see Figs. 5 and 6).

Off-line FDLMP Parameters

Quantitative interpretation of photopasteographic data is desirable to allow numerically expressed differentiation between starches of even

subtly varying functionalities. Further analysis of the off-line data obtained on the chemically modified waxy corn starches allows one to select a well-specified method to quantitatively differentiate members of this particular group.

Table 4 gives the pasting parameters of off-line FDLMP at different time exposures to shear. The initial diameter (median diameter at 40°C) was practically not affected by the shearing, but the maximum median diameter was. The maximum median diameter of WM-0 was rather fluctuating and did not show the steady decrease of WM-.05 and WM-.08. This could be due to the fact that at 78-80°C when most of the WM-0 granules had been fragmented, the median diameter value was more dictated by fewer particles. The decrease in maximum PHV of WM-.05 and WM-.08 with exposure to shear was accompanied by the decrease in median diameter; the increase in maximum PHV of WM-.13 was accompanied by an increase in median diameter. It is probable that the maximum diameter obtained with the off-line FDLMP is closer to the true value than with gravity flow because of the absence of the bubble and condensing water vapor problems in the former method which at higher temperatures (72°C and above) plagued gravity flow.

The order of maximum relative PHV obtained by extrapolation to zero time (WM-.08 > WM-.05 > WM-.13 > WM-0) was not identical to that of gravity flow (WM-.08 > WM-.13 > WM-.05 > WM-0). It was due either to the difficulty and possible error in the extrapolation of the steep curves or to the oft-mentioned uncertainty of measurement with gravity flow. The writer is inclined to trust the off-line data more than that of the latter. After 27 seconds of shear, the order of maximum relative PHV became identical to that of gravity flow; but from 53 seconds on, the order became that of the conventional FDLMP.

Table 4

Off-line FDLMP Parameters

Exposure to shear (seconds)	Starch Sample	Diameter			Temperature °C				Max. PHV (cm ³ /g)	Max. RPHV
		Ini. (μ m)	Max. (μ m)	Change (μ m)	Ini. Rise Diam.	Max. Diam.	Ini. Rise PHV	Max. PHV		
0	WM-0	----	----	----	----	----	----	71	.522	5.80
	WM-.05	----	----	----	----	----	----	87	.922	22.50
	WM-.08	----	----	----	----	----	----	89	.952	25.05
	WM-.13	----	----	----	----	----	----	89	.753	19.85
27	WM-0	15.1	31.9	16.8	66	79	65	71	.415	4.86
	WM-.05	15.2	42.1	26.9	67	85	67	75	.743	18.13
	WM-.08	13.8	37.8	24.0	67	79	67	87	.810	20.70
	WM-.13	14.6	31.9	17.3	65	83	65	89	.756	19.88
53	WM-0	15.3	27.4	12.1	67	78	65	71	.369	4.25
	WM-.05	14.5	40.1	25.6	65	79	65	75	.683	16.67
	WM-.08	14.1	38.4	24.3	67	81	67	75	.713	18.75
	WM-.13	14.3	32.7	18.4	63	83	65	89	.764	20.32
66	WM-0	14.7	30.7	16.0	67	79	65	71	.368	4.09
	WM-.05	15.0	39.0	24.0	67	81	65	75	.636	16.08
	WM-.08	14.2	37.8	23.6	67	85	67	75	.690	18.15
	WM-.13	14.4	32.1	17.7	63	85	63	89	.777	20.44
79	WM-0	14.9	31.7	16.8	66	78	65	71	.342	4.00
	WM-.05	14.4	37.6	23.2	63	79	67	75	.636	15.52
	WM-.08	14.1	36.9	22.8	67	83	67	75	.654	17.20
	WM-.13	14.3	33.1	18.8	65	85	65	89	.785	20.65

Table 15 (continued)

	Starch Sample	Diameter			Temperature °C				Max. PHV (cm ³ /g)	Max. RPHV
		Ini. (μm)	Max. (μm)	Change (μm)	Ini. Rise Diam.	Max. Diam.	Ini. Rise PHV			
105	WM-0	14.9	32.1	17.2	67	80	63	71	.330	3.86
	WM-.05	14.6	36.5	21.9	65	79	67	75	.544	13.71
	WM-.08	13.8	36.5	22.7	67	77	67	75	.637	16.75
	WM-.13	14.4	33.0	18.6	65	83	65	89	.803	21.12
157	WM-0	14.9	29.6	14.7	64	79	65	71	.307	3.59
	WM-.05	14.5	33.5	19.0	67	75	67	75	.478	12.32
	WM-.08	14.1	36.3	22.2	67	81	65	75	.590	15.52
	WM-.13	14.1	33.7	19.6	65	85	65	89	.821	21.59
209	WM-0	15.0	26.3	11.3	67	78	65	71	.292	3.42
	WM-.05	14.8	32.6	17.8	65	75	67	75	.447	10.91
	WM-.08	13.8	34.2	20.4	67	79	67	75	.558	14.68
	WM-.13	14.1	34.6	20.5	65	83	65	89	.847	22.28
235	WM-0	14.8	26.7	11.9	67	77	65	71	.294	3.44
	WM-.05	15.1	30.7	15.6	65	73	65	73	.445	10.86
	WM-.08	14.0	33.7	19.7	67	75	67	75	.540	14.20
	WM-.13	14.1	34.6	20.5	65	83	65	89	.863	22.70

Determination of the Degree of Crosslinking by Off-line FDLMP

Fig. 27 shows the relationship between the amount of crosslinking reagent used and the maximum relative PHV at the different time exposures to shear. The change of the curves with time exposure to shear implies the need for a standard procedure emphasizing the time factor if the off-line FDLMP is to be used. Fig. 27 also reveals that the linear relationship between maximum relative PHV and crosslinking was attained after 209 seconds of shearing time. However if measures are to be taken during the entire pasting process after 209 seconds of shear at every other degree centigrade as was done here in order to obtain the maximum relative PHV, the method would still be needlessly time and energy consuming (nearly 3½ hours/sample if the 1°C/4 min ramp is used). It would be much simpler and more efficient if measurements could be made only at two temperatures; one before pasting and another during pasting. Fig. 28 indicates that a temperature of 77°C and a shearing time of 209 seconds give the linear relationship between relative PHV and degree of crosslinking.

In itself Fig. 28 is a calibration curve for determining degree of crosslinking of modified waxy corn starches. The same curve could have been prepared by using the following procedure: Heat ca. 210 ml of water to 40°C. To this add a suitable amount of weighed starch sample (1.0 g for WM-0, .5 g for the crosslinked starches). Provide for a gentle stirring and constant rate of heating of the slurry. Allow the starch to disperse for about 10 seconds and pipet 100 ml of the slurry into the sample bowl of the Microtrac Analyzer which had previously been zeroed. After 202 seconds, take a reading. Continue to heat the slurry (in this work a temperature ramp of 1°C/4 min was used) to 77°C, then repeat what was done at 40°C. Divide the PHV reading at 77°C by that at 40°C to get the

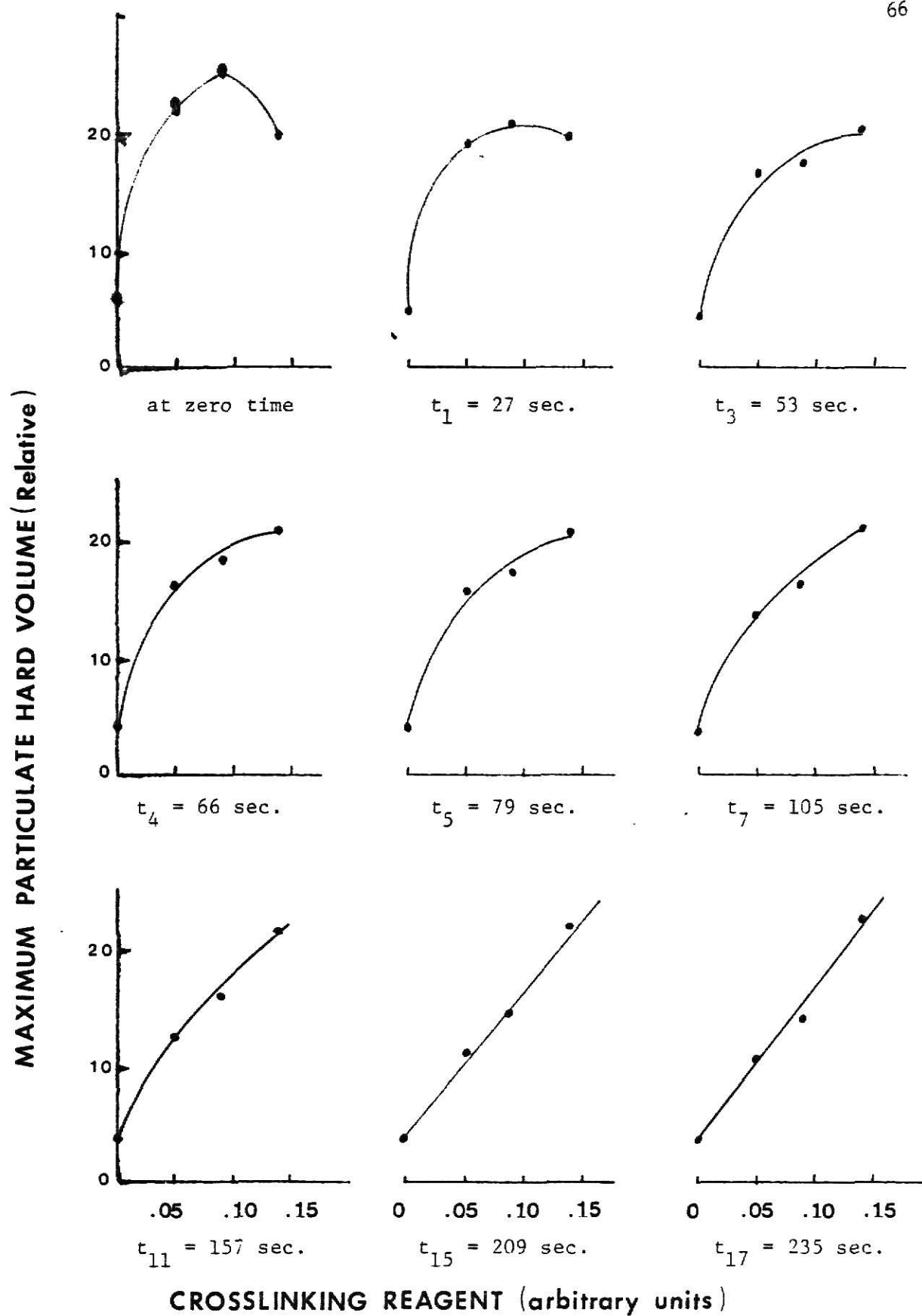


Fig. 27 Maximum relative particulate hard volume vs. amount of crosslinking reagent at different time exposures to shear.

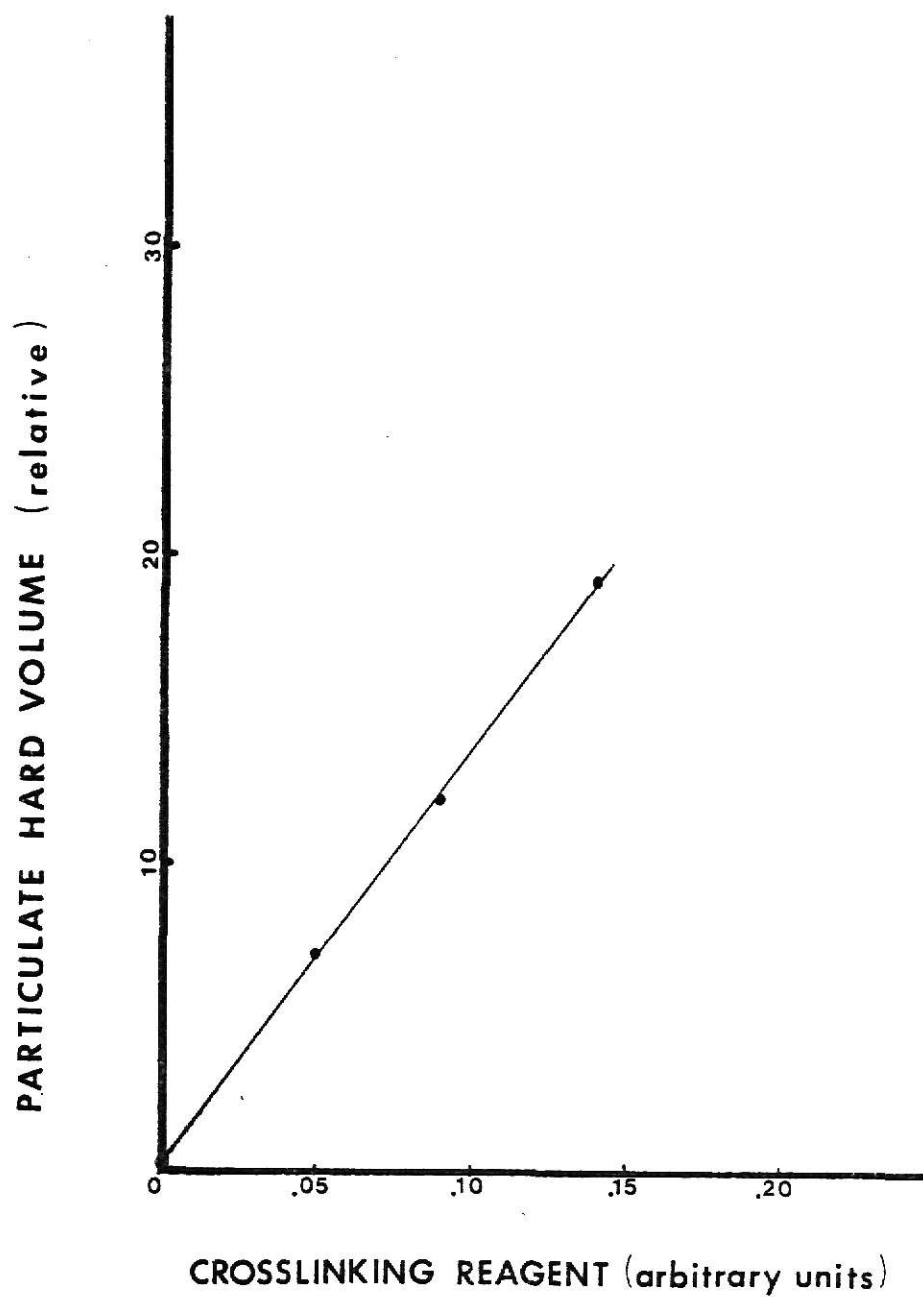


Fig. 28. Relative particulate hard volume of crosslinked waxy corn starch at 77°C and shearing time of 209 seconds vs. amount of crosslinking reagent.

relative PHV at 77° . Plot this value against the degree of crosslinking.

Recommendations

It is not possible to dictate from this study alone standard times, concentrations, temperatures or treatments for quantitative photopasteography to directly compare starches or individual members of all starch groups, but some suggestions can be given. Even the foregoing procedure for crosslinked corn starches should still be improved. The temperature ramp of $1^{\circ}\text{C}/4$ min. needs looking into. The writer thinks it is too slow a rate of heating if practicality, economics and realistic conditions are to be considered. Cook and Axtmayer (46) found 1.5 to 2 min./ $^{\circ}\text{C}$ as satisfactory. Kainuma et al. (10) employed a $2^{\circ}\text{C}/\text{min.}$ ramp. The temperature before pasting at which measurement was made (40°C) should perhaps be raised to 55°C or even higher as no significant changes seemed to happen below that temperature. It might even be probable with more careful weighing to totally eliminate taking a measurement at a temperature below pasting. Another point that perhaps needs consideration is the pH at which measurements should be made since pH is an important factor in starch pasting.

In general, any procedure to be developed will have to depend on the functional properties to be attained by the product for which the starch pasting measure is to be made. Considerations might be taken as to what temperature the water or suspension medium is to be heated before adding the starch sample. This can lead to much time saving. The rate of heating is important as unnecessary slow rates should be avoided. The amount of starch sample needed will depend on up to what temperature measures are to be taken and optimum slurry concentration. It is well to use a

slurry concentration that at maximum pasting will approach maximum PHV that the detector and micro-processor can take without overloading.

For roots and tuber starches, for starches in which modification leads to hastened swelling, for slurries to which reagents like acid has been added hastening granule expansion too, it might be necessary to begin taking measures at as low as 55°C or lower and anticipate a low stopping point (about 80°C). For cereal starches and for starches in which modification and/or addition of chemicals to the sample slurry inhibits or retards swelling, it might be practical to begin taking measures at 60°C or higher and also anticipate a higher temperature (about 95°C or higher) at which to stop if the entire process down to fragmentation of the granule is to be characterised. Taking readings at every other degree centigrade though convenient might be unnecessary. A 4 or 5°C interval at the lower temperatures and 3 or 2°C as maximum pasting is approached might be better.

Time allowed for the dispersion of the sample in the mixing bowl before taking the first reading is very important and must be kept constant for each procedure developed.

Conclusion

To summarize, this work indicated:

1. That the determination of gelatinization temperature range is subjective and inadequate to indicate the extent of crosslinking of the starches.
2. That FDLMP can give an approximation of gelatinization temperature range.
3. That as expected, crosslinking in the particular starches used

decreased peak viscosity and helped maintain high viscosity as was shown by the Brabender amylograms.

4. That the conventional FDLMP data did not reflect realistic values of granule size increase on pasting because the Microtrac impeller pump was shearing the pasted granules.

5. That the conventional FDLMP gave linear response to the degree of crosslinking because it measured the fragility of the pasted granules and crosslinking increases granule strength.

6. A model for differentiation among members of starch sets by an off-line modification of the conventional FDLMP.

The writer believes that further improved, the conventional FDLMP and its off-line modification can be a powerful tool not only in capturing the "elusive" starch granule and shedding light on the "anomalies" of starch chemistry, but also in the less glamorous but equally important task of controlling quality in production.

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APPENDIX A

Brabender Amylograph Data

1. With 700 g cm cartridge

Starch Sample	Sample No.	Peak/Shoulder Viscosity (B. U.)	Final Viscosity (B. U.)	Temperature of Initial Rise (°C)
WM-0	1	685 (p)	245	82.1
WM-.05	1	520 (s)	590	81.5
	2	520 (s)	605	82.0
	3	520 (s)	580	81.2
WM-.08	1	435 (s)	520	81.5
WM-.13	1	57 (s)	195	82.2
Monarch	1	120 (p)	80	85.2
	2	120 (p)	90	85.2
	3	105 (p)	67	86.0

2. With 350 g cm cartridge

Starch Sample	Sample No.	Temperature of Initial Rise (°C)
WM-0	1	80.3
	2	80.4
	3	81.0
WM-.05	1	80.8
	2	80.8
	3	80.8
WM-.08	1	80.9
	2	80.8

continued

Starch Sample	Sample No.	Temperature of Initial Rise (°C)
WM-.13	3	80.8
	1	80.3
	2	80.6
	3	80.4
Monarch	1	83.5
	2	83.5
	3	84.0

APPENDIX B
FDLMP Pasting Parameters for Multiple Runs
1. With Gravity Flow

Starch Sample	Sample No.	Diameter		Temperature °C				Max. PHV cm ³ /g	Max. RPHV
		Ini. (m)	Max. (m)	Change (m)	Ini. Rise Diam.	Max. Diam.	Ini. Rise PHV		
WM-0	1	17.0	33.7	16.7	*	75	66	.567	8.59
	2	17.1	35.0	17.9	66	73	66	.651	9.30
WM-.05	1	15.7	36.5	20.8	*	**	62	**	**
	2	15.4	66.7	51.3	*	**	63	**	**
WM-.08	1	16.8	**	**	62	**	62	**	**
	2	16.5	**	**	61	**	63	**	**
WM-.13	1	14.8	**	**	62	**	63	**	**
	2	14.9	**	**	62	**	63	**	**
	3	14.8	**	**	61	**	65	**	**
	4	14.8	**	**	62	**	65	**	**

*Too fluctuating to be definite.

**Overloaded below 80°C, so the maximum values could not be ascertained.

FDLMP Pasting Parameters for Multiple Runs

2. Off-line FDLMP

Starch Sample	Sample No.	Diameter			Temperature °C				Max. PHV cm ³ /g	Max. RPHV
		Ini. (m)	Max. (m)	Change (m)	Ini. Rise Diam.	Max. Diam.	Ini. Rise PHV	Max. PHV		
WM-0 (at 27 sec.)	1	15.1	31.9	16.8	66	79	66	71	.415	4.86
	2	15.1	30.4	15.1	66	78	65	71	.405	4.53

Relative PHV's of Off-line FDLMP at Different
Time Exposures to Shear

1. At 75°C

Starch Sample	t ₅ 79 seconds	t ₇ 105 seconds	t ₁₁ 15 seconds	t ₁₅ 209 seconds	t ₁₇ 235 seconds
WM-0	.8	.76	.67	.61	.60
WM-.05	15.52	13.71	11.93	10.91	10.05
WM-.08	17.20	16.75	15.52	14.68	14.20
WM-.13	17.78	18.09	18.75	18.73	18.88

2. At 77°C

Starch Sample	t ₁₁ 15 seconds	t ₁₅ 209 seconds	t ₁₇ 235 seconds	t ₁₈ 248 seconds
WM-0	.39	.37	.34	.35
WM-.05	8.78	7.15	6.49	6.30
WM-.08	12.99	12.18	11.26	11.05
WM-.13	19.17	19.44	19.46	19.83

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FRAUNHOFER DIFFRACTION LASER MULTICHANNEL PHOTOPASTEOGRAPHIC
(FDLMP) MEASUREMENT OF CROSSLINKING IN CHEMICALLY
MODIFIED WAXY CORN STARCH

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The pasting of waxy corn starch and its crosslinked modification was observed and measured using Fraunhofer diffraction laser multi-channel photopasteography (FDLMP), viscometry, and microscopy. FDLMP gave quantitative and linear responses to the degree of crosslinking and an approximation of the gelatinization temperature range. The Brabender amylograph showed that crosslinking decreased peak viscosity but helped retain high viscosity. The determination of gelatinization temperature by microscopy proved inadequate to indicate extent of crosslinking.

FDLMP data appeared unrealistic in the median diameter values of the pasted granules and its response to pasting. The unrealistic data was found to be due to the pasted starch granules being sheared by the impeller pump of the Leeds and Northrup Microtrac Particle Size Analyzer, the basic instrument for FDLMP, by using gravity flow in place of the impeller pump for the circulation of the starch sample.

A simpler and more flexible off-line modification of the conventional FDLMP was developed. The method involves heating the dispersion medium off-line, dispersing the weighed starch sample into it, pipetting an aliquot of the slurry into the Microtrac Analyzer mixing bowl, taking a reading after 202 seconds; in the meantime heating the slurry to 77°C at which measurement similar to that at 40°C is made. The optical response at 77°C is divided by that at 40°C and read against a similarly prepared calibration curve of optical response vs. degree of crosslinking.