Final Report

THE ADDITION OF LIGNIN FROM GASOHOL PLANTS TO ASPHALTS

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Abstract

Proposed increases in highway maintenance and decreases in gasoline consumption may combine to create asphalt shortages. Fuel shortages could encourage the large-scale conversion of biomass to alcohol fuels, which would generate substantial quantities of by-product lignins. This study examined the use of lignin from exploded wood as an extender for asphalt in paving mixtures. Uniform blends of up to 50 percent lignin in AC-10 and AC-20 asphalts were achieved by mechanical mixing. The effect of increasing lignin content was to increase viscosity and to decrease ductility and aging index of the binders. The lignin in asphalt binders was combined with aggregate to prepare molded samples for Marshall tests, which measure the maximum compressive load (stability) and the corresponding deformation (flow). With 6 percent total binder content in the pavement mixture, stability increased with increasing lignin content of the binder, whereas flow was relatively unaffected by lignin level. For binders containing 30 percent lignin, stability reached a maximum near 6 percent total binder content. The viscosity and Marshall properties were comparable for 30 percent lignin in AC-10 asphalt and for unmodified AC-20 asphalt.

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Background and Objectives

The increasing price and decreasing reserves of petroleum in the United States are encouraging development of substitutes for petroleum-based materials. Asphalt has experienced a rapid increase in price in recent years and its long-term availability may be limited. Although many extenders have been tested in asphalt, they have not received widespread acceptance because of cost, supply or performance. Lignin from biomass is a potential substitute for part of the binder in asphalt pavements.

Lignin constitutes about 20 percent of photosynthetic biomass and represents an abundant renewable resource. The conversion of cellulose and hemicellulose components of biomass to alcohol fuels is currently under extensive investigation. As these processes become commercial, substantial quantities of by-product lignin will be generated. The total national quantity of biomass which is recoverable annually is estimated to be over 305 million dry tons. Assuming 10 percent of this total is used as a feedstock for alcohol plants, 10-15 million tons per year of by-product lignin will be produced.

The form and structure of these new biomass lignins will depend upon the source of biomass, the conversion process and the conditions of operation. For example, one of the more promising processes for alcohol fuels involves pressurized treatment of biomass with steam followed by rapid decompression to disrupt the structure. This pretreatment permits removal of the lignin from the biomass by solvation in alcohol or caustic. The lignin is then precipitated from solution in the form of small spherical particles. The resulting lignin is water insoluble, has a number average molecular weight near 700, and has UV and IR spectra similar to native lignin.

Although the chemical structure of native lignin is not entirely known, it is generally agreed that lignin is a complex polymer based on phenylpropane units. The complexity of lignin results from the many ways in which these groups can be linked together. Lignins have structural similarities to the resin fraction of asphalt mixtures in that both contain considerable unsaturated aromatic rings joined by alkyl chains. Since lignin also has adhesive properties, its use as an extender in asphalt is suggested.

There are strong economic reasons for evaluating lignin as an asphalt component. Presently lignin is mainly worth its fuel value of about 4¢/lb since no large-volume alternative uses have been commercialized. In contrast, the current price of asphalt is about 2 times the fuel value of lignin. The market for asphalt is sufficient to absorb significant amounts of lignin with a resulting savings in binder costs. In addition, as alcohol and other synfuels replace part of the petroleum derived gasoline, the quantity of asphalt produced from crude oil will decrease. To help ensure adequate supplies of asphalt paving materials, the use of asphalt extenders, such as lignin, should be explored.

The pulp and paper industry produces large quantities of lignin by kraft and sulfite processes. Although sulfite lignin has several low-value applications, most kraft lignin is burned to recover energy and pulping chemicals. A literature search revealed only one major research study on the use of pulp and paper lignins as extenders for asphalts. Terrel and Rimsritong (Ref. 2) combined powdered kraft lignin with an AC-5 asphalt by hand, mixing with a spatula. They found that lignin-asphalt blends containing 30 percent lignin exhibited good qualities with respect to coating, workability, compaction and fatigue resistance. Based on several mixture characteristics, such as density, Hveem stability, resilient modulus and voids, they concluded that the optimum binder contents were 4.5 percent for AR-4000 asphalt, 4.5 percent for AC-5 asphalt and 7.2 percent for 30 percent lignin, 70 percent AC-5 blends. Thus, the optimum lignin-asphalt mixture contained about 5 percent asphalt, which did not represent a savings in asphalt content over the mixtures with asphalt alone. The implication is that the lignin acted as fines in the mix rather than as a binder extender. Since the technologies of the proposed biomass to alcohol plants differ from those used in pulp and paper operations, the new biomass lignins will have different structures and properties,which may provide advantages in asphalt binders.

The objectives of the program were to develop blends of biomass lignins with asphalt and to evaluate the properties of these blends in pavement mixtures. The performance of the lignin-asphalt binders will be judged on the basis of standard laboratory tests for viscosity and stability.

Materials and Methods

Materials

The AC-10 and AC-20 asphalt cements were provided by John Hudson Company. The viscosities of these asphalts at 60°C were 110 $N \cdot S/m^2$ (1100 poise) for the AC-10 and 240 $N \cdot S/m^2$ (2400 poise) for the AC-20.

The lignin was supplied in powdered form by the Iotech Corporation of Canada. This lignin had been produced by steam-exploding aspen wood chips, extracting the lignin into caustic solution, and precipitating the lignin by pH adjustment. The lignin as received was dried in an oven at 100°C and, for most runs, was ball milled for two hours to break up agglomerates. About 90 percent of the milled lignin was between 60 and 200 mesh as shown in Fig. 1. In several subsequent figures, this lignin is indicated as MAS (milled aspen lignin).

The mineral aggregate used to prepare the Marshall sample utilized a blend of natural sand and traprock dust for fine aggregate and traprock for coarse aggregate. For most runs, the aggregate mixture contained 25 percent natural sand, 25 percent stone dust, and 50 percent trap rock. A typical particle size distribution for the aggregate is shown in Fig. 2.

Mixing Methods

The initial mixing method involved heating the lignin and asphalt to about 140°C on a hot plate, and mixing them with a spatula for several minutes. The mixture was then poured into a container for storage. Although the blend appeared homogeneous during mixing, lumps of lignin floated to the top of the storage container upon reheating.

To improve the compatibility of the lignin in asphalt, organic liquids were added to the mixture. Creosote and kerosene were effective in improving dispersion of lignin in the asphalt. Since the presence of volatile organics in the binder presented potential problems, other mixing methods were tried.

To increase the shear during mixing, a mortar and pestle were used. The lignin was added to hot asphalt in a mortar and the pestle was then used to disperse the lignin in the asphalt. The mortar and pestle were both preheated to aid in maintaining a uniform temperature. The lignin and asphalt were mixed at temperatures from 110 to 140°C. By limiting the mixing temperature to 120°C and the mixing time to 7 minutes, uniform blends were obtained without excessive oxidation of the asphalt. The hot lignin-asphalt blends were poured into containers, which were purged with nitrogen before sealing.

Another mixing method employed a ball mill to provide the shearing action. The temperature was controlled by heating the outside of the ball mill with a quartz heater. The ball mill could be purged with nitrogen before a run to provide an inert atmosphere. At a temperature of 120°C, 35-45 minutes of rotational mixing were needed to obtain a uniform blend that did not segregate upon reheating.

An electric mixer provided a convenient and consistent mixing technique. The asphalt was heated to about 120°C in a 250 ml glass bottle. A flat mixing blade was inserted into the asphalt and the rotational speed of the blade was adjusted to produce a vortex in the asphalt. The lignin powder was poured slowly into the vortex of the asphalt to promote rapid dispersion without agglomeration. The blend was then mixed for five minutes under a nitrogen atmosphere.

Measurements

Viscosities of the lignin-in-asphalt binders were measured with a Haake rotational viscometer using a Couette geometry (concentric cylinders). Several cup and rotor combinations were used with gap width ranging from 1 to 6 mm. The heated binder was poured into the annular region between the cylinders. Viscosities were measured at 60°C (140°F) and 135°C (275°F) over a range of shear rates.

Rolling thin-film oven tests were made according to ASTM D 2872. In this test, a glass bottle containing asphalt was rotated on a rack inside an oven at 163°C. The rotating bottle continuously exposed a fresh film of asphalt to air. During each rotation, the opening of the bottle passed before the orifice of an air jet, which renewed the supply of air inside the bottle. After 75 minutes exposure at 163°C, the asphalt was removed from the oven and the viscosity of the aged asphalt was measured with the Haake viscometer at 60°C.

Ductility was measured by ASTM procedure D-113, in which one end of a molded briquet of asphalt at 25°C was pulled away from the other at a rate of 5 cm/min. The sample was 1 cm thick by 1 cm wide at the center. The ductility was the change in length of the asphalt briquet in cm at the time of breakage.

Stability and flow of the binders in bituminous concrete mixtures were measured by the Marshall Test (ASTM D 1559). Specimens for testing were prepared by mixing the binder with aggregate at a temperature giving a binder viscosity of 0.2 $N \cdot S/m^2$, followed by compaction by 50 blows on each side of the specimen. The molded samples were 4 inches in diameter and about 2.5 inches in height. The Marshall samples were stored overnight at room temperature and tested after heating for 30 minutes in a water bath at 60°C. The test involved measuring the compressive force on the sample at a strain rate of 2 in/min. Results from the deformation curve are expressed in terms of maximum load (stability in lb) and deformation at this load (flow in hundredths of inches).

Results and Discussion

Mixing Methods

Considerable effort was devoted to developing techniques for mixing lignin with asphalt. Low shear mixing with a spatula was unsatisfactory, since small clumps of lignin appeared in the binder upon reheating. Although organic liquids, such as creosote, improved dispersion of the lignin, their use was abandoned because of environmental concerns with volatile organics.

Higher-shear mixing with a mortar and pestle gave uniform blends for lignin contents up to 50 percent by weight. The stiffness of the mixture increased with increasing lignin content. Since the 50 percent blend was very viscous and difficult to mix, lignin contents above 40 percent by weight may be impractical. The blends produced by mixing lignin and asphalt in the mortar and pestle at 120°C rarely showed lignin clumps upon reheating. This method was used to prepare the lignin-asphalt blends for viscosity and ductility tests.

The heated ball mill also gave uniform blends of lignin in asphalt, but longer mixing times were needed than with the mortar and pestle. The ball mill also enabled control of the atmosphere during mixing. Separation of the asphalt blends from the ceramic balls was difficult.

The mechanical mixing technique was simple, easily controlled, reproducible and minimized oxidation. The electric stirrer was considered the best of the mixing methods and was used to prepare the samples for the aging and Marshall tests. Should quantities of lignin become available, high-shear mixers can be readily adapted for commercial use.

Binder Viscosity

The viscosities of lignin dispersed in AC-10 and AC-20 asphalts were measured at 60°C, 100°C and 135°C with the rotational viscometer. The viscosities at 60°C and 135°C are plotted as a function of shear rate in Figs. 3 and 6. There is more scatter of the data at 135°C because the instrument was near the limit of its sensitivity. For a given lignin content, viscosities decreased with increasing shear rate over the range studied. Similar non-Newtonian behavior of asphalt has been observed in other studies. Viscosities of the AC-10 and AC-20 asphalts were measured as received (pour control) and after 5 minutes mixing in a mortar and pestle (mix control). Exposure to air during mixing caused only a slight increase in the viscosity of the asphalt.

The effect of temperature on viscosity at low shear rates (called initial viscosity) is shown in Figs. 7 and 8. These curves were extrapolated to estimate the temperatures where binder viscosities were 0.2 $N \cdot S/m^2$, thus determining the temperatures used in preparing the Marshall samples.

The viscosity increased rapidly with increasing lignin content of the asphalt. In Figs. 9 and 10, relative viscosities are plotted versus lignin content for the two asphalts at 100°C and 135°C. Relative viscosity is defined as the viscosity of a lignin-asphalt mixture divided by the viscosity of the pure asphalt at a given temperature and shear rate. The high relative viscosities at 40 percent lignin content suggest that lignin levels above 30 percent may be impractical.

At 60°C, the viscosity of 20 percent lignin in AC-10 asphalt was comparable to the viscosity of AC-20 asphalt alone. These results indicate that 20 to 30 percent lignin in AC-10 asphalt may give rheological behavior in service that is similar to AC-20 asphalt.

Aging of Binder

The rolling thin film oven test provides information on hardening of the asphalt blends as a result of exposure to air at 163°C. The viscosities at 60°C of aged and unaged binders are listed in Table 1. The aging index, defined as the ratio of aged viscosity to unaged viscosity, is also given in Table 1. The aging index for both AC-10 and AC-20 binders decreased with increasing lignin content of the binder.

It is of interest to note that the viscosity of aged AC-10 binder with 30 percent lignin is nearly the same as the viscosity of aged AC-20 asphalt alone. This result again suggests rheological similarity between lignin-modified AC-10 and pure AC-20 asphalt binders.

Ductility of Binder

The ductility test involves pulling on a molded sample of binder until the sample breaks. The change in length of the sample at the time of rupture is reported as ductility. The ductility of AC-10 and AC-20 binders is plotted versus lignin content of binder in Fig. 11. The ductility of both asphalts decreased significantly with increasing lignin content of the binders. The low ductility in the presence of lignin may result from the presence of agglomerated lignin particles, which create weak regions in the elongated strand. If the lignin remains as discrete particles in the blend, the presence of such particles in the material would tend to impede flow of the binder into the very small ductility thread.

Marshall Tests

The Marshall test measures the compressive force applied to a cylindrical sample at a constant rate of strain. A typical recording from a Marshall test is shown in Fig. 12. The ordinate is the force applied to the sample in pounds and the abscissa is the deformation expressed in hundredths of an inch. The stress goes through a maximum as a result of fractures within the pavement structure. The applied force at the peak of the curve is called stability and the corresponding deformation is called flow.

The major variables examined in the Marshall tests were grade of asphalt, lignin content of binder and binder content of pavement mixture. All lignin binders were prepared by mechanical mixing of the lignin and asphalt since this mixing procedure gave higher stabilities and more reproducible curves than mixing by ball mill or mortar and pestle. The Marshall tests were made in sets of 6 to 10 specimens with replicates in each set. Most data points represent the average of tests on 3 or more samples.

The effect of lignin content of the binder on Marshall stability and flow was examined at a total binder content of 6 percent. The lignin content of the binder refers to the weight percent of lignin in the lignin-asphalt binder, whereas the binder content refers to the total weight percent of lignin plus asphalt in the pavement mixture. Thus, a Marshall pavement mix with 6 percent of a 30 percent lignin binder would contain 4.2 wt. percent asphalt (0.7 x 6) and 1.8 wt. percent lignin (0.3 x 6).

The stability of Marshall samples increased with increasing lignin content of the binder using both AC-10 and AC-20 asphalts (Fig. 13). The stabilities of samples made with AC-20 asphalt averaged about 250 pounds higher than those made with AC-10 asphalt. The effects of lignin content and type of asphalt on stability are expected, since stability usually increases with increasing viscosity of the binder. All binders satisfied the minimum stability specification of 1200 pounds for the State of Connecticut.

The Marshall flow values were fairly constant up to 30 percent lignin content of the binder and then decreased markedly (Fig. 14). The flow values averaged about 1 unit (0.01 inch) higher for binders made with AC-20 asphalt. The flow at 40 percent lignin content is probably too low for satisfactory pavement performance.

Air void space and voids in mineral aggregate (VMA) were estimated using approximate values for specific gravity of the components and for binder absorption on the aggregate. VMA is the total volume occupied by binder and air voids, expressed as a percentage of total bulk volume of the sample. Estimated values of air voids and VMA increased with increasing lignin content of the binder, as shown in Figs. 15 and 16. The air voids were greater in AC-20 binders up to 20 percent lignin content, but were greater in AC-10 binders at 30 and 40 percent lignin content. All VMA values exceeded the common specification of 15 percent for mixes with aggregate up to 1/2 inch. This implies that the viscosity was too high during compaction. The air void values for the pure AC-10 and AC-20 binders were below the usual criterion of 3 to 5 percent for surface pavement. This indicates the asphalt content is too high.

The viscosity and Marshall flow results suggest that the maximum practical lignin content of the binder is 30 percent. Therefore, the effect of total binder content on Marshall performance was determined with binders containing 30 percent lignin. For comparison, the effect of total binder content was also studied with binders consisting of unmodified AC-10 and AC-20 asphalts.

Marshall stability and flow of samples containing 4.5 to 6.0 percent of unmodified AC-10 or AC-20 binder are shown in Figs. 17 and 18. The highest stability and flow values occurred at 6 percent binder content for both AC-10 and AC-20 asphalts. Stabilities did not vary much with asphalt content over the range studied, but flow values declined with increasing asphalt content. The stabilities of mixes made with AC-20 exceeded those made with AC-10 by an average of about 400 pounds.

The Marshall samples made with 30 percent lignin binder exhibited a maximum stability near 6 percent total binder content (Fig. 19). Stabilities of binders containing AC-20 were greater than those containing AC-10 by an average of about 300 pounds. For a given type of asphalt, stabilities did not change greatly for binder contents between 5 and 8 percent. The flows increased with increasing binder content up to 7.5 percent (Fig. 20). Between 5.5 and 7.0 percent binder content, the AC-10 and AC-20 binders had nearly the same flow values.

The estimated air voids and VMA's decreased with increasing binder content for both pure asphalt and lignin-modified binders, as shown in Figs. 21 to 24. The decrease in voids with increasing binder content is expected since additional binder fills voids and usually permits better compaction.

It is of interest to note that at 6 percent total binder content, stability and flow were nearly the same for Marshall samples made with either 30 percent lignin in AC-10 binder or with unmodified AC-20 binder. Similar viscosities before and after aging were also observed with these binders. With the exception of ductility, then, 30 percent lignin in AC-10 binder had properties comparable to AC-20 asphalt. Since the pavement mixtures with 30 percent lignin binder contained 4.2 percent AC-10 asphalt rather than 6.0 percent AC-20 asphalt, a savings in asphalt may be achieved. However, the high air voids of the 30 percent indicates a need for a higher temperature during compaction. This should be expected as temperature was controlled during mixing rather than during compaction. At the higher temperature required for the 30 percent lignin mix, more heat was lost during mixing and handling and temperature was proportionately lower during compaction.

Conclusions

1. The viscosity of lignin-modified asphalt binders increased with increasing lignin content.
2. A binder with 30 percent lignin in AC-10 asphalt had similar rheological behavior to unmodified AC-20 asphalt, both before and after aging.
3. Ductility decreased with increasing lignin content of the binder.
4. At 6 percent total binder content, stability increased with increasing lignin content but flow declined above 30 percent lignin content in the binder.
5. For 30 percent lignin in asphalt binders, the maximum stability occurred at 6 percent total binder content.
6. Stability and flow were nearly the same at 6 percent total binder content for pure AC-20 asphalt and for 30 percent lignin in AC-10 asphalt.
7. A mix utilizing 30 percent lignin in AC-10 should be placed 20°C hotter than a similar mix using unmodified AC-20.
8. Field testing of pavement produced with lignin modified binder is recommended when sufficient lignin becomes available.

Bibliography

1. H. Abraham, Asphalts and Allied Substances, D. Van Nostrand Co.

2. Ronald L. Terrel and Sveng Rimsritong, Wood Lignins Used as Extenders for Asphalt in Bituminous Pavements. AAPT, Vol. 48, 1979, pp. 111-134.

TABLE 1

Results of Rolling Thin Film Oven Tests

Asphalt Type	Lignin Content %	Unaged Viscosity Pa•s at 60°C	Aged Viscosity Pa•s at 60°C	Aging Index
AC-10	0	110	306	2.78
AC-10	10	175	395	2.25
AC-10	20	257	494	1.93
AC-10	30	353	596	1.69
AC-20	0	240	627	2.62
AC-20	10	356	875	2.46
AC-20	20	456	1101	2.42
AC-20	30	638	1319	2.07

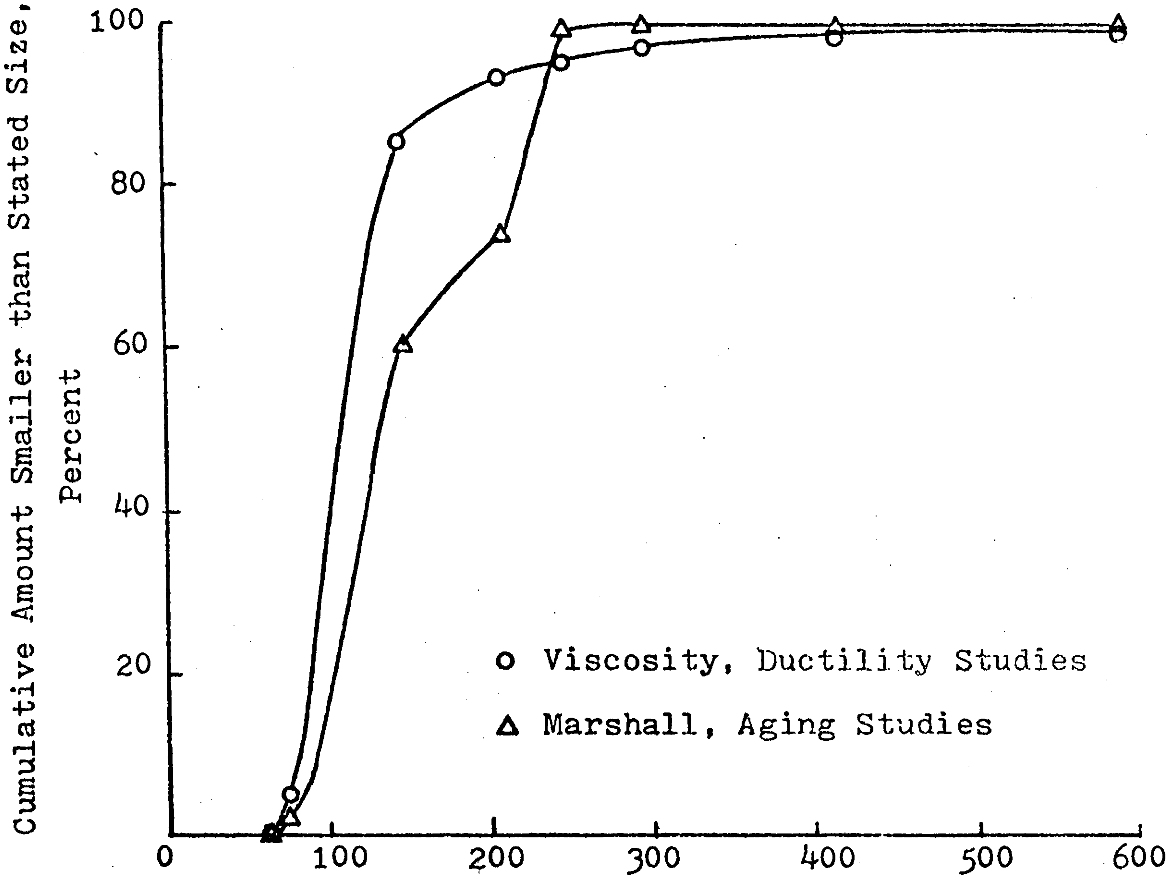

Figure 1: Particle Size Cumulative Distribution Curves for Two Batches of IOTECH Lignin.

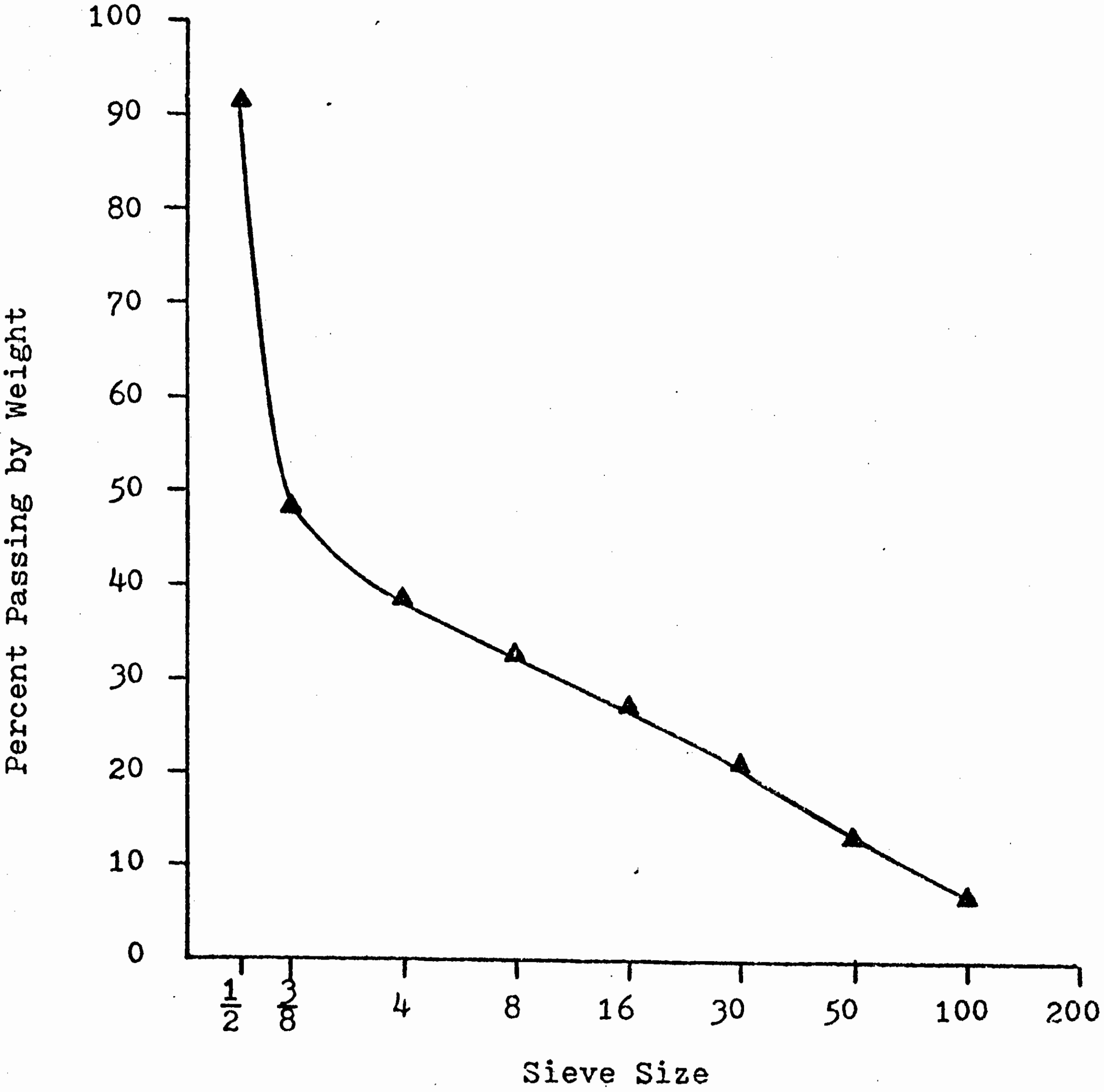

Figure 2: Overall Particle Distribution of Marshall Aggregate.

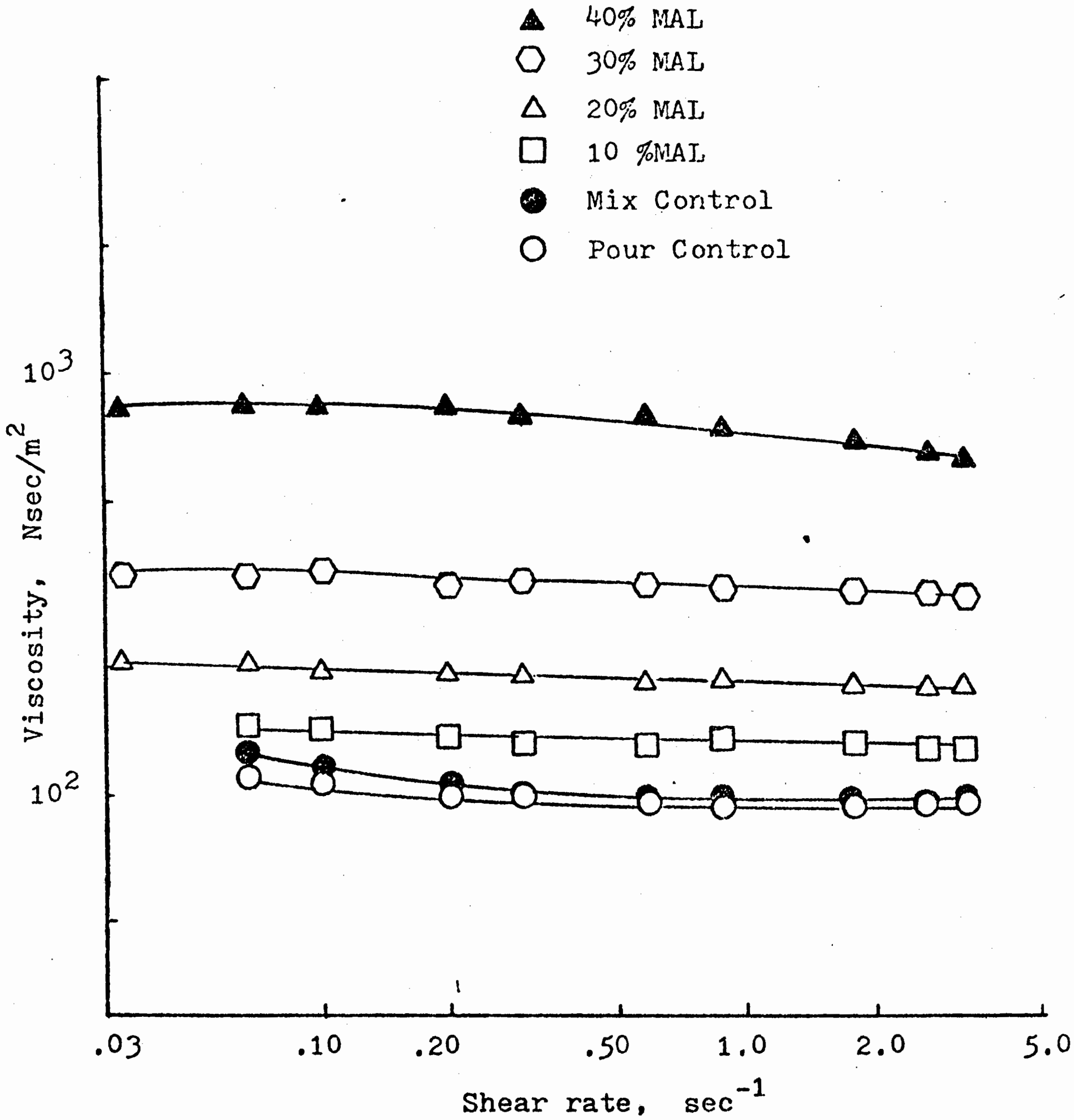

Figure 3: Viscosities of AC-10 Binders at 60 C.

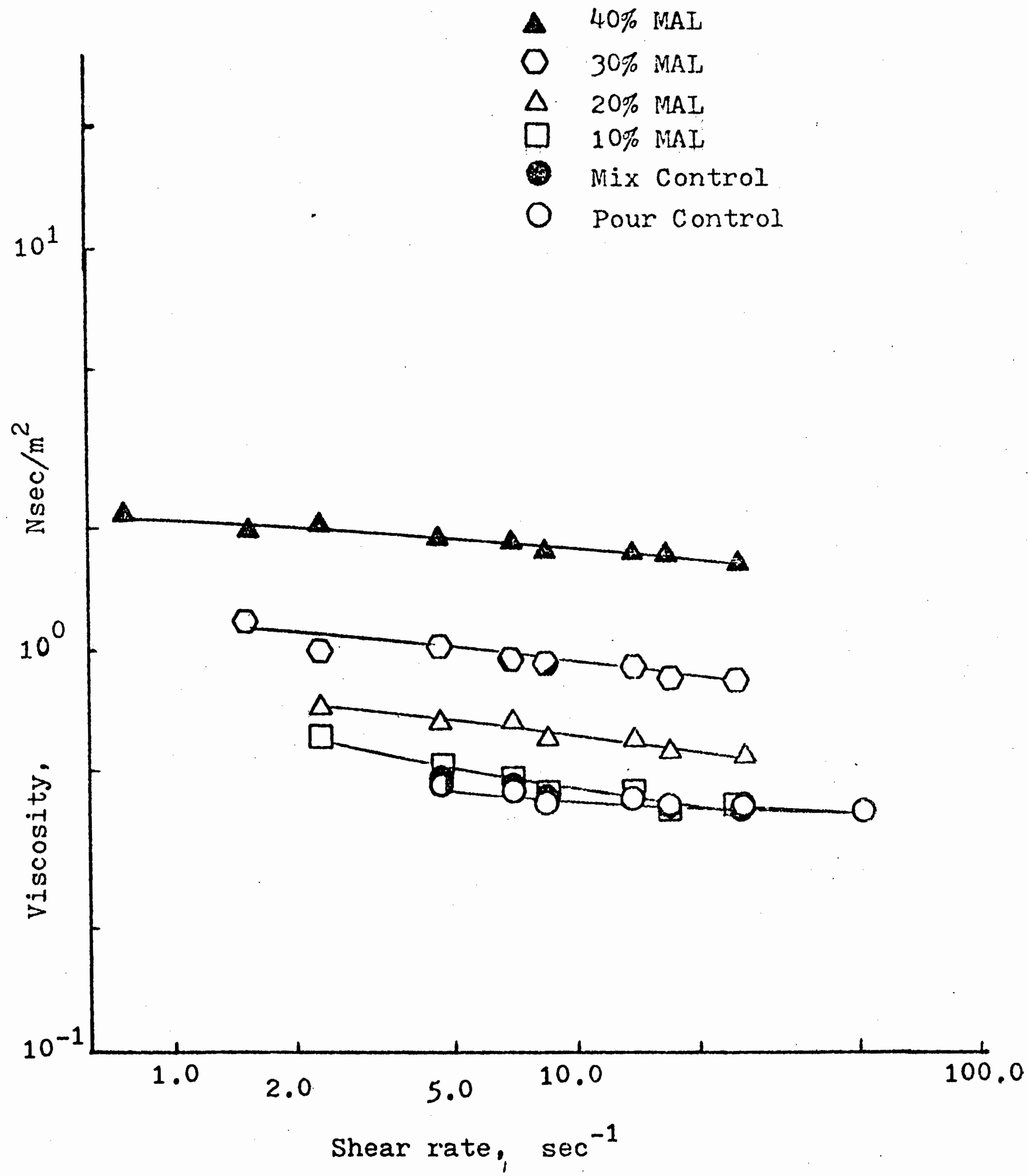

Figure 4: Viscosities of AC-10 Binders at 135 C.

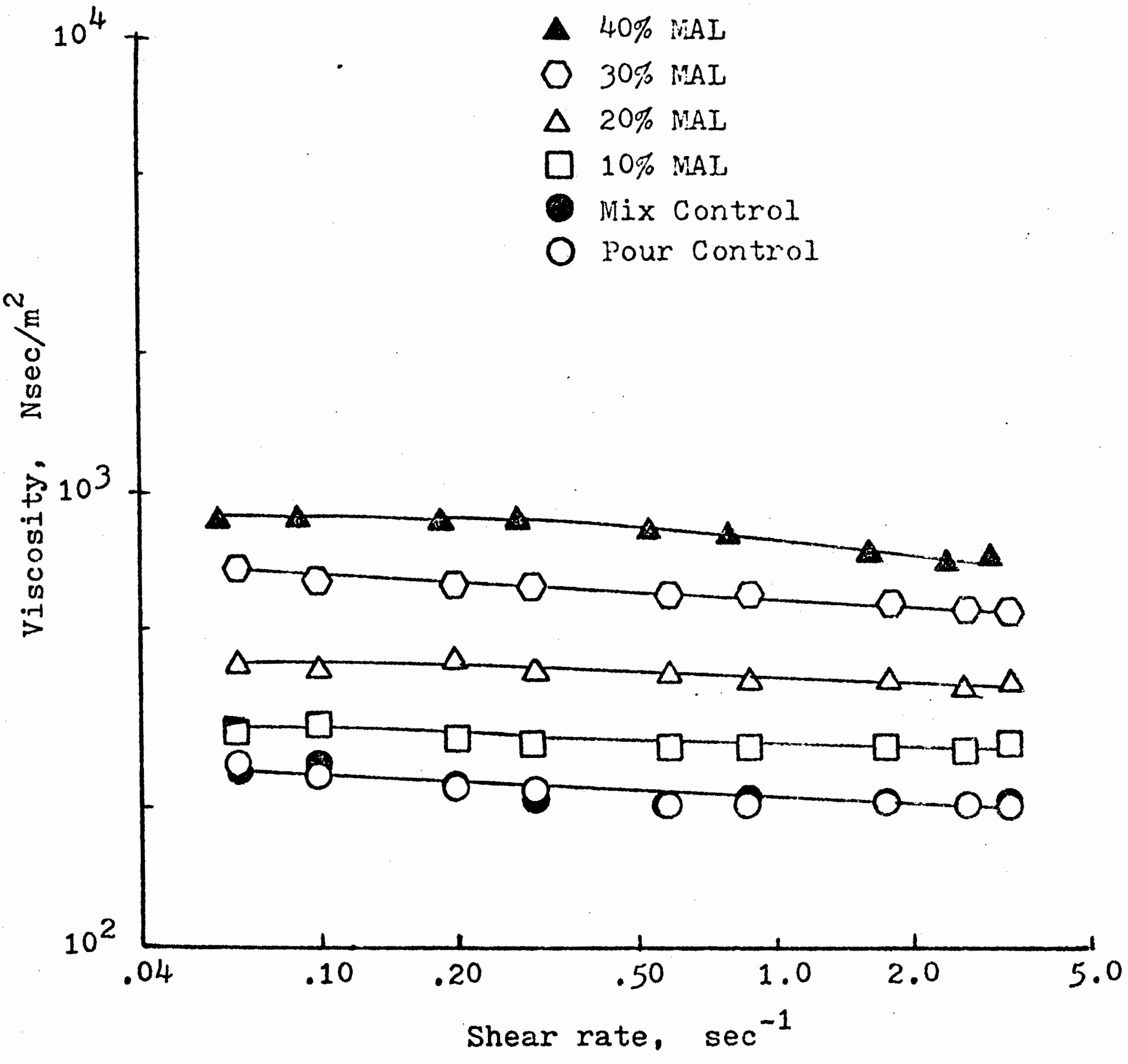

Figure 5: Viscosities of AC-20 Binders at 60 C.

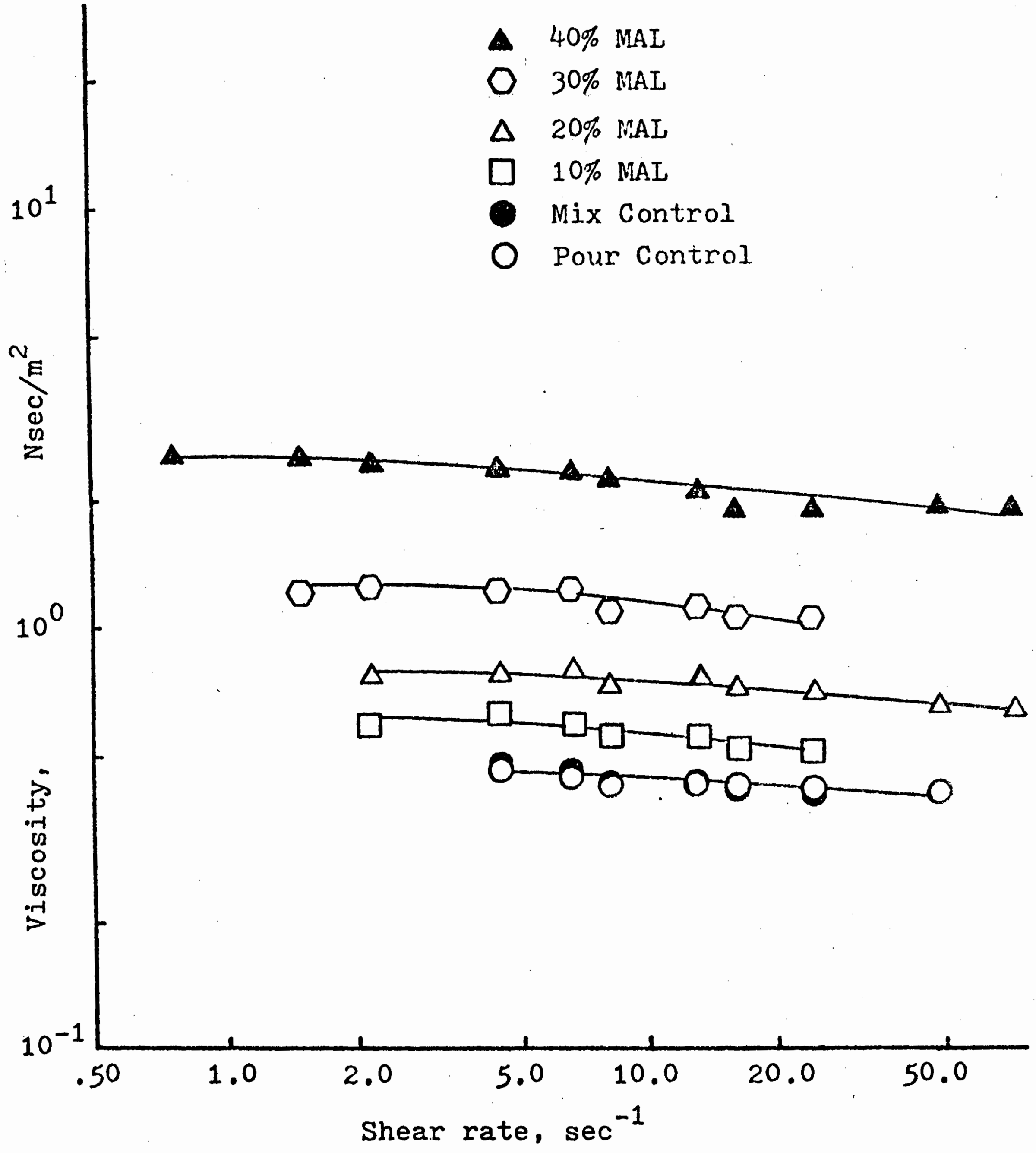

Figure 6 : Viscosities of AC-20 Binders at 135 C.

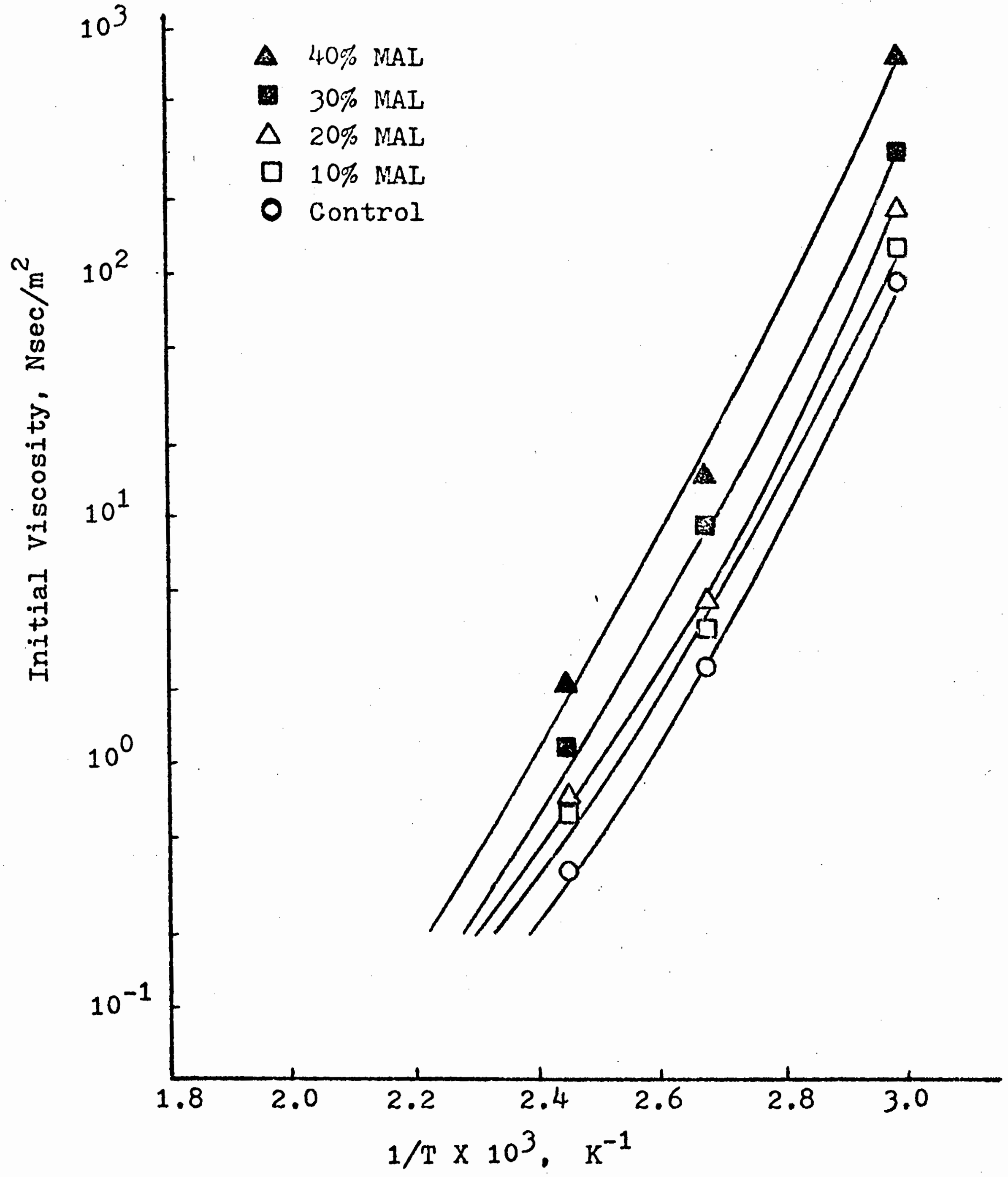

Figure 7 : Effect of Temperature on Initial Viscosities of AC-10 Binders.

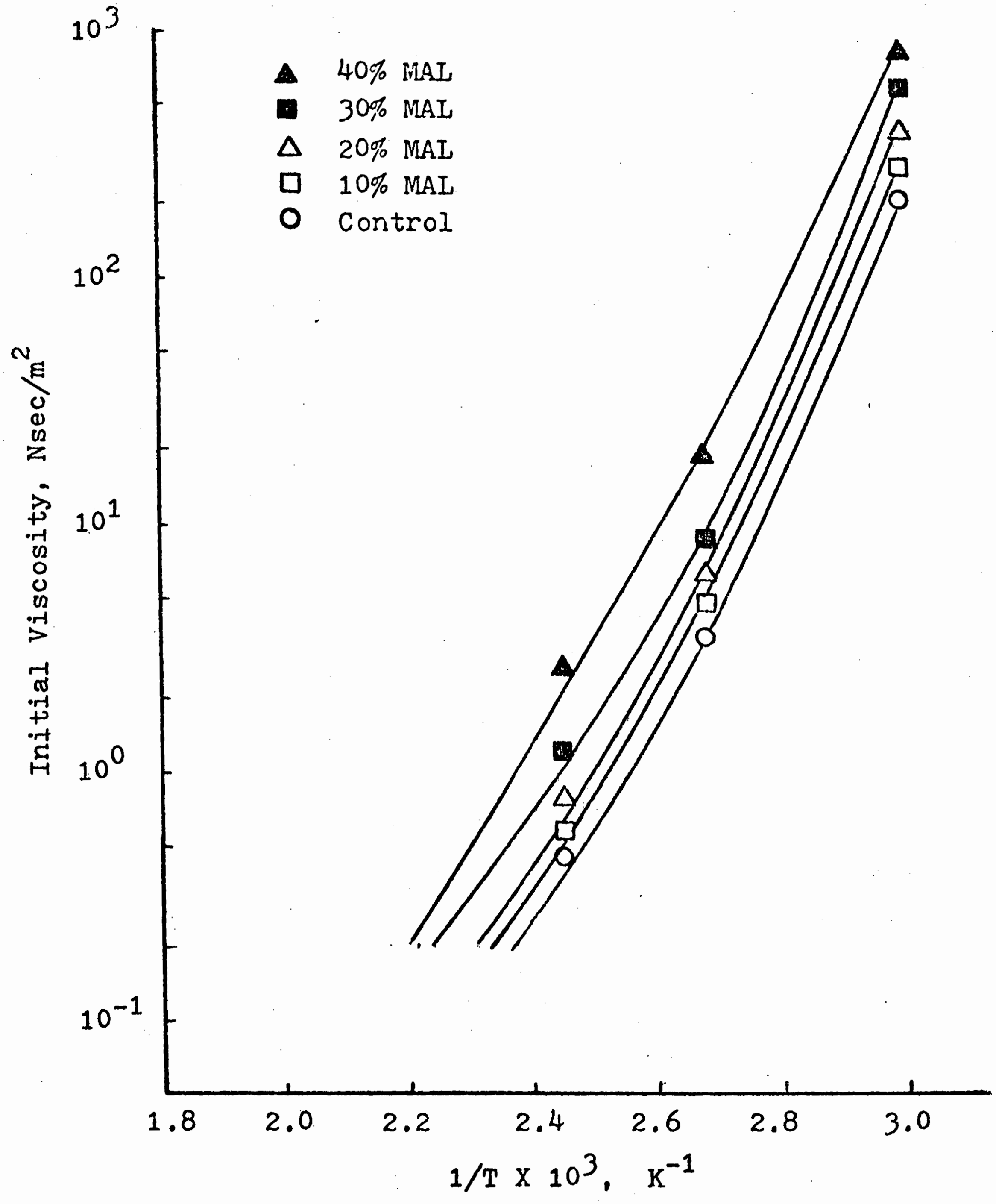

Figure 8: Effect of Temperature on Initial Viscosities of AC-20 Binders.

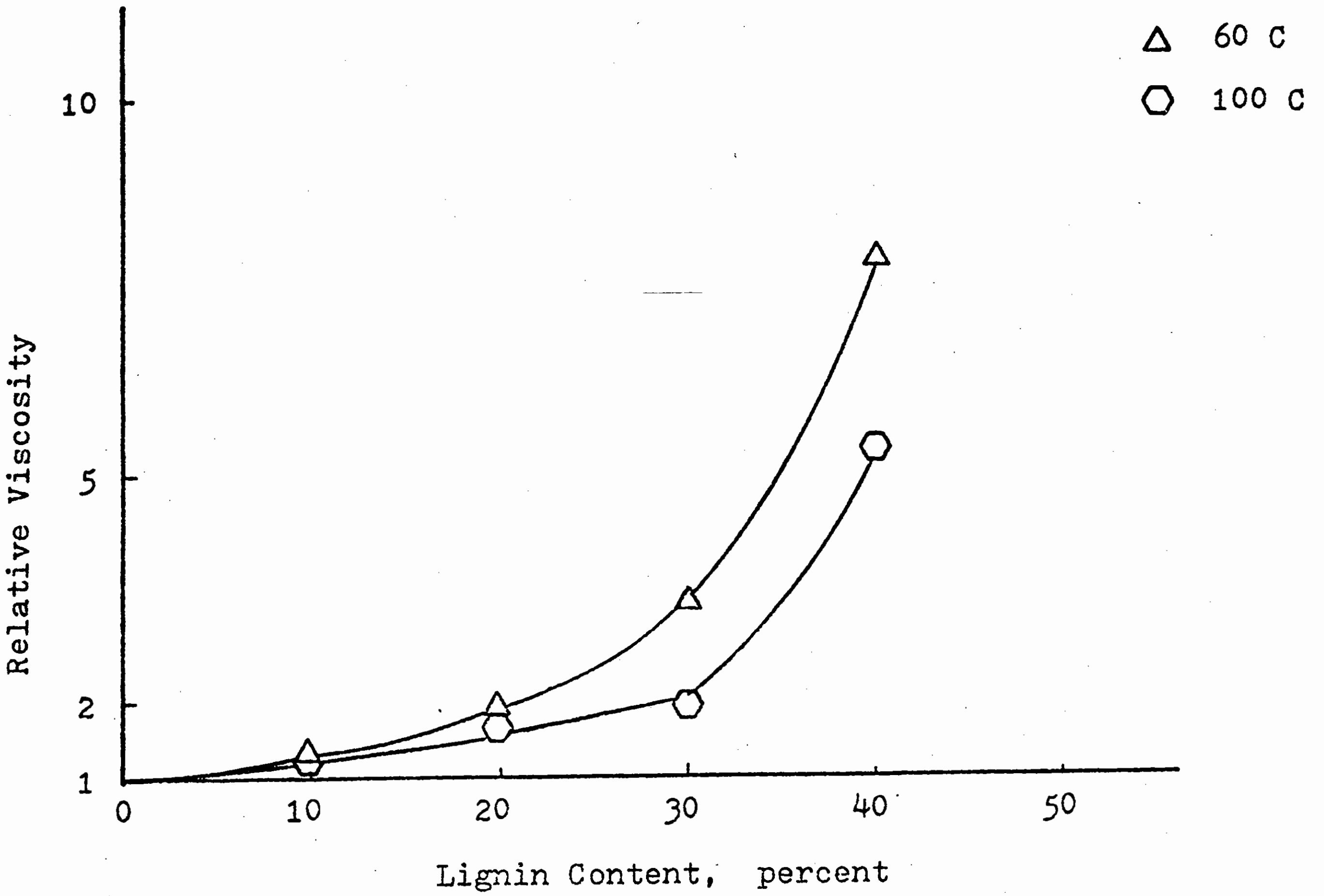

Figure 9: Effect of Lignin Content of AC-10 Binder on Relative Viscosities at 1.0 sec^{-1}

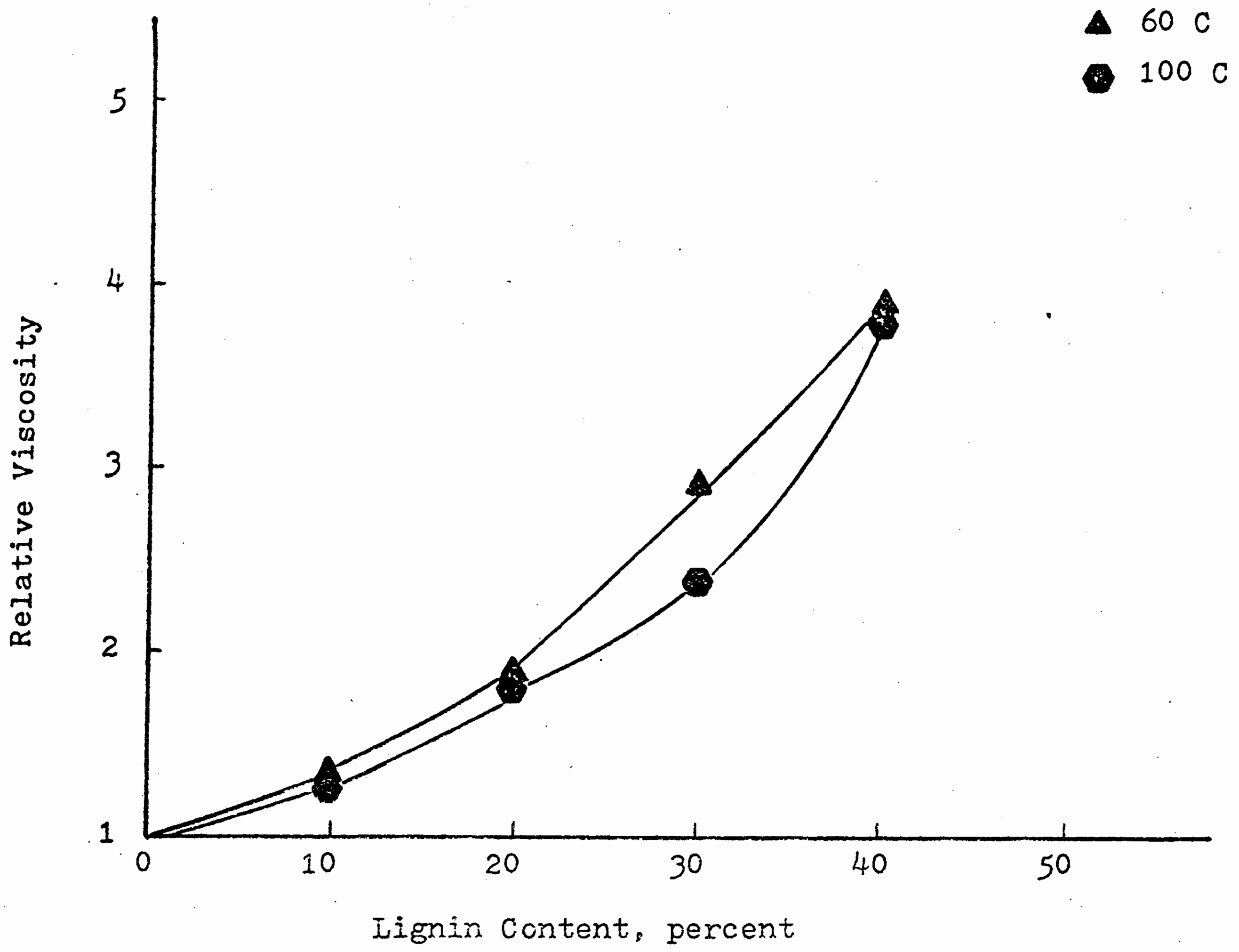

Figure 10 : Effect of Lignin Content of AC-20 Binder on Relative Viscosities at 1.0 sec^{-1}.

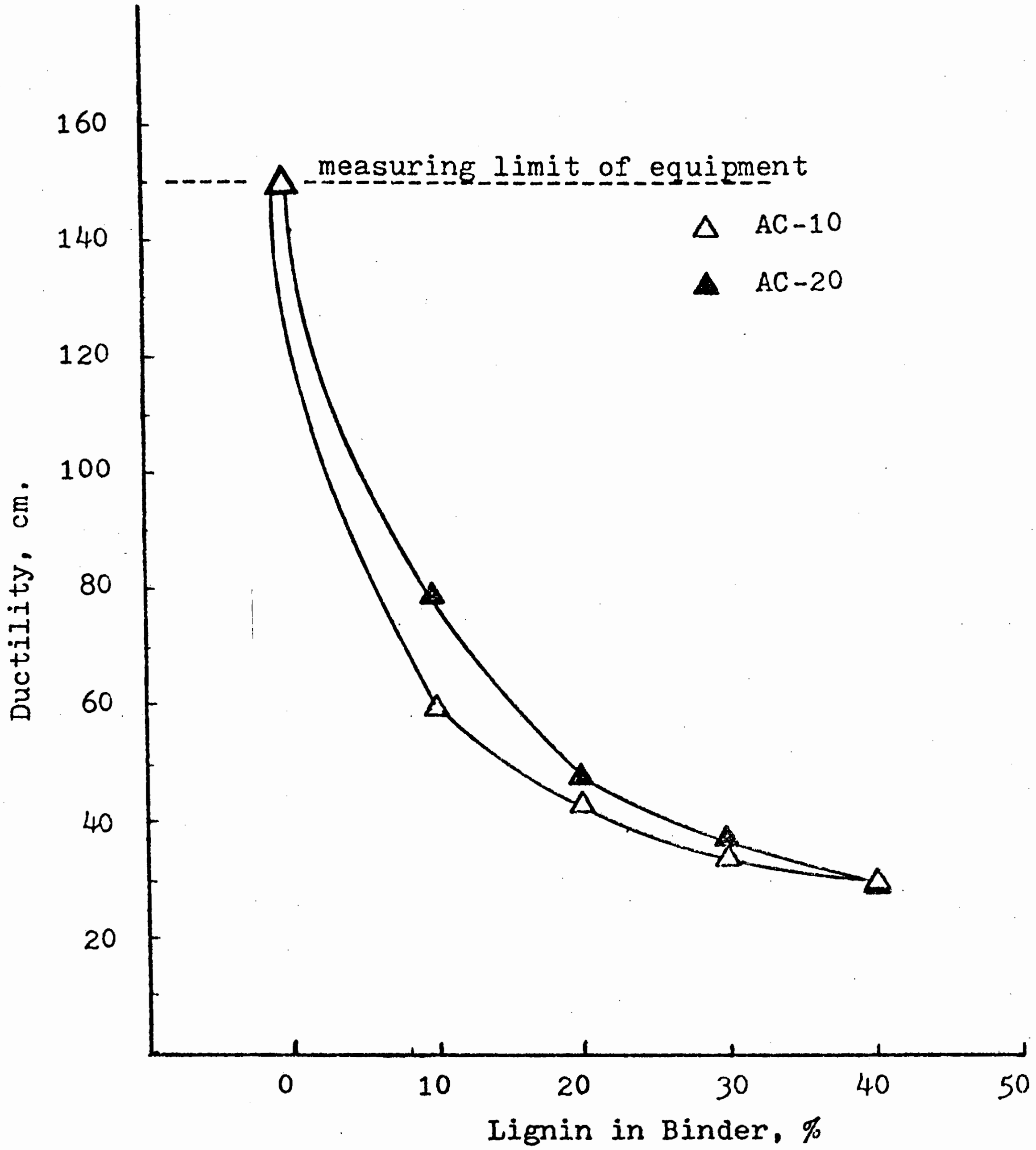

Figure 11: Effect of Lignin Content of Binder on Ductility.

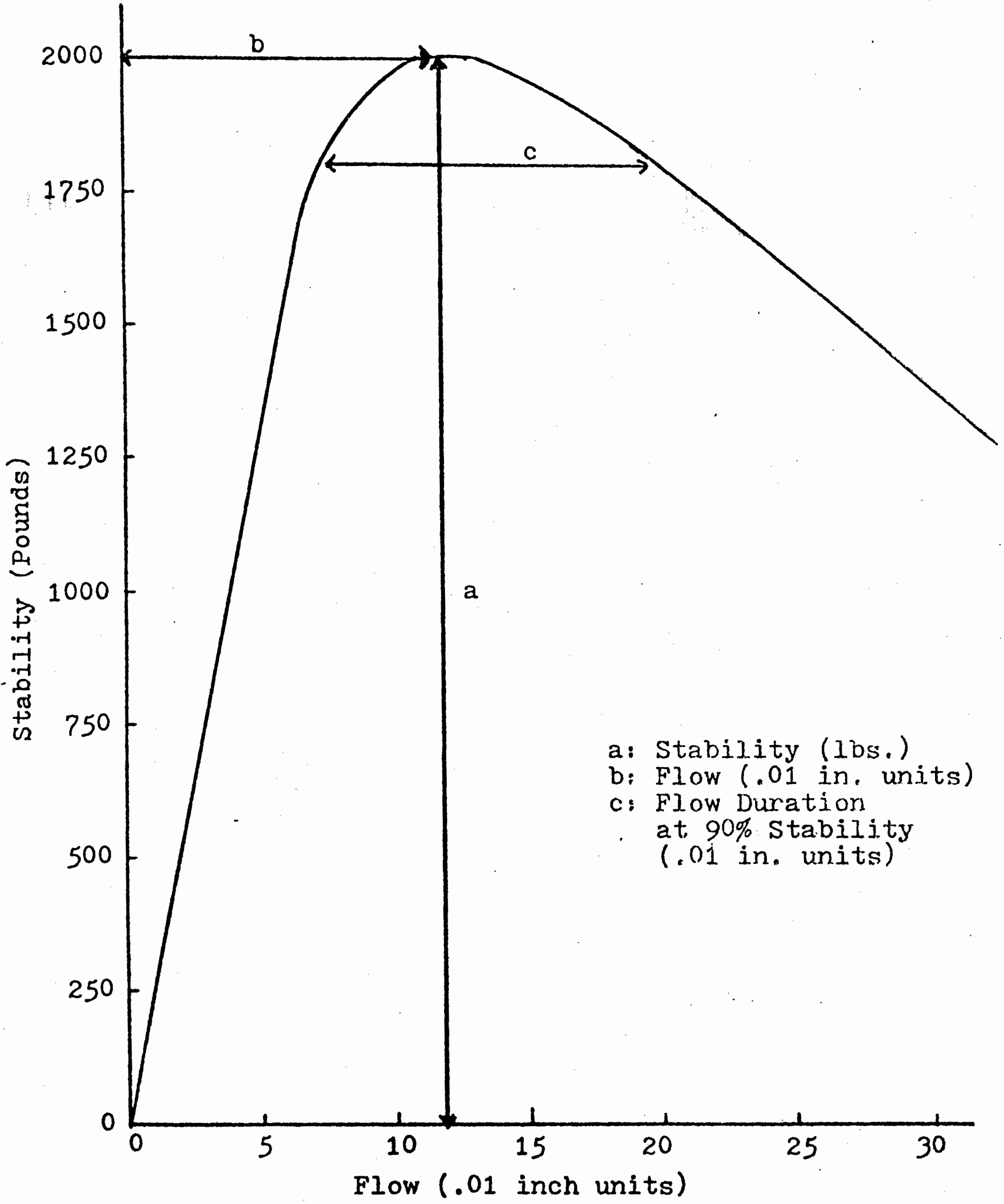

Figure 12: Typical Marshall Fracture Recording.

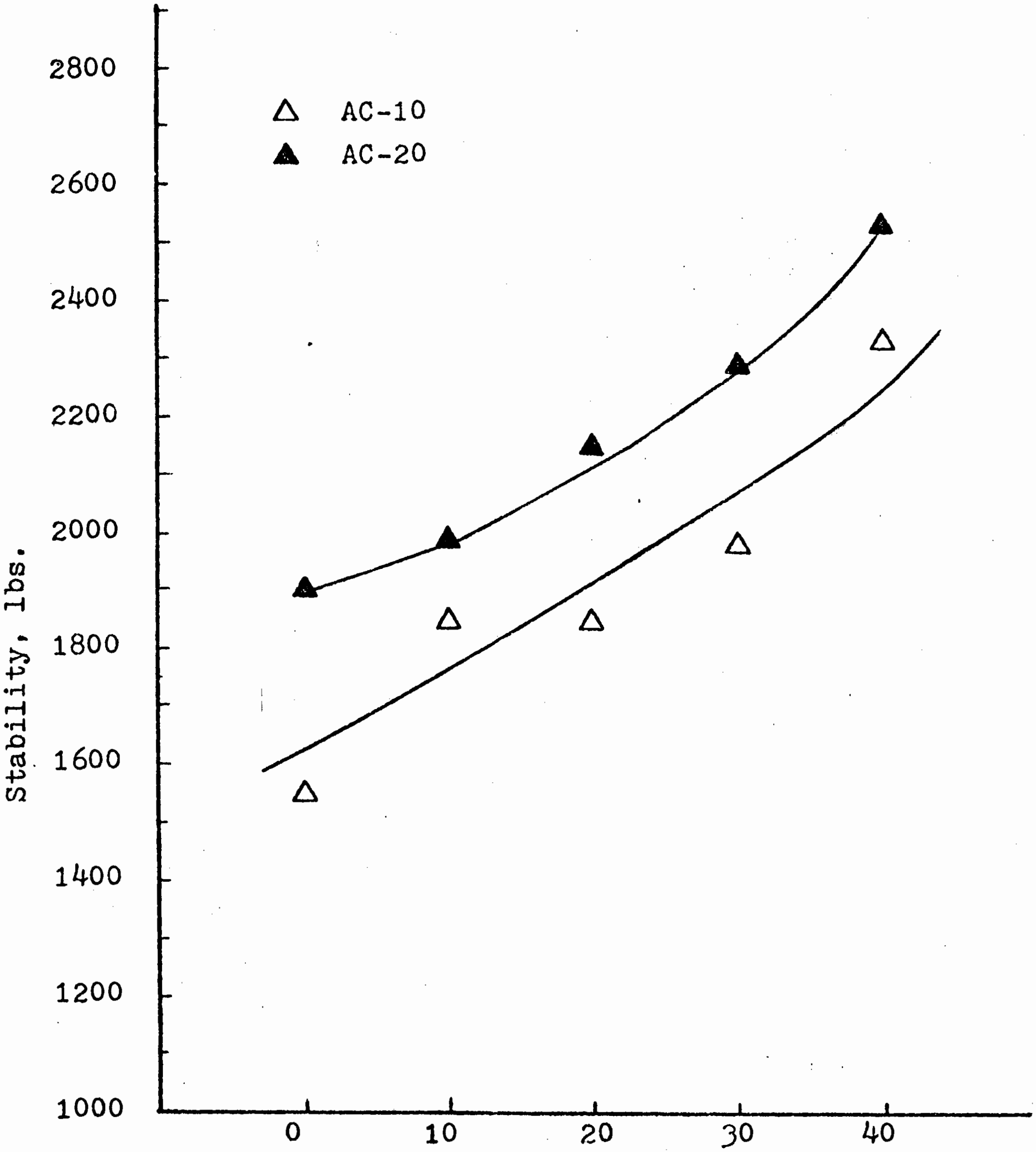

Figure 13: Effect of Lignin Content of Binder on Marshall Stability of Pavement Mixtures Containing 6% Binder.

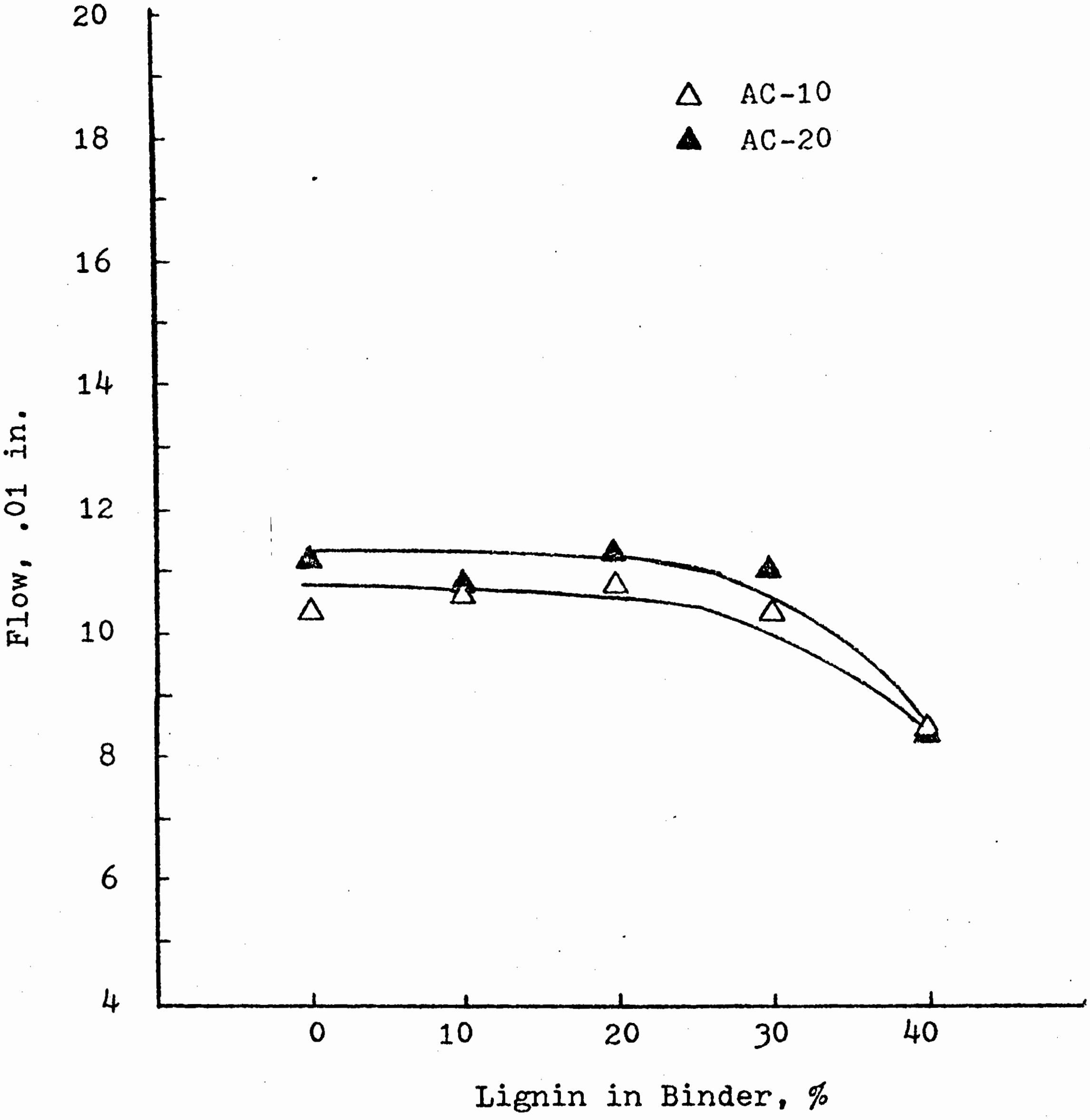

Figure 14: Effect of Lignin Content of Binder on Marshall Flow of Pavement Mixtures Containing 6% Binder.

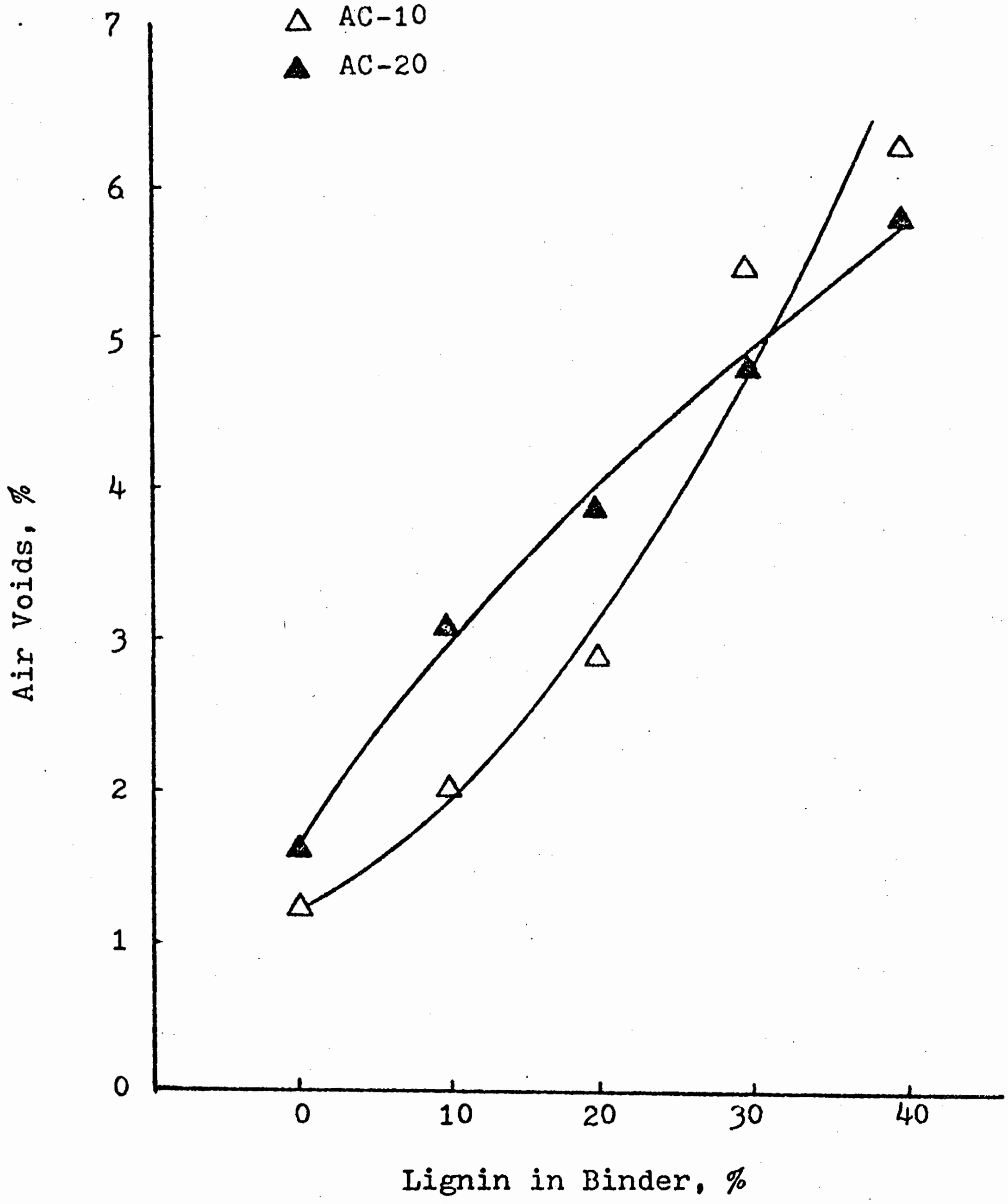

Figure 15 : Effect of Lignin Content of Binder on Air Voids for Pavement Mixtures Containing 6% Binder.

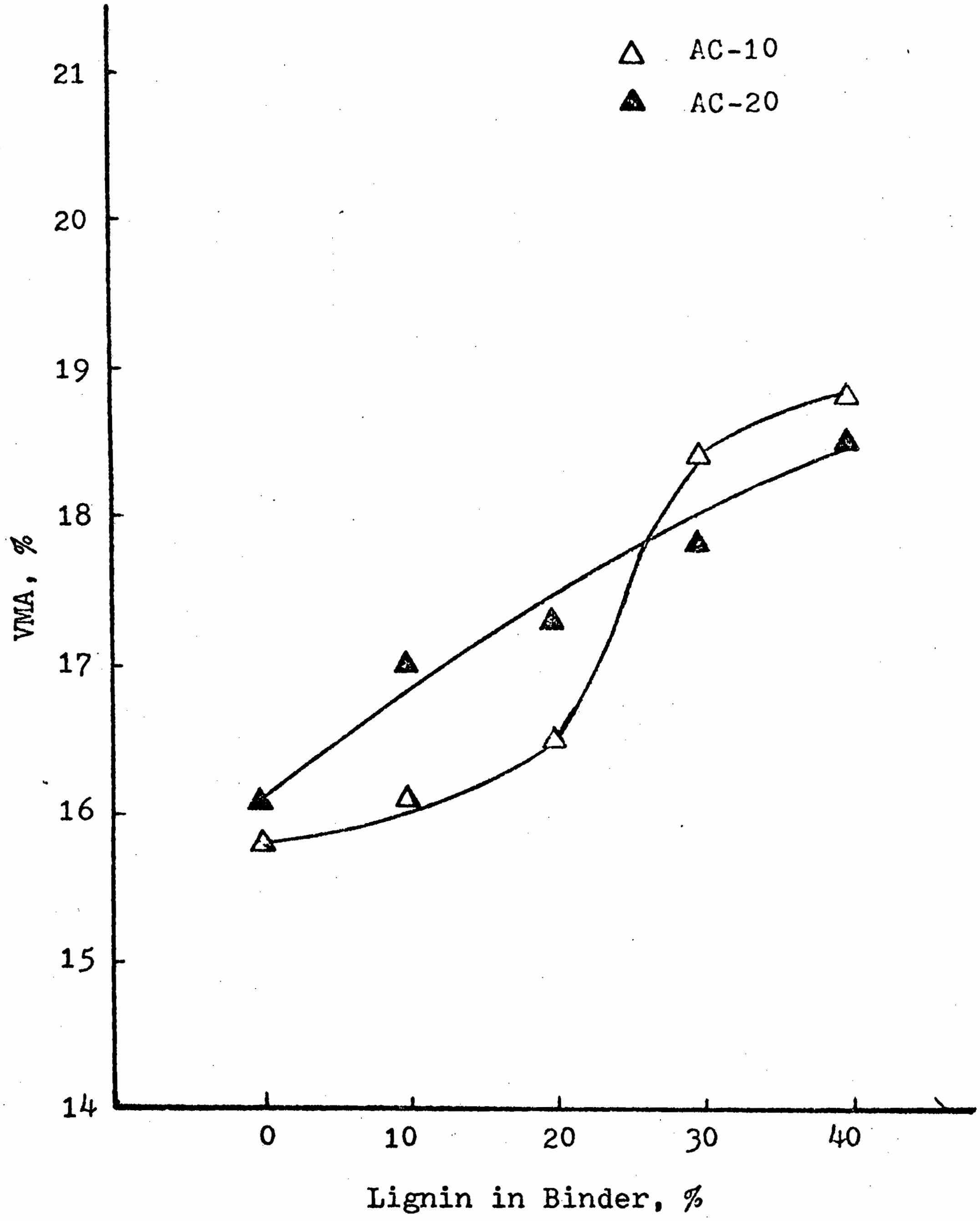

Figure 16 : Effect of Lignin Content of Binder on Voids in Mineral Aggregate for Pavement Mixtures Containing 6% Binder.

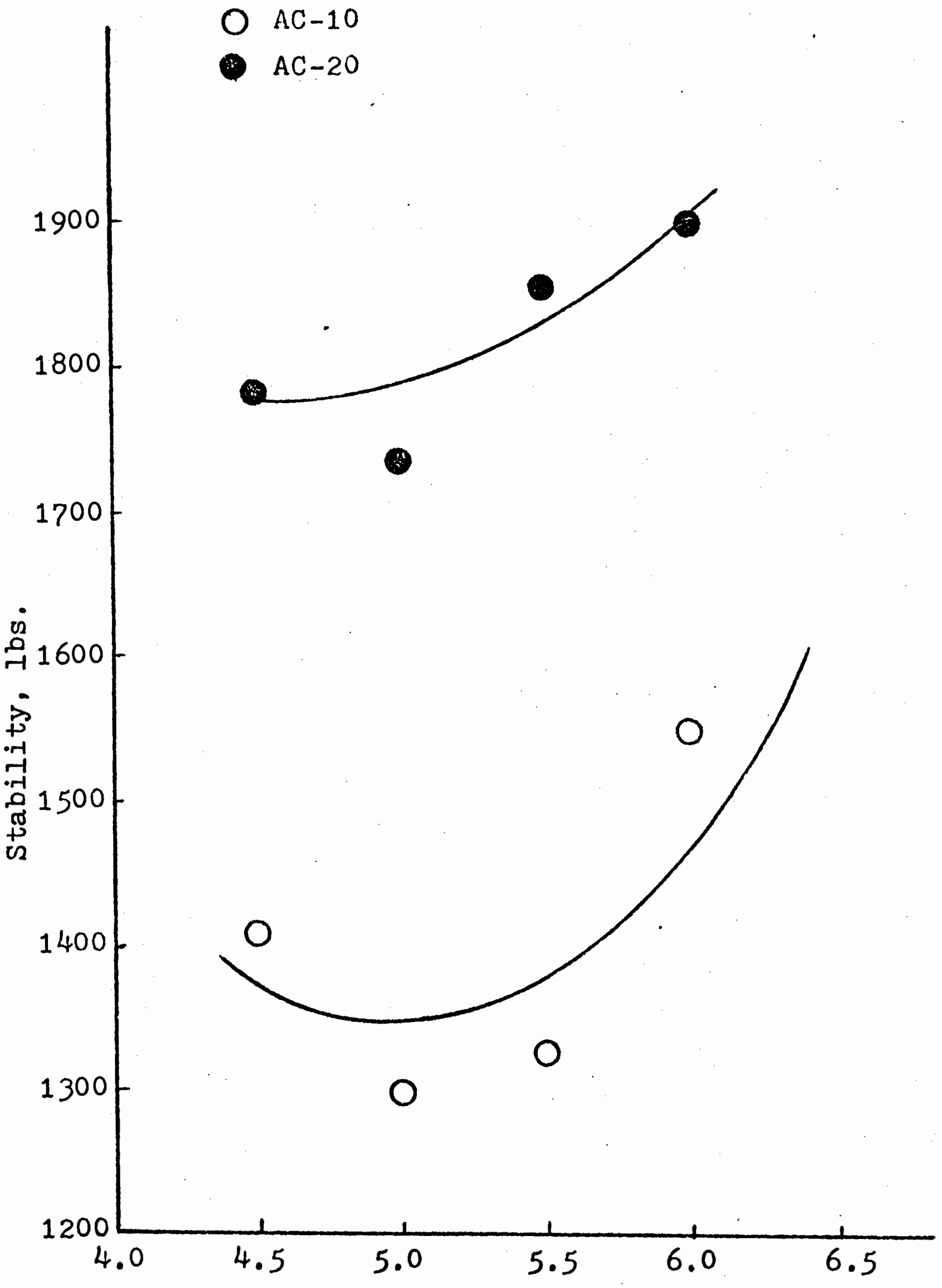

Figure 17: Effect of Binder Content of Pavement Mixture on Marshall Stability for Unmodified Bituminous Binders.

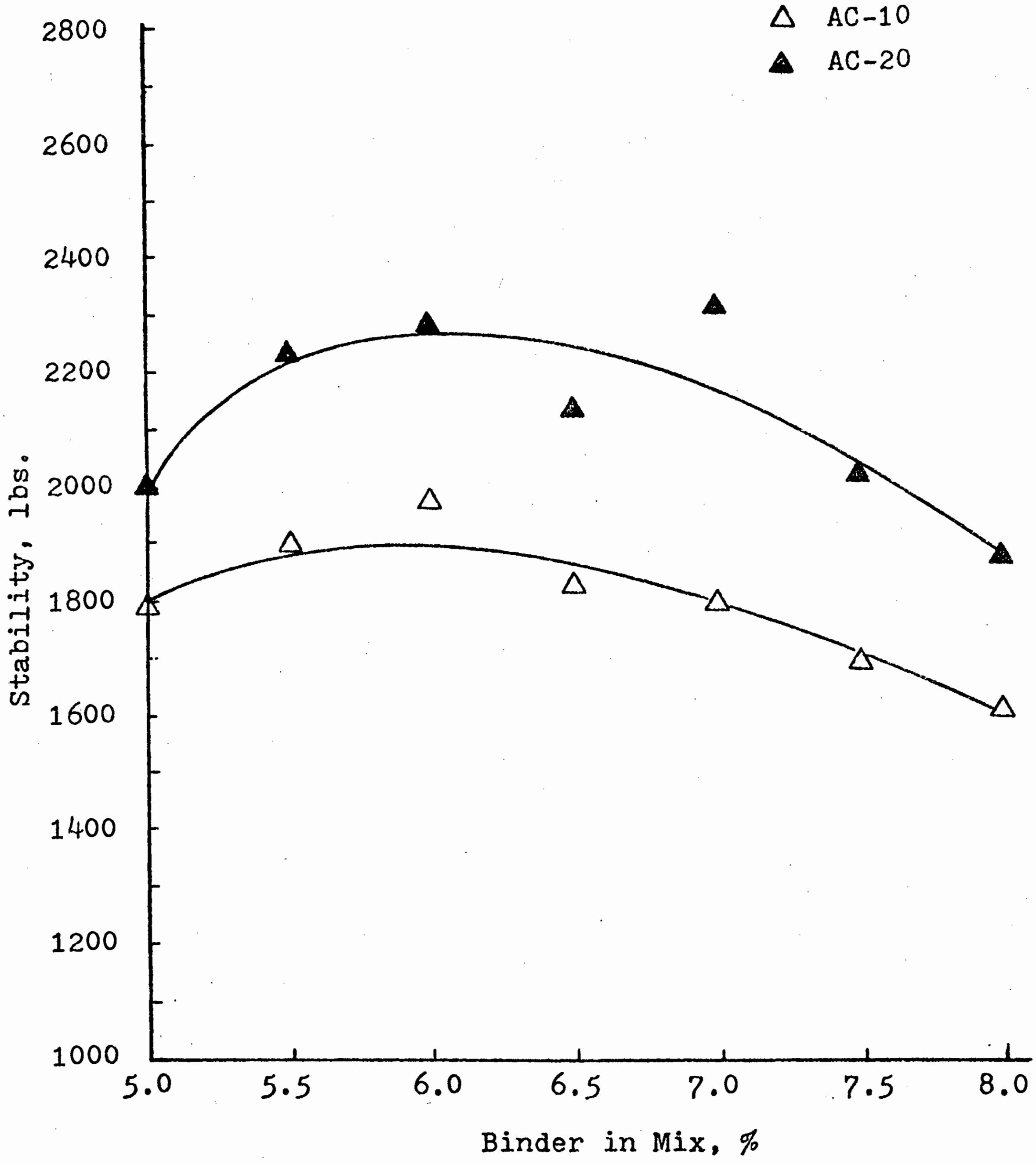

Figure 19: Effect of Binder Content of Pavement Mixture on Marshall Stability for Binders Containing 30% Milled Lignin.

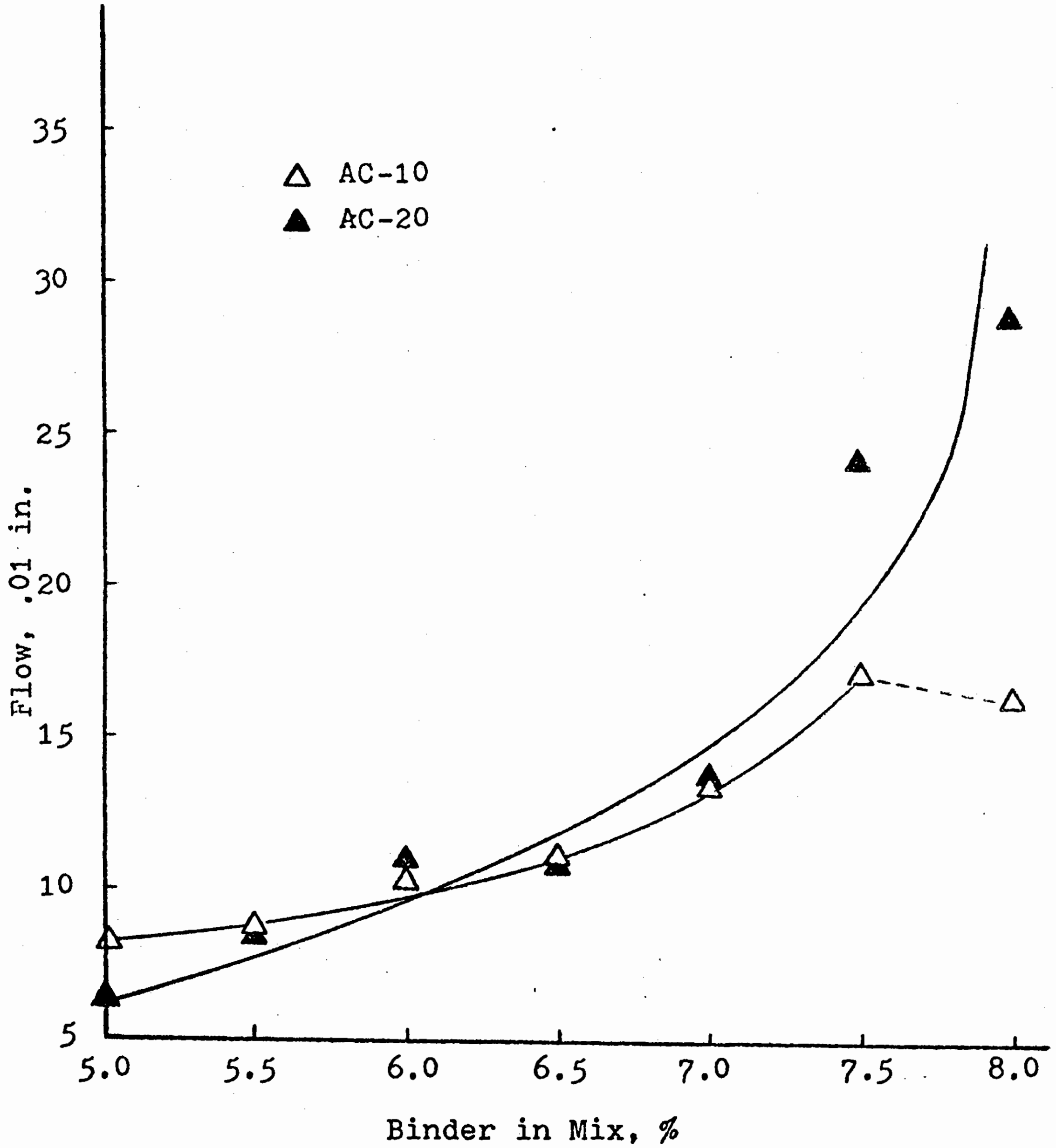

Figure 20 : Effect of Binder Content of Pavement Mixture on Marshall Flow for Binders Containing 30% Milled Lignin.

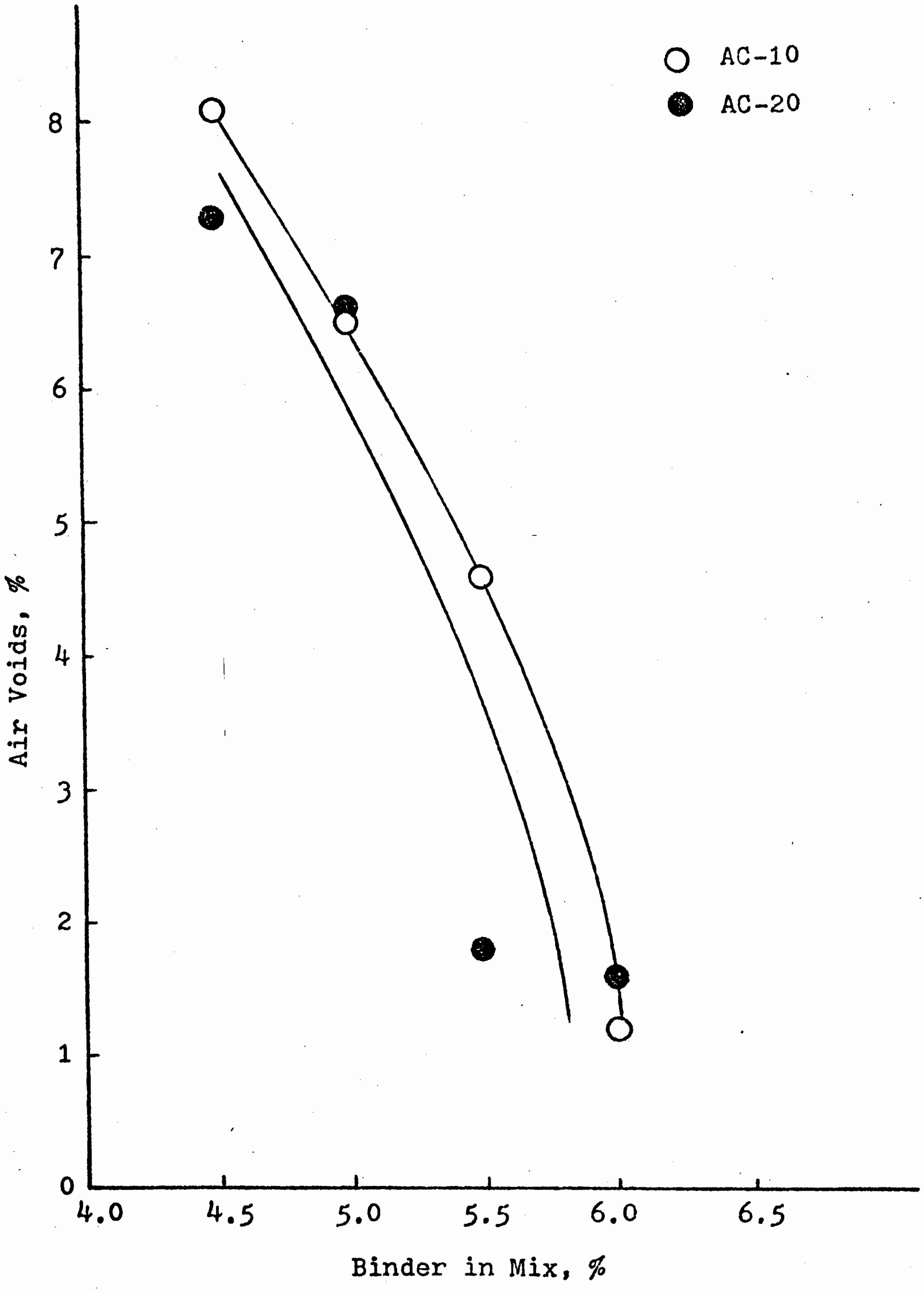

Figure 21: Effect of Binder Content of Pavement Mixture on Air Voids for Unmodified Bituminous Binders.

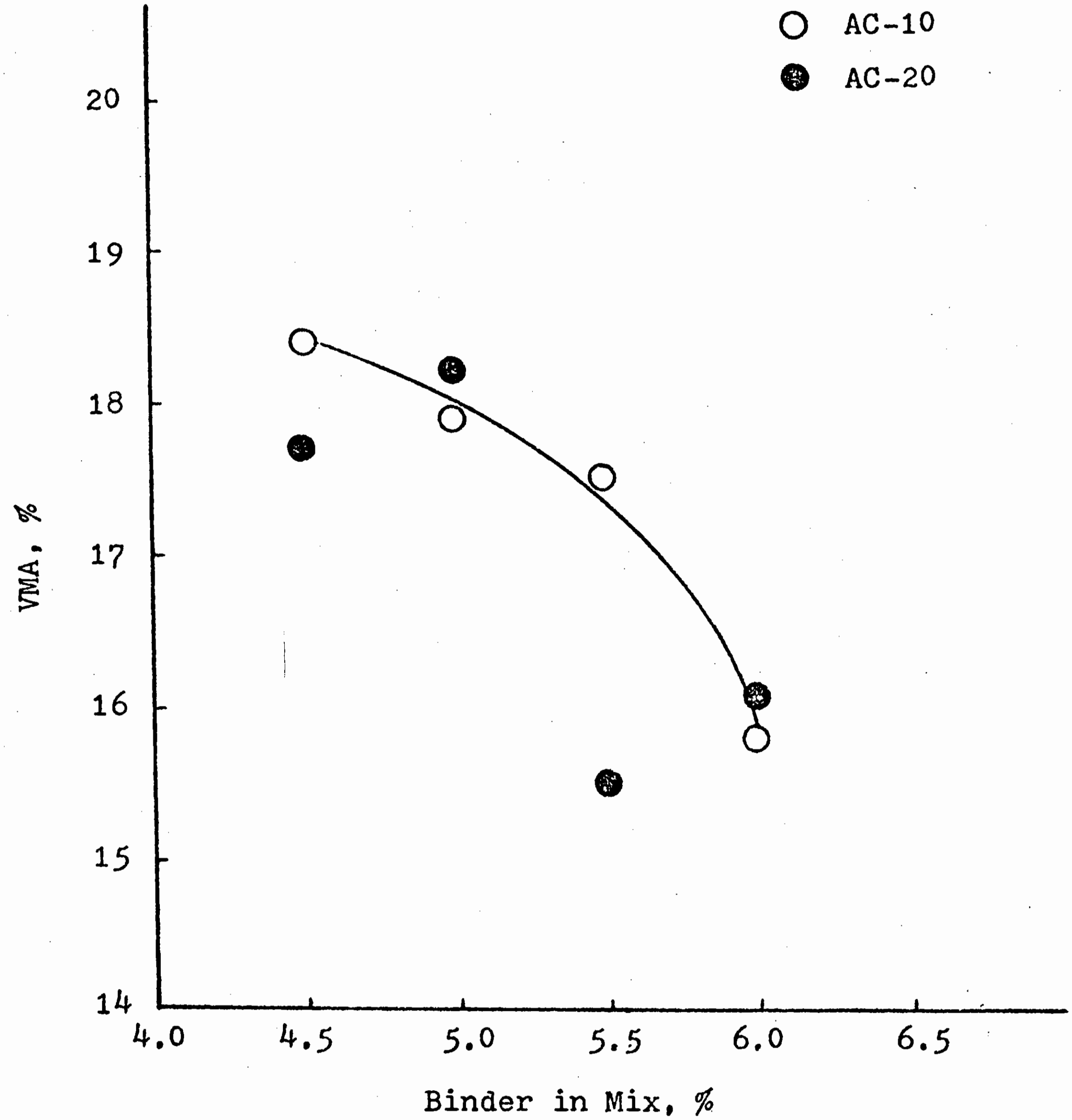

Figure 22: Effect of Binder Content of Pavement Mixture on Voids in Mineral Aggregate for Unmodified Bituminous Binders.

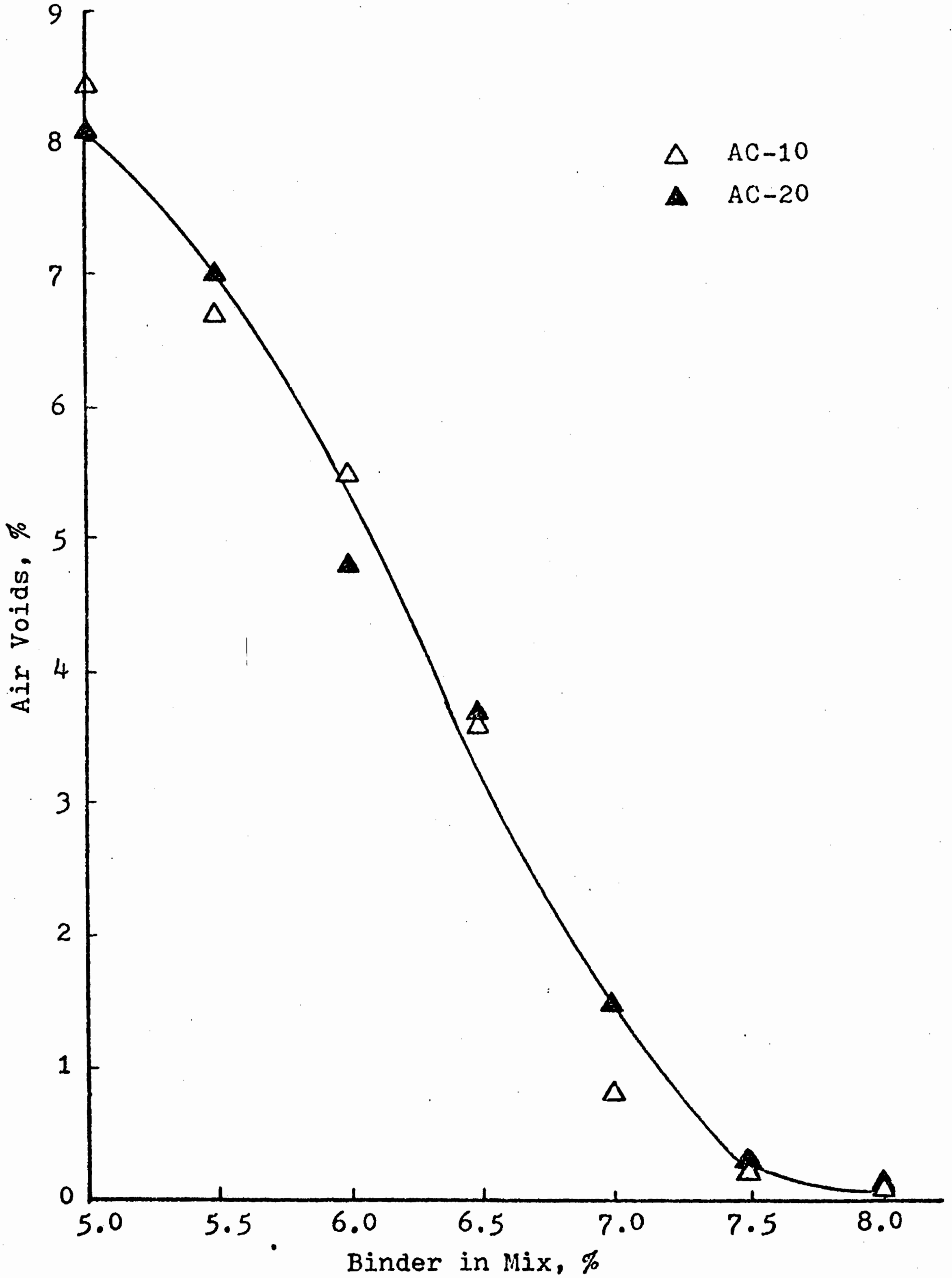

Figure 23: Effect of Binder Content of Pavement Mixture on Air Voids for Binders Containing 30% Milled Lignin.

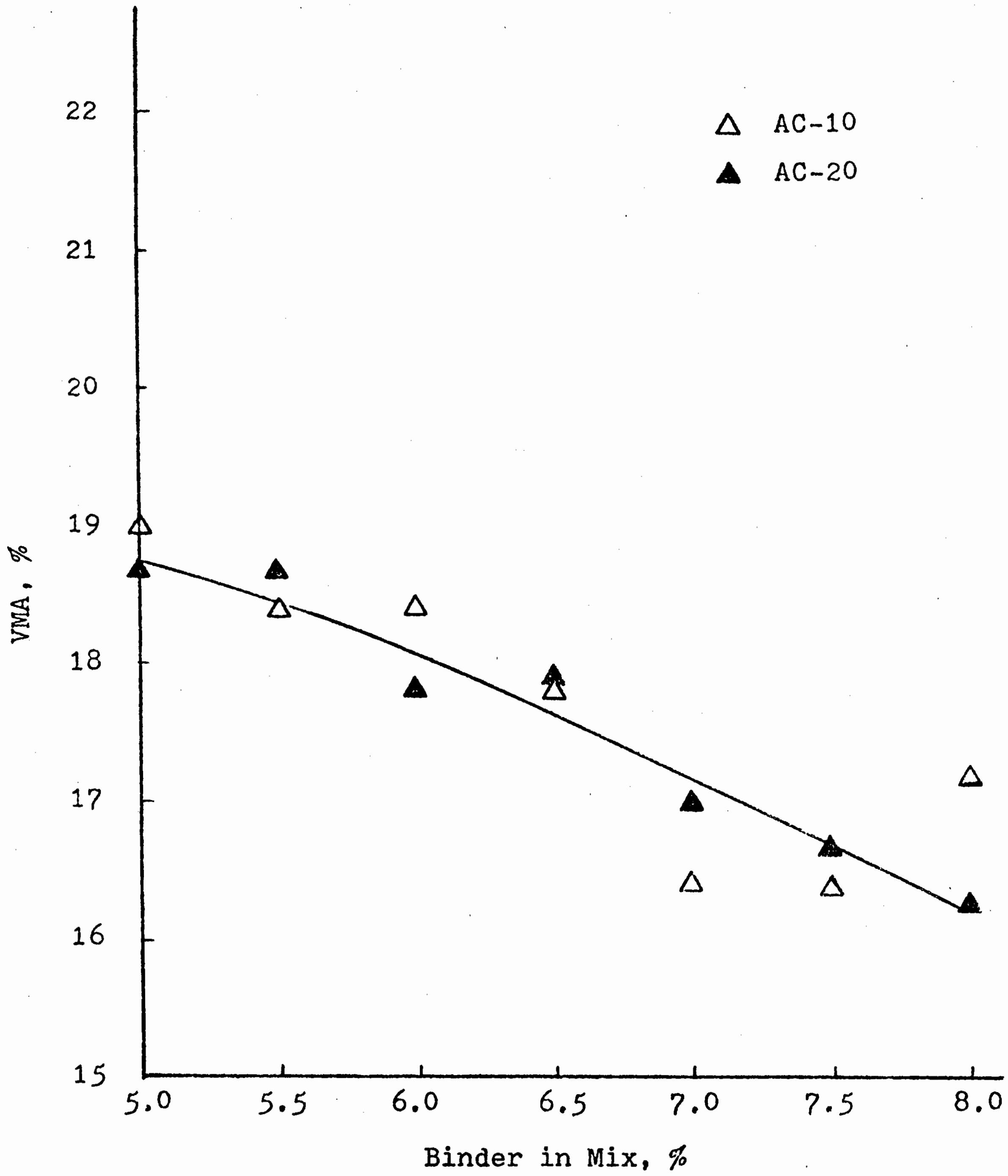

Figure 24: Effect of Binder Content of Pavement Mixture on Voids in Mineral Aggregate for Binders Containing 30% Milled Lignin.