37853 #2

FILLED POLYPROPYLENE. I

DEVELOPMENT OF TALC-FILLED GRADES

by N. E. Frailey

Technical Progress Report WPR 8-66

Uniform Research Project Code No. 66229

This report is based on work from October 1965 to March 1966.

Written and Reviewed:	N. E. Frailey and D. K. Peterson
Approved:	M. E. Doyle
Participant:	G. W. Powers
Reference:	Laboratory Record Book No. CWLR 127

PLASTICS TECHNICAL CENTER
WOODBURY, NEW JERSEY
PRIVATE AND CONFIDENTIAL

TECHNICAL PROGRESS REPORT

DISTRIBUTION

Head Office

Technical Information Services (19)
Manager, Union Laboratories

Industrial Chemicals Division

Director, Houston Research & Development Laboratory

Plastics and Resins Division

Manager, Woodbury Plant
Manager, Polystyrene Operations, Wallingford

Synthetic Rubber Technical Center

Manager, Research and Development
Research Director, Torrance Research Laboratory

Shell Oil Company

Manager, Manufacturing Research Dept, New York
Research Director, Houston
Research Director, Wood River

Shell Development Company

President, New York (2)
Emeryville Research Center (14)
Director, Modesto

Shell Pipe Line Corporation

Manager, Technical Development Laboratory, Houston

For Information:

Shell Canada, Limited

Manufacturing Department, Toronto, Ontario

Export of this document is subject to license under the Export Control Act of 1949.
SCC-4

TABLE OF CONTENTS

ABSTRACT

Experimental filled polypropylene grades with properties to satisfy a range of requirements have been developed. These are based on 40% Mistron Vapor talc in propylene homopolymer and copolymer. Talc particle size has more effect on the physical properties of filled polypropylene than does particle shape.

INTRODUCTION

A filler is added to a polymer to improve certain mechanical properties for a specific end-use. Generally, these properties are flexural modulus, heat distortion temperature, and creep resistance. Most fillers are capable of significantly improving these properties; in almost every case, however, there is a concurrent sacrifice in impact strength, end-use oxidative stability, water absorption, and color in the blend. Perhaps of equal importance, incorporation of the filler into the polymer must be readily accomplished (preferably in conventional equipment) for a filled grade to be economically attractive. Thus, the ideal filler must impart an unusual balance of properties to the filled system.

At the present time, the market for filled polypropylene is growing rapidly, and is expected to increase from approximately 7 MM lb in 1965 to an estimated 15-20 MM lb per year by 1967. Automobile manufacturers are employing filled polypropylene for air ducts, fan and radiator shrouds, and electrical components; while the appliance industry is using it for various washing machine, dishwasher, and garbage disposal parts. At present Shell Polypropylene WM-650, which contains 32.1% asbestos, 6.4% zinc oxide, and 3.6% carbon black in propylene homopolymer, is our only semi-commercial grade of filled polypropylene. This material has been sampled to the automotive industry for use in the applications mentioned above; however, approval has been limited by three major deficiencies - impact strength, oxidative stability, and weld strength. Studies have, therefore, been conducted to overcome these deficiencies by making various modifications to the standard WM-650 formulation; the results are included in the present report.

EXPERIMENTAL

Initially in our study, several formulations, described in Table 1, were prepared by the outside compounder[1)] whom the plant presently employs for WM-650 production. Based on these results, four grades of talc of varying particle size and shape (described in Table 2) were evaluated in propylene homopolymer and copolymer. The formulations, shown in Table 3, were prepared via extrusion compounding using a twin-screw Welding Engineers Incorporated (WEI) extruder. The polypropylene powder and fillers were blended in a Henschel mixer for two minutes prior to crammer-feeding and extruding. These experimental samples and two competitive grades of talc-filled polypropylene were injection molded into ASTM specimens and tested for selected physical properties. Double-gated tensile bars were also prepared from various samples and tested for tensile strength in the weld line area. The oven life of 110-mil plaques was measured at 150°C on selected samples.

1) The equipment train used by the compounder consists of a batch-intensive mixer (Banbury-type) and a pelletizing extruder.

RESULTS AND DISCUSSION

Substituting talc for asbestos in the WM-650 formulation results in an improved product (10A18), as shown in Table 1. The impact strength and oven stability of the talc-filled material are superior to that of WM-650, while the other physical properties are comparable. A comparison between the physical properties of this same experimental formulation prepared by the outside compounder and prepared by extrusion compounding further indicates that a talc-filled system can be prepared via extrusion compounding.

The formulations discussed above contain carbon black and zinc oxide; both are expensive fillers compared to talc or asbestos. Therefore, samples with asbestos or talc substituted for zinc oxide and/or carbon black were evaluated. As shown by the data in Table 1, the non-black asbestos formulation has properties fully equivalent to the standard WM-650. Moreover, talc can be substituted for both the zinc oxide and carbon black (compare samples 3B32 and 3B33). Compared to WM-650, the homopolymer sample containing 40% talc has superior impact strength and oven stability without significant sacrifices in flexural modulus or heat distortion temperature. The weld strength is also marginally better than that of WM-650.

Two experimental samples based upon the standard WM-650 formulation but with a copolymer substrate were also evaluated. The addition of either talc or asbestos to Shell Polypropylene V-526 (high impact tailblock copolymer) results in significant increases in flexural modulus and heat distortion temperature. However, the talc-filled system has significantly better oven stability.

Based upon these results, four grades of talc of varying particle size and shape were evaluated in propylene homopolymer and copolymer to select the best grade of talc to be incorporated in these systems. As shown in Figures 1, 2, and 3, the talc particle size has more effect on the flexural modulus, impact strength, and yield elongation of the filled copolymer (V-526) than does the particle shape. The significant increase in notched Izod impact strength and the comparatively small reduction in yield elongation, illustrated in Figures 2 and 3, obtained with the addition of Desertalc 57 is a result of orientation of the large particles in the ASTM test specimens. The impact strength of 60-mil compression-molded plaques prepared from the Desertalc 57 filled systems was comparable to those of the other talc-filled systems, as shown in Table 3. No significant relationship was observed between talc particle size and the other measured physical properties.

The results of this study agree remarkably well with results reported in the literature by H. Alter.[1] In his study, it was shown that the mechanical properties of filled polyethylene are linear functions of the reciprocal of the filler particle diameter (d) and are independent of the chemical composition of the filler. The explanation given is that the 1/d function is an expression of the dependence on the surface-to-volume ratio of the filler. The filler is a diluent in polymer; so the modulus is inversely proportional to the filler volume. However, the polymer also adheres to the filler surface, forming a network and increasing the modulus in proportion to the number of attachments or to the filler surface area. The net result is the dependence on the diameter of the filler. The significant independence of the nature of the filler suggests that the polymer-filler adhesion, per unit available, is the same for all of the fillers. This seems reasonable if the non-polar polymers wet the higher surface energy fillers.

Figures 4 through 7 show the effect of talc (Mistron Vapor) addition on the flexural modulus, impact strength, and heat distortion temperature at 264 psi for Shell Polypropylene 55XX and V-526. In addition, an estimate of the effect of talc content on each property of talc-filled Shell Polypropylene V-521 (medium-impact tailblock copolymer) is also shown in these figures. Based upon economic considerations and improvements in physical properties, a loading of 40% Mistron Vapor talc appears to be optimum in filled homopolymer and copolymer for use in present applications. Moreover, these relationships will permit us to alter the balance of properties for future specific end-uses.

Compared to the competitive grades of talc-filled polypropylene, our experimental talc-filled systems have a superior balance of impact strength and flexural modulus. The other physical properties are comparable. This is shown in Table 4, which also shows an average of some of the physical property specifications employed by the various automobile manufacturers for such applications as fan shrouds. As shown by the data, 40% talc in polypropylene meets all of the automotive specifications, while WM-650, our asbestos-filled system, fails to meet the impact specification.

1) "Filler Particle Size and Mechanical Properties of Polymers", H. Alter, Journal of Applied Polymer Science, Vol 9, pp 1525-1531 (1965).

CONCLUSIONS

Substituting talc for asbestos in Shell Polypropylene WM-650 results in improved impact strength and oxidative stability without significant sacrifices in other physical properties. Talc particle size has a more significant effect on the flexural modulus, impact strength, and heat distortion temperature of filled polypropylene, than does the particle shape. From the study, three experimental talc-filled systems (40% talc in Shell Polypropylene 55XX, V-521, and V-526) have been developed. Samples of the 40% talc in homopolymer, designated TC8-1, have been submitted to the automotive industry for their evaluation. Initial results are favorable.

Further studies are planned with different types of mineral fillers of varying particle size and with various surface active agents.

APPENDIX

Table 1. SELECTED PROPERTIES OF FILLED POLYPROPYLENES

Grade Lot No. Sample Prepared by	WM-650 10HWJ301 Banbury	Experi- mental 10A17 Banbury	Experi- mental 10A18 Banbury	Experi- mental 3B33 WEI Extruder	Experi- mental 3B32 WEI Extruder	Experi- mental 10A16 Banbury	Experi- mental 10A19 Banbury	Homopolymer (MF 5) Typical -	Shell Polypro- pylene V-526 Typical -
Formulation									
Shell Polypropylene 55XX (MF 4), %	57.0	58.0	57.0[1)]	57.0	60.0	-	-[1)]	-	-
Shell Polypropylene V-526, %	-	-	-	-	-	57.0	57.0	-	-
Asbestos AMP-1, %	32.1	34.5	-	-	-	32.1	-	-	-
Mistron Vapor Talc, %	-	-	32.1	32.1	40.0	-	32.1	-	-
Zinc Oxide, %	6.4	6.6	6.4	6.4	-	6.4	6.4	-	-
Carbon Black, %	3.6	-	3.6	3.6	-	3.6	3.6	-	-
Butyl Zimate, phr	0.9	0.9	0.9	0.9	0.9	0.9	0.9	-	-
IONOX 330, phr	0.10	0.10	0.10	0.10	0.10	0.10	0.10	-	-
Calcium Stearate, phr	0.10	0.10	0.10	0.10	0.10	0.10	0.10	-	-
DLTP, phr	0.35	0.35	0.25	0.35	0.35	0.35	0.25	-	-
DSTP, phr	0.15	0.15	-	0.15	0.15	0.15	-	-	-
Physical Properties									
Ten Yld at 0.2 in./min, psi	4300	4700	4700	4400	4500	3400	3800	4500	3100
Yld Elong at 0.2 in./min, %	3.3	-	-	2.8	3.3	-	-	12	12
Flex. Modulus, 10^5 psi	6.0	6.5	6.3	5.3	5.5	4.6	4.8	2.2	1.5
Unnotched Izod Impact at 73°F, ft-lb/in.	4.0	4.0	6.4	7.9	7.5	-	19	≈ 20	-
Hardness, Rockwell "R"	90	-	-	98	95	-	-	90	81
Heat Distortion Temp, °F									
at 264 psi	192	212	190	185	182	185	165	140	130
at 66 psi	285	-	-	-	-	-	-	240	225
Ten Yld at the Weld Line, psi									
at 0.2 in./min	2900	-	2800	-	-	-	-	-	-
at 2.0 in./min	1900	-	-	-	2100	-	-	-	-
Oven Stability at 150°C on 110 mil plaques, days	29	30	50	-	65	30	50	-	-

1) Also contains 0.25 phr IONOL CP.

ABS-043943

8

Table 2. DESCRIPTION OF TALCS

Description	Mistron Vapor	Mistron Super Frost	Mistron Frost	Desertalc 57
Chemical Composition[1]				
SiO_2, %	62.51	59.15	59.15	58.10
MgO, %	30.59	27.96	27.96	29.21
CaO, %	0.22	5.17	5.17	4.46
Fe_2O_3, %	0.99	0.26	0.26	0.35
H_2O^+ (Chem combined), %	4.73	3.83	3.83	-
Na_2O, %	0.09	1.61	1.61	1.10
CO_2, %	0.44	2.29	2.29	-
Particle Size, μ				
Maximum	6.0	6.0	10.0	16.0
Average	1.0	0.8	3.0	7.0
Particle Shape[2]	P	AP	AP	AP
Surface Area,[3] $in.^2/g$	19.5	25.5	16	5-7

1) Major components only.
2) P = Platy AP = Acicular Platy
3) Measured by N_2 Adsorption.

Table 3. PROPERTIES OF EXPERIMENTAL TALC-FILLED POLYPROPYLENE

Lot No.	3B8	3B9	3B10	3B11	3B12	3B13	3B14	3B15	3B16	3B17	3B18	3B19	4B11	3B32	1B7-2
Sample Formulation															
Shell Polypropylene 55XX (MF 4) %	-	-	-	-	-	-	-	-	-	-	-	-	50	60	80
Shell Polypropylene V-526, %	60	70	80	60	70	80	60	70	80	80	70	60	-	-	-
Mistron Vapor Talc, %	40	30	20	-	-	-	-	-	-	-	-	-	50	40	20
Mistron Super Frost, %	-	-	-	40	30	20	-	-	-	-	-	-	-	-	-
Mistron Frost, %	-	-	-	-	-	-	40	30	20	-	-	-	-	-	-
Desertalc, %	-	-	-	-	-	-	-	-	-	20	30	40	-	-	-
Physical Properties															
Ten Yld at 0.2 in./min, psi	3500	3500	3400	3300	3200	3200	3200	3200	3200	3500	3500	3600	-	4500	4500
Yld Elong at 0.2 in./min,%	3.9	5.0	5.5	3.0	3.7	4.6	3.2	4.0	4.8	10	10	10	-	3.2	5.2
Flex Modulus, 10^5 psi	4.64	3.58	3.04	4.64	3.53	2.95	4.16	3.81	2.88	2.49	2.93	3.83	7.64	5.51	3.92
Unnotched Izod Impact at 73°F, ft-lb/in.[1)]	26	2)	2)	26	2)	2)	24	2)	2)	2)	2)	2)	4.9	7.6	16
Notched Izod Impact at 73°F, ft-lb/in.	1.8	2.2	2.5	2.0	2.3	2.7	1.9	2.2	2.3	4.4	4.3	3.7	-	0.65	0.65
Hardness, Rockwell "R"	78	82	81	83	83	84	82	82	83	81	79	83	91	95	91
Heat Distortion Temp at 264 psi	167	163	157	176	166	159	163	167	155	154	148	160	187	182	165
DIF, 60-mil Compression Molded Plaques, ft-lb/in.^{2}	-	130	145	-	-	-	-	-	-	140	-	115	-	-	-

1) Measured on heat distortion bars.
2) Did not break.

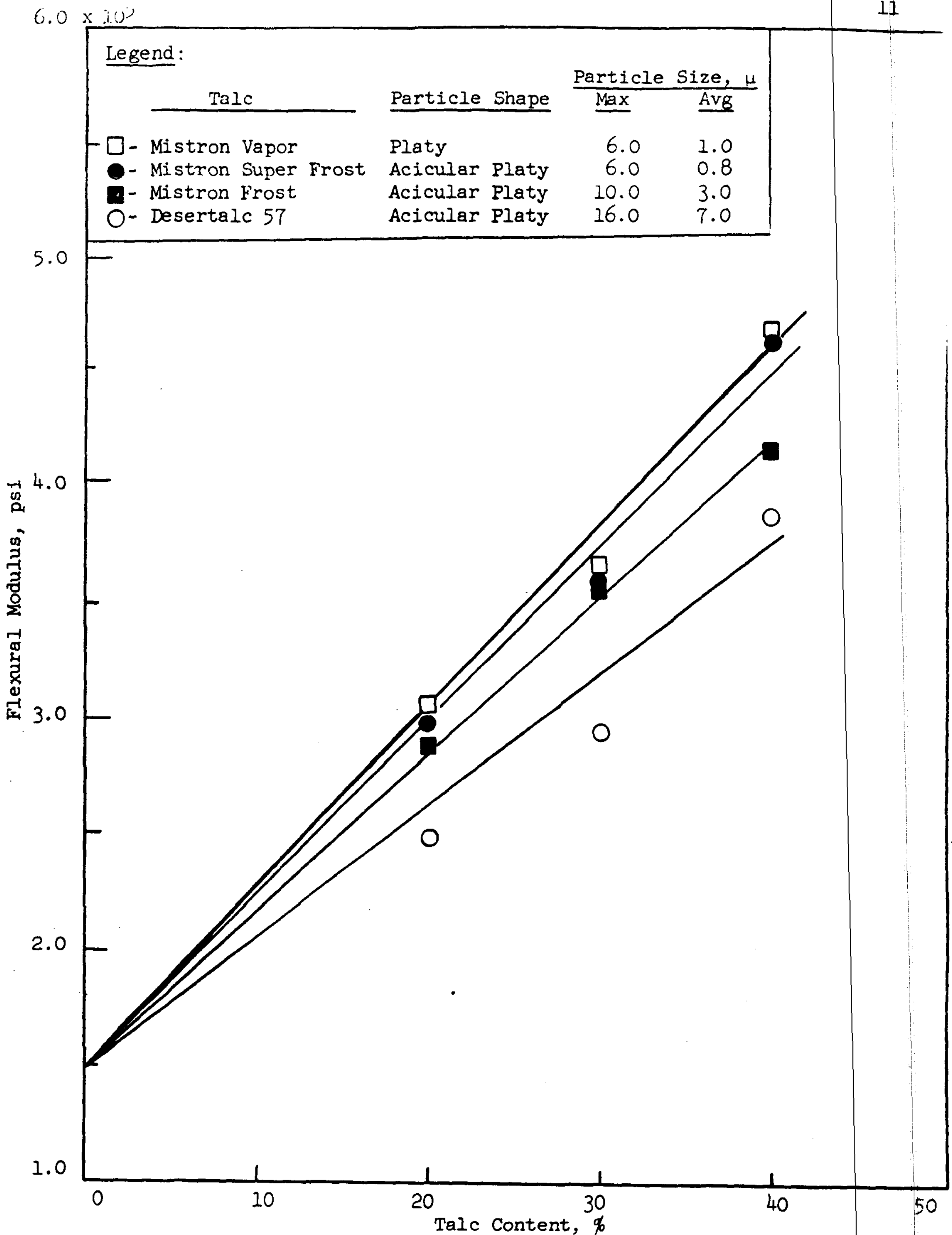

Figure 1. INFLUENCE OF TALC CONTENT, SHAPE, AND PARTICLE SIZE ON FLEXURAL MODULUS OF FILLED SHELL POLYPROPYLENE V-526

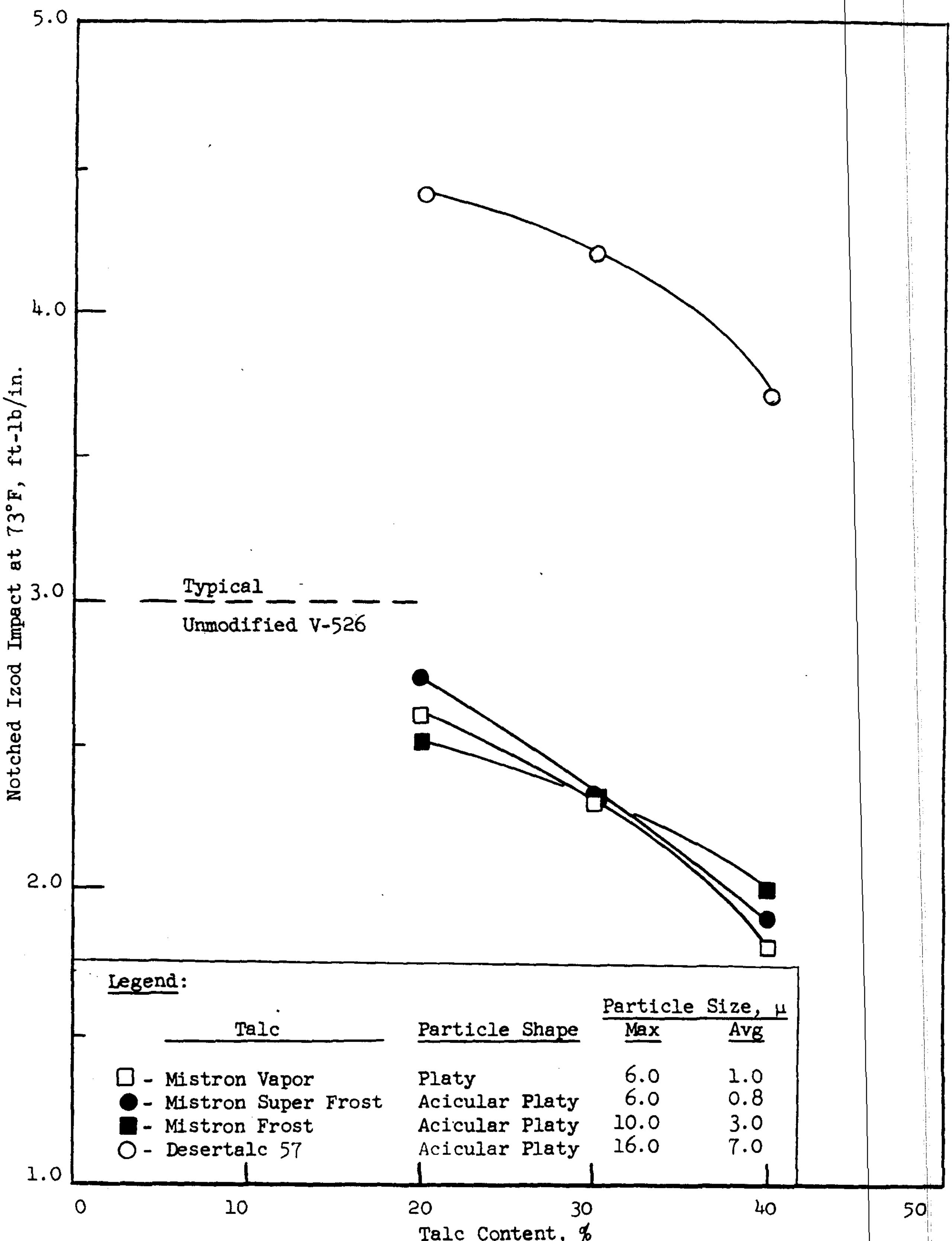

Figure 2. INFLUENCE OF TALC CONTENT, SHAPE, AND PARTICLE SIZE ON NOTCHED IZOD IMPACT STRENGTH AT 73°F OF FILLED SHELL POLYPROPYLENE V-526

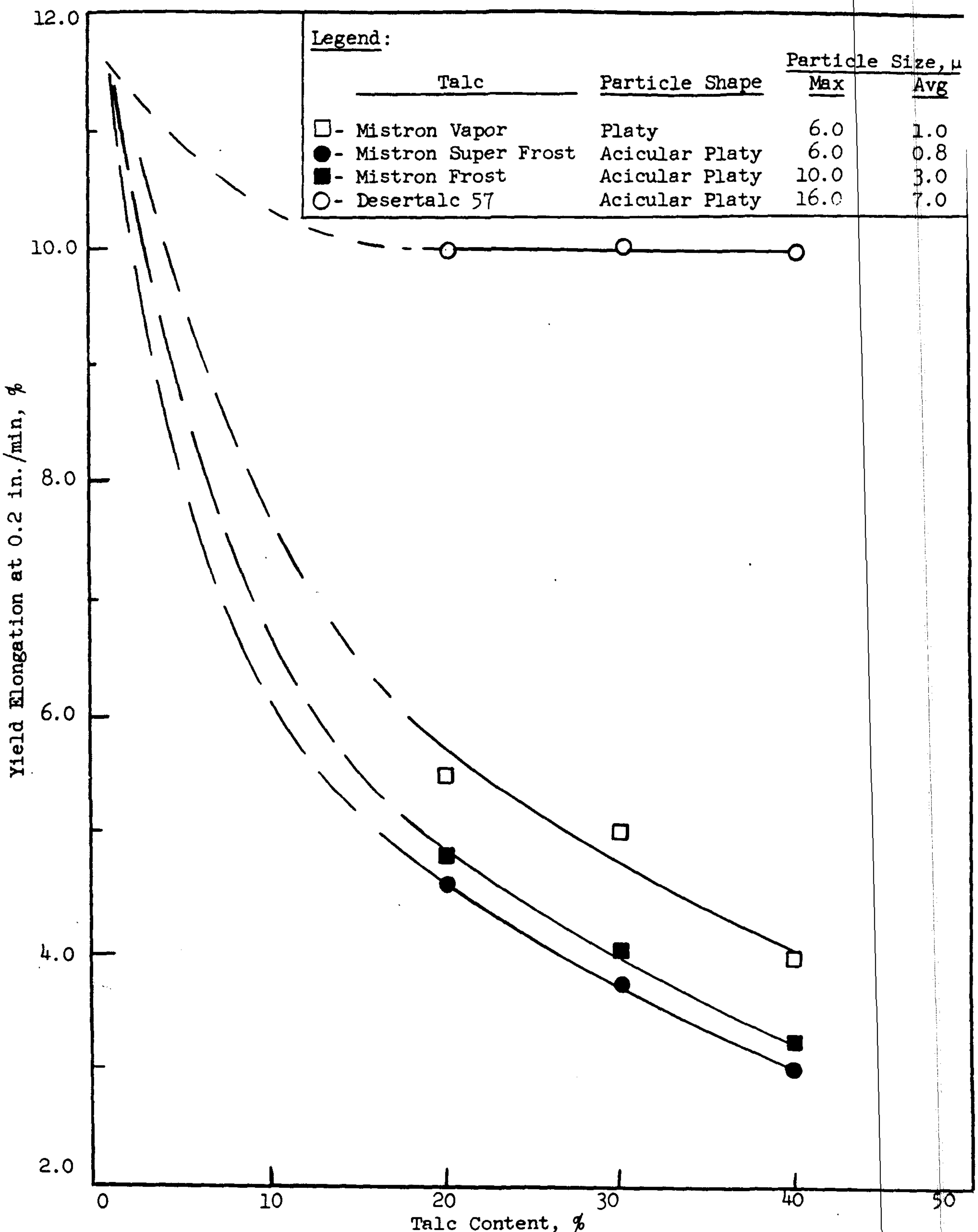

Figure 3. INFLUENCE OF TALC CONTENT, SHAPE, AND PARTICLE SIZE ON YIELD ELONGATION AT 0.2 IN./MIN OF FILLED SHELL POLYPROPYLENE V-526

ABS-043948

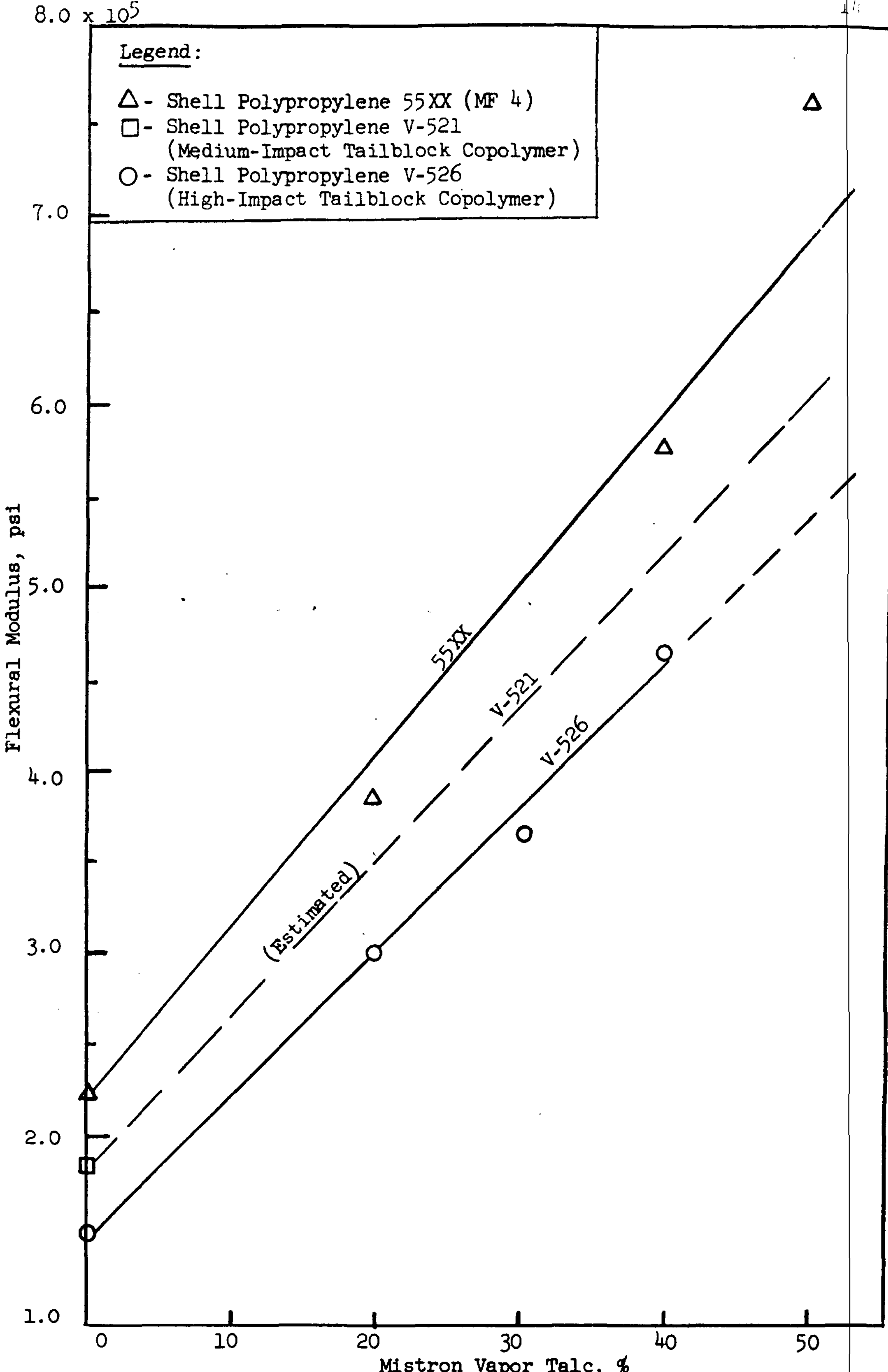

Figure 4. INFLUENCE OF TALC CONTENT ON FLEXURAL MODULUS OF FILLED PROPYLENE POLYMERS

ABS-043949

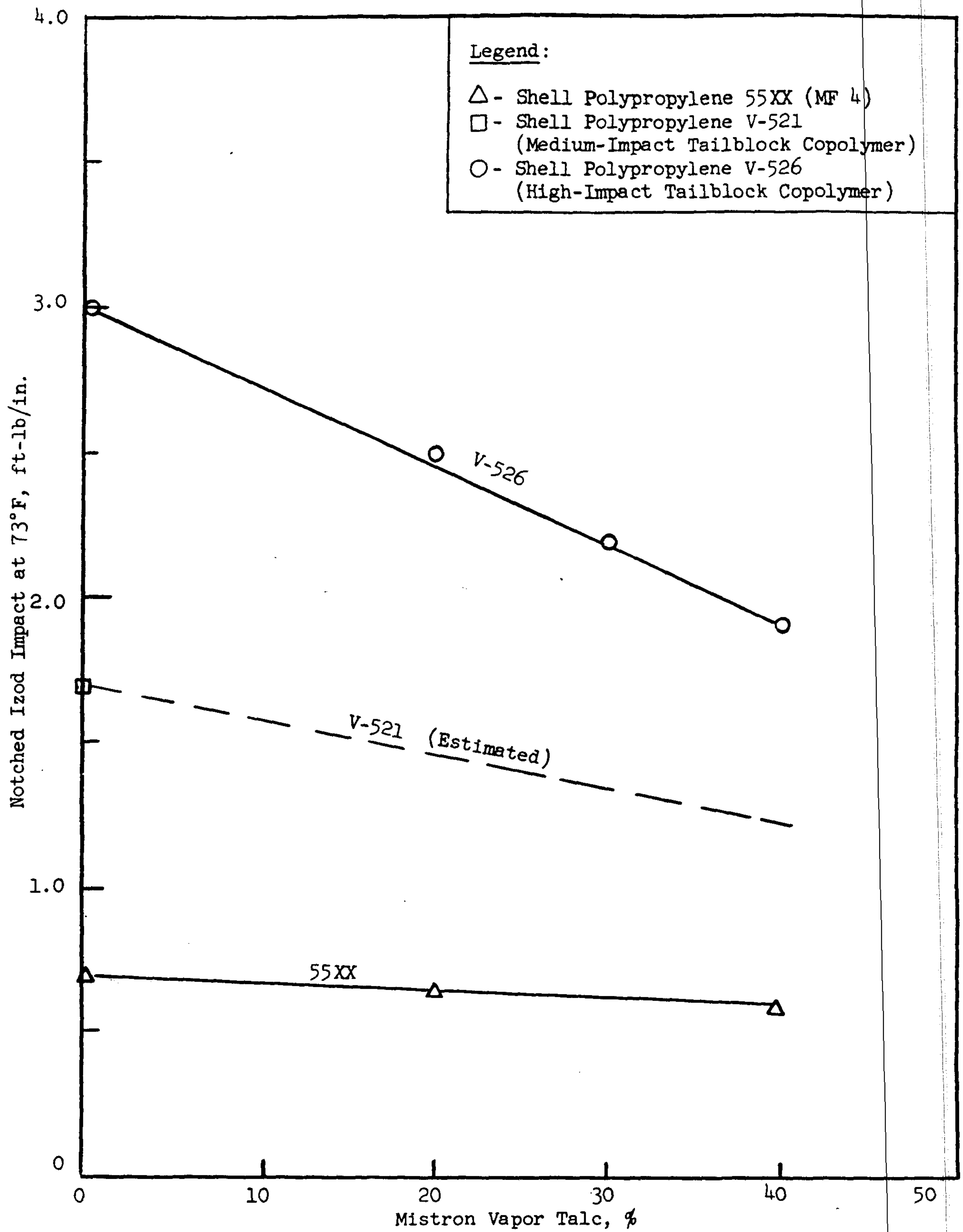

Figure 5. INFLUENCE OF TALC CONTENT ON NOTCHED IZOD IMPACT STRENGTH AT 73°F OF FILLED PROPYLENE POLYMERS

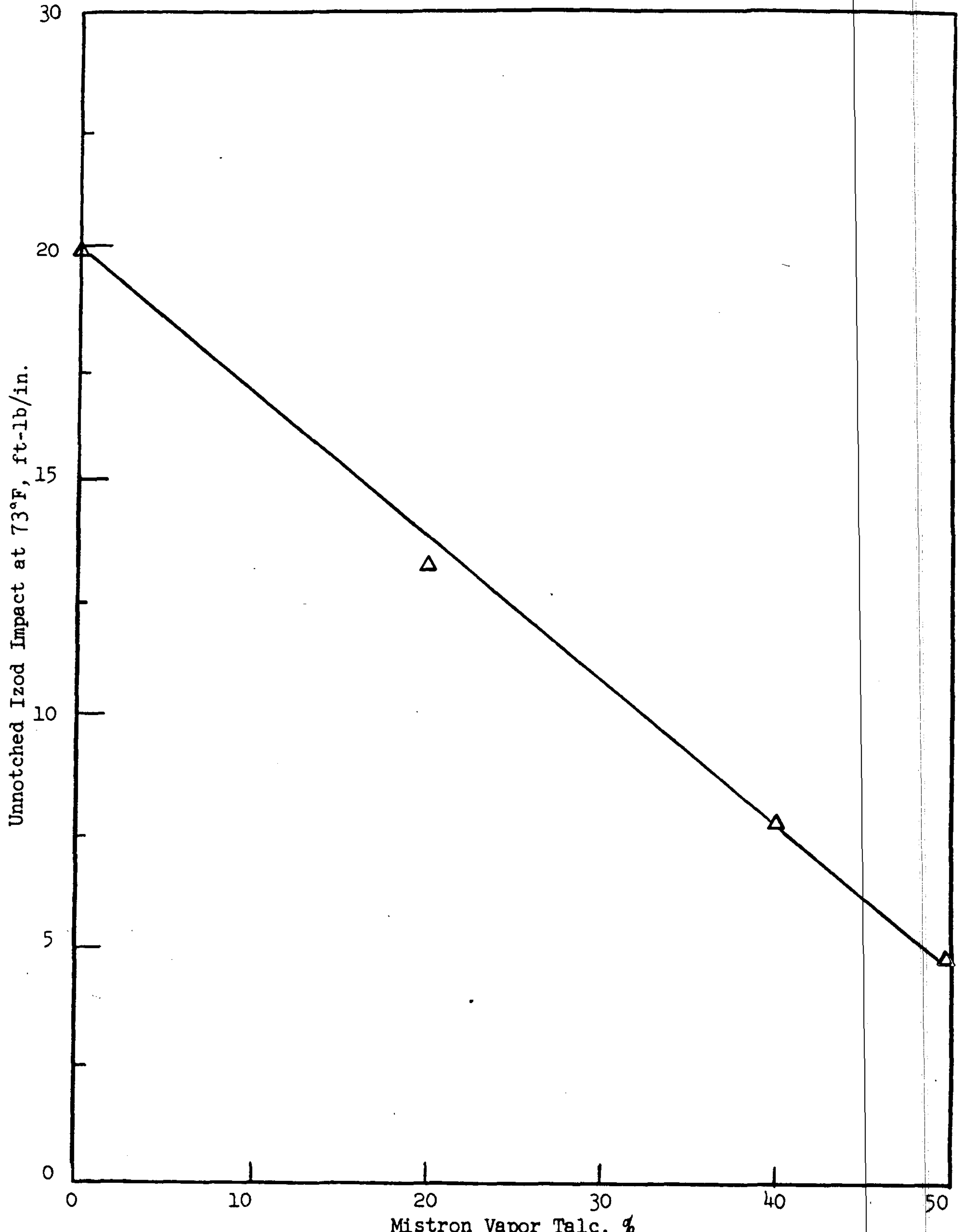

Figure 6. INFLUENCE OF TALC CONTENT ON IMPACT STRENGTH OF FILLED SHELL POLYPROPYLENE 55XX

Unnotched Izod Impact Measured on Heat Distortion Bars at 73°F

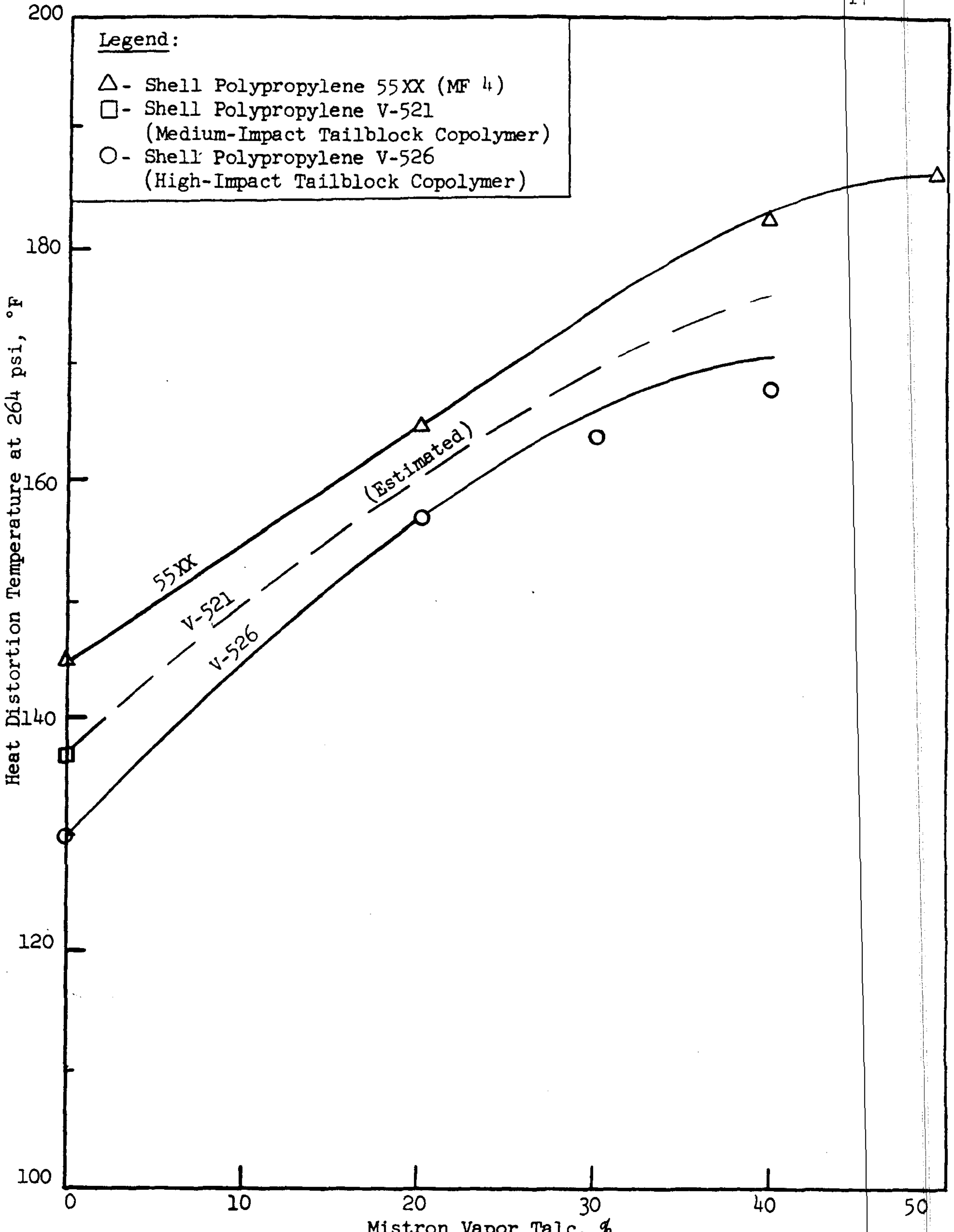

Figure 7. INFLUENCE OF TALC CONTENT ON HEAT DISTORTION TEMPERATURE AT 264 PSI OF FILLED PROPYLENE POLYMERS

ABS-043952

Table 4. SELECTED PROPERTIES OF FILLED POLYPROPYLENES

Sample	WM-650	Talc-Filled 55XX	Talc-Filled V-521	Talc-Filled V-526	Avisun[1] TD-231	Avisun[1] TD-235	Nominal Automotive Specification
Filler Content, %	42.1	40	40	40	36.5	38.5	35-45
Tensile Strength at 2 in./min, psi	4700	5000	≈ 4400	3900	4600	3900	4000-4400
Flexural Modulus, 10^5 psi	6.0	5.5	≈ 5.0	4.6	5.2	4.2	4.3-4.5
Unnotched Izod Impact[2] at 73°F, ft-lb/in.	3.8-4.1	7.5	≈ 15	25	6.8	11.0	4.0-4.5
Hardness, Rockwell "R"	93	95	≈ 86	78	-	-	90-100
Hardness, Shore "D"	75	75	≈ 74	72	-	-	65-75
Heat Distortion Temperature							
at 264 psi, °F	192	182	≈ 175	167	-	-	180-190
at 66 psi, °F	285	283	≈ 280	275	277-284	277-284	260-290
Vicat Softening Point, °F	315	311	-	293	-	-	> 280
Melt Flow, g/10 min	5-6	≈ 4.0	≈ 4.0	≈ 4.0	6.0	4.0	4.0-7.0
Density, g/cc	1.23	1.23	≈ 1.23	1.23	-	-	1.15-1.30
Water Absorption, %	0.006	0.014	-	0.027	-	-	< 0.05

1) Materials are talc-filled, rubber-modified homopolymers.
2) Measured on heat distortion bars.