

## The Gelation of Plastisols: An Automatic Method for the Determination of Plastisol Temperature-Rheology Characteristics\*

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### INTRODUCTION

It has long been recognized that the performance of a plastisol (a suspension of finely divided poly(vinyl chloride) resin in an oil plasticizer) in various applications is dependent on the characteristics of the plastisol's gelation, and that these characteristics can be expressed as the viscosity-temperature curve or gel curve. A plastisol's viscosity-temperature characteristics are particularly important in making vinyl foam or in the rotational casting of plastisols. For example, in the Elastomer foam process, a plastisol is mixed with an inert gas (e.g., CO<sub>2</sub>) under pressure and discharged as a wet foam, either into a mold or onto a moving belt.<sup>1,2</sup> When the wet plastisol foam is heated to set, either in a conventional or RF oven, the plastisol's viscosity-temperature characteristics will be very important in determining whether the foam will fuse or collapse to a soupy gel. As will be discussed later, the gel curve can be used to predict the gelation characteristics and performance of a plastisol when the plastisol is used for rotational casting.

There has been a previous report describing the use of a Brookfield viscometer to determine gel curves.<sup>3</sup> There are many disadvantages in using a Brookfield viscometer for this type of measurement. Principally, the instrument is not sensitive to small changes, it is inaccurate when the viscosity is changing rapidly, it is tedious to use, and its use is restricted to low rates of heating. At these low rates of heating, the technique may be measuring accelerated heat aging rather than the sharp gelation experienced in practice. A rapid technique was developed in order to study plastisol gel characteristics for foam and other applications. The new

technique makes use of standard, readily available equipment and is precise, rapid, and automatic. The viscosity is measured with an Ultra-Viscoson viscometer and the temperature with a thermocouple. The outputs from these transducers are fed to suitable recording equipment.

In discussing this technique for measuring a plastisol's rheology-temperature characteristics, a distinction must be made between "gel" and "fusion." Gel curves are reported here, and the gel region is where the curve approaches a vertical line. This is separate and distinct from the fusion point which occurs at a much higher temperature, in the neighborhood of the "clear point."<sup>4</sup> The gel temperature is ambiguous, as it is impossible to assign a single temperature to a region of a curve.

### EXPERIMENTAL TECHNIQUES

A Bendix Ultra-Viscoson viscometer is used to measure the viscosity. The method of measurement relies on the viscous damping of a magnetostricting probe operating at 28 kcycles/sec.; the instrument's meter reads directly [in centipoise (grams/cubic centimeter)]. Because of the high frequency of the probe, the measured viscosity can not be expected to match the viscosity measured by a Brookfield viscometer. The important feature of the Ultra-Viscoson viscometer is that it can continuously and automatically measure a viscosity and viscosity changes. Whatever it measures can be recorded on conventional equipment.

The temperature of the plastisol is measured by means of a thermocouple. Figure 1 shows the specially designed, thin-walled, stainless-steel tube which holds both the plastisol and the viscometer probe. The thermocouple is so set into the tube with epoxy cement that the end of the thermocouple is immersed in the plastisol rather than in the wall of the tube. The probe of the Ultra-viscoson viscometer fits easily into the tube and is held in

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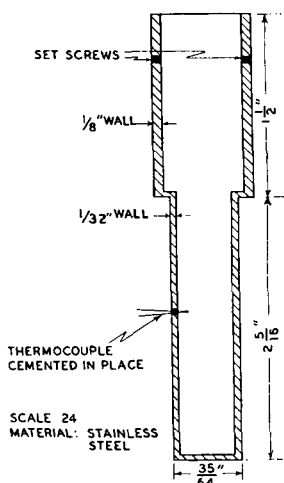


Fig. 1. Tube for plastisol and Ultra-Viscoson viscometer probe.

place by a thumbscrew. The steel tube requires less than 8 cc. of plastisol.

Operating procedure is to zero the Ultra-Viscoson viscometer, calibrate the instrument with SAE 80 oil or similar fluid at constant temperature, check the setting of the viscosity recorder, clean the probe, place it in the plastisol in the steel tube, and immerse the tube-probe assembly in a stirred oil bath. The oil bath is heated from room temperature at a prescribed rate. The calibration and recorder setting steps are important if precise results are to be obtained.

Figure 2 illustrates the oil bath used. It consists of a 600 ml. stainless steel beaker placed inside of a 1500 cc. stainless steel beaker. The beakers are insulated from each other with glass wool. An Aminco 750-watt immersion heater is coiled as so to fit into the smaller beaker, and a mechanical stirrer is placed near the coil. Silicone or other

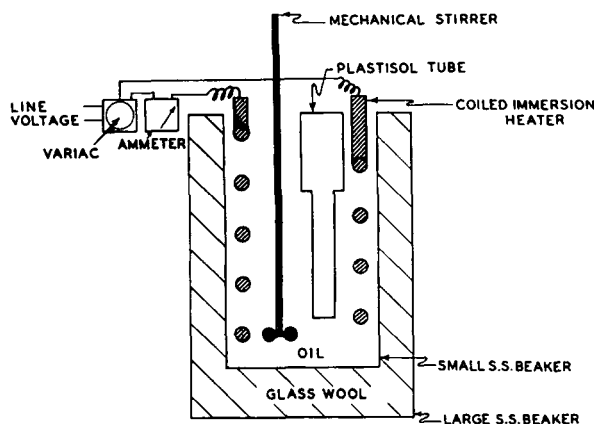


Fig. 2. Oil bath for plastisol heating.

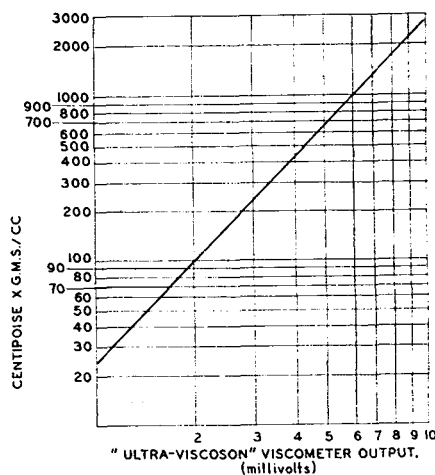


Fig. 3. (Viscosity-density) vs. Ultra-Viscoson viscometer output.

oil capable of being safely heated to 150°C. is used to fill the inner container. The heater is optionally in series with an ammeter and is operated through a variable transformer so as to control current input. This seemingly elaborate oil bath was found to be a convenient and inexpensive way of insuring uniform and controlled rates of heating. With a little practice, the Variac can be used to control the rate of heating over a wide range.

The temperature can be recorded directly on a recorder as degrees Centigrade. The output from the Ultra-Viscoson viscometer is recorded on a 10-mv. recorder which records the output voltage rather than the viscosity-density product. The voltage output is proportional to (viscosity  $\times$  density)<sup>1/2</sup> so that plotting voltage output versus temperature expands the more important part of the gel curve in the low viscosity region. (Recorders and recorder papers are available that enable the viscosity-density product to be read directly.) On the curves that follow, viscosity is plotted as Ultra-Viscoson viscometer output voltage; by means of Figure 3 conversions from voltage to (viscosity  $\times$  density) units can be made.

EXPERIMENTAL RESULTS

Figures 4 and 5 indicate the precision of the Ultra-Viscoson viscometer-thermocouple method for measuring gel curves. Figure 4 shows duplicate determinations of the gel curves for a polyvinyl chloride-di-2-ethylhexyl phthalate (PVC-DOP) plastisol, (100/70 by weight), and Figure 5 shows duplicate determinations for a plastisol intended for flexible foam manufacture. Data points are taken

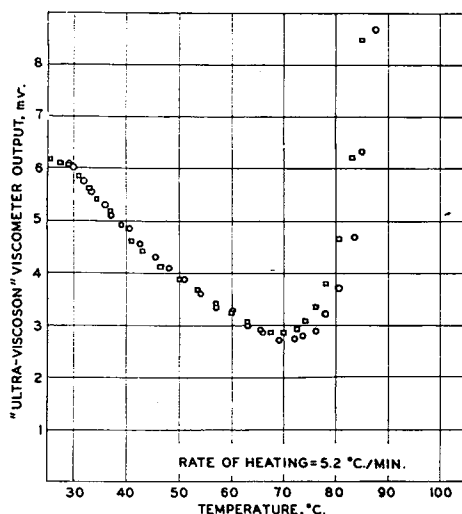


Fig. 4. Duplicate determination of PVC-DOP gel curve.

from 30-sec. intervals on the recorder charts. The precision of the gel curve determination is within  $\pm 0.05$  mv. which is equivalent to within  $\pm 20$ – $30$  (viscosity  $\times$  density) units, depending on the viscosity. Since instrument precision is within  $\pm 2\%$  of full scale, and measurements are usually made in the 0–5000 unit scale, the precision of the gel curve determination is within the precision of the Ultra-Viscoson viscometer. Care must be exercised in changing viscometer probes, since an additional error can be introduced. All curves reported here were determined with a single probe. When a second probe was employed, a discrepancy of as much as 0.04 mv. and  $5^\circ\text{C}$ . was noted.

Figure 6 illustrates the effect of rate of heating on a foam plastisol and on a PVC-DOP (100/70 by

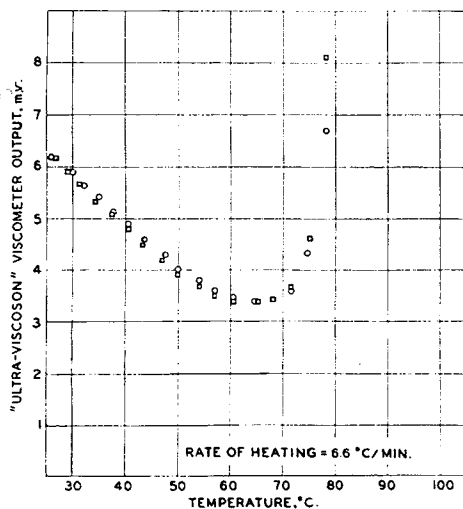


Fig. 5. Duplicate determination of a foam plastisol gel curve.

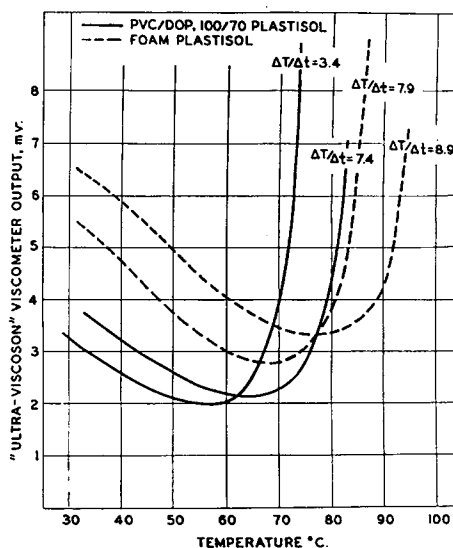


Fig. 6. Effect of rate of heating ( $\Delta T/\Delta t$ ) on plastisol gel curves.

weight) plastisol. When the plastisol is heated at a rate as high as  $9^\circ\text{C}/\text{min}$ ., the gel curves are reproducible. It is believed that accelerated heat aging, rather than gelation, is measured when very low rates of heating are used and that thermal equilibrium is not attained at very high rates of heating. The slower the heating rate, the longer the plastisol is maintained at a high temperature, and the greater the opportunity for viscosity buildup. Gel curves obtained with the Ultra-Viscoson viscometer must be compared at the same rate of heating, and this rate of heating need not coincide with process conditions, although this would be a help.\* The gel curve measurement, as described here, requires about 10 min. heating to gel the plasticizer; this coincides with some process conditions. The length of time necessary to gel the plastisol can be judged from these curves, and the information may be used to plan production cycles.

In formulating for a plastisol application, both resin characteristics and plasticizer activity will contribute to the plastisol's suitability. (This is not to imply these are the only factors.) The effect of various resin types is shown in Figure 7,

\* Preliminary work indicates that it may be possible to correct for rate of heating differences between runs by correcting for the temperature lag between the thermocouple and probe. The correction is established by replacing the Ultra-Viscoson probe by a second thermocouple and plotting the temperature difference between thermocouples against the rate of heating as measured by the permanent thermocouple. The author is indebted to Mr. L. A. McKenna for establishing this.

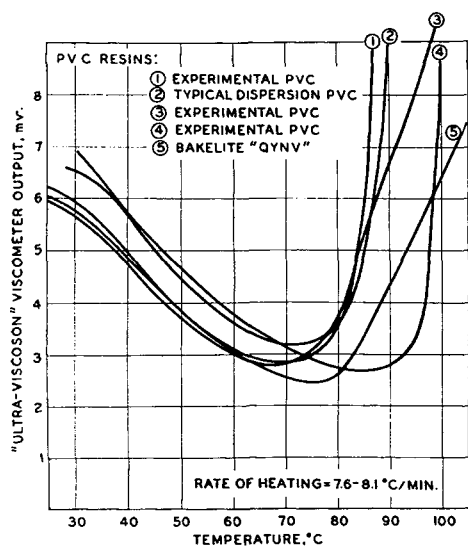


Fig. 7. Plastisol gel curves for different PVC samples: (1) experimental PVC; (2) typical dispersion PVC; (3) experimental PVC; (4) experimental PVC; (5) Bakelite QYNV.

which shows gel curves for five PVC samples of different molecular weights and molecular weight distributions and of about the same particle size distributions. Resins 1, 2, and 4 have a fairly narrow molecular weight distribution and are characterized by sharp gelation. Resins 3 and 5 have a much broader distribution. The broad distribution results in slower gelation. The temperature range over which the narrow distribution resin gels is a function of the molecular weight which may be judged from the intrinsic viscosities listed in Table I. The polymers having a wide molecular weight distribution are characterized by a curve with a broad minimum and not too steep a vertical arm. The polymers with a narrow molecular weight distribution are characterized by a narrow gel curve with a very sharp viscosity increase at gelation. The temperature of the gel region is proportional to the molecular weight. There is no doubt there are other factors affecting gelation, for

TABLE I

No.	Resin	Intrinsic viscosity in cyclohexanone, at 20°C.
1	Experimental PVC	1.16
2	Typical commercial dispersion PVC	1.23
3	Experimental PVC	1.48
4	Experimental PVC	1.36
5	Bakelite QYNV	1.58

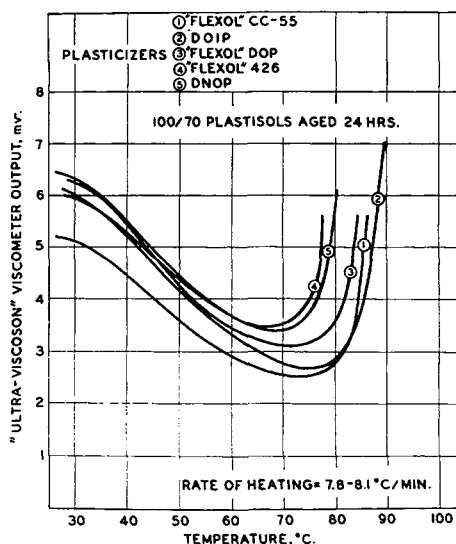


Fig. 8. Gel curves for phthalate plasticizers: (1) Flexol CC-55; (2) DOIP; (3) Flexol DOP; (4) Flexol 426; (5) DNOP.

example, resins must be compared at similar particle size distributions, as is done in Table I.

Figure 8 illustrates gelation characteristics of plasticizers of related chemical structure. The plasticizer chemical compositions are tabulated in Table II, and their relative activities can be judged from the gel curves.

Figure 9 indicates the relative activity of a number of commercial plasticizers. Table III shows the chemical composition of the plasticizers.

TABLE II

Plasticizer indicated in Figure 8	Chemical composition
DNOP	Di- <i>n</i> -octyl phthalate
Flexol <sup>a</sup> DOP	Di-2-ethylhexyl phthalate
Flexol CC-55	Di-2-ethylhexyl hexahydrophthalate
Flexol 426	Butyl-ethylhexyl phthalate mixed ester
DOIP	Di-2-ethylhexyl isophthalate

<sup>a</sup> Trademark of Union Carbide Chemicals Co.

TABLE III

Plasticizer indicated in Figure 9	Chemical composition
Flexol A-26	Di-2-ethylhexyl adipate
Flexol TOF	Tri-2-ethylhexyl phosphate
TCP	Tricresyl phosphate
Santicizer <sup>a</sup> 141	Alkyl aryl phosphate

<sup>a</sup> Trademark of Monsanto Chemical Co.

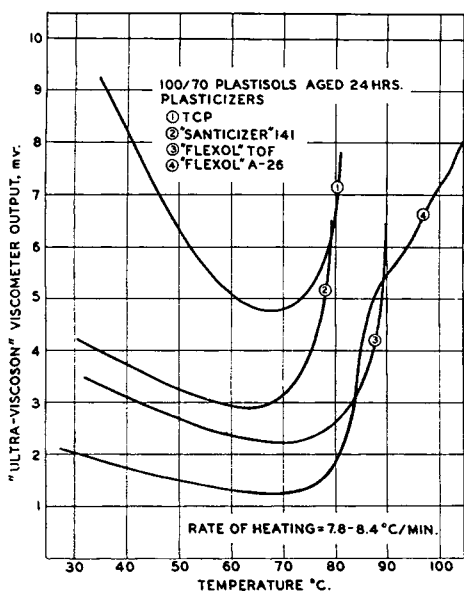


Fig. 9. Plastisol gel curves for 100/70 plastisols aged 24 hr. with various plasticizers: (1) TCP; (2) Santicizer 141; (3) Flexol TOF; (4) Flexol A-26.

The gel curves in Figures 7-9 are for plastisols containing 100 parts by weight resin to 70 parts by weight plasticizer. The plastisols were prepared by the stir-in technique and aged 24 hr. at room temperature before the gel curves were determined.

Figure 10 shows the gel curves for two plastisols that have been evaluated as starting materials for flexible vinyl foam in the Elastomer process. Plastisol 1 was readily made into a superior foam, gelling rapidly and fusing to an integral piece. Plastisol 2 could not be fused as a foam and collapsed to a

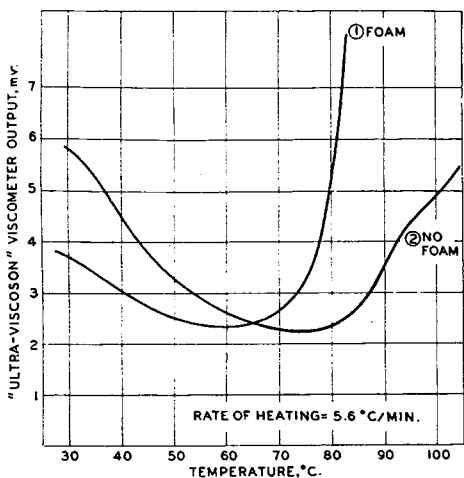


Fig. 10. Plastisol gel curves for foam formulations.

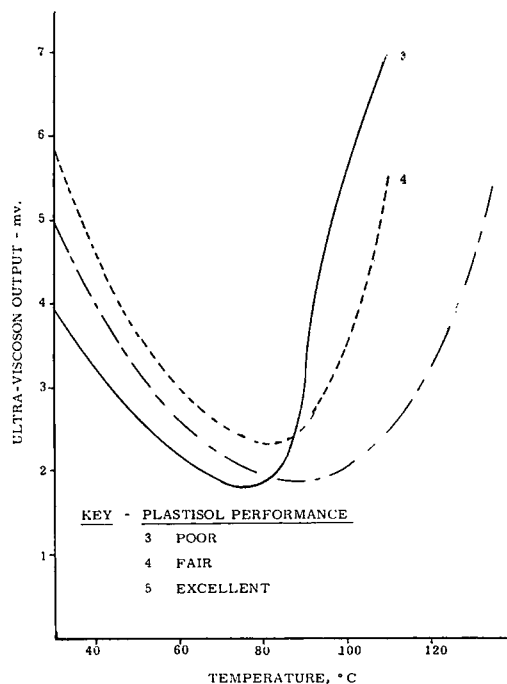


Fig. 11. Plastisol gel curves for rotational casting plastisols: plastisol performance (3) poor; (4) fair; (5) excellent.

viscous syrup when heated. Plastisol 1 is capable of being made into a flexible foam because it gels quickly, at a fairly low temperature, and the viscosity does not go through too broad or low a minimum which avoids premature foam collapse. Plastisol 2 was a poor choice for foam, and the gel curve, with its slow, upward rise after a deep, broad minimum, shows why this particular plastisol collapsed before it could be gelled and fused to a foam. Before gelling, the plastisol experienced a broad area of low viscosity and could not support a foam structure.

Figure 11 illustrates one application of the gel curve determination to plastisols for rotational casting. Plastisol 4 was somewhat superior to Plastisol 3, in that it more readily filled a spherical mold before gelling. However, both plastisols gelled to a molded piece with ridges and with unevenly thick walls. These imperfections were due to too rapid gelation of the plastisol. The curves suggest that a plastisol for rotational casting should possess certain gelation behavior. It may be judged that a suitable plastisol should have a gel curve with a broad minimum and not too rapid rate of gelation so that the fluid material can fill the mold adequately while it is being heated. Plastisol 5 was formulated on this basis and found to be an excellent choice for the application. Its use re-

sulted in a molded article having smooth, uniformly thick walls, despite the higher temperature needed for gelation. Further applications and extensions of the gel curve technique should be obvious.

### DISCUSSION

A precise, rapid, sensitive, and automatic method for the determination of plastisol viscosity-temperature curves is presented. The method is convenient, requiring about  $1\frac{1}{2}$ -2 hr. per determination, including time for clean-up and replotting of data if an X-Y recorder is not available. The method, in simultaneously measuring rate of solution and rate of viscosity buildup, clearly distinguishes between good and poor formulations for plastisol applications and gives an indication of necessary process times. Differences among various resins and plasticizers are clearly defined; this leads to a means of formulating from viscosity-temperature curves instead of inadequate gel data or guesswork. The gel curves can give an insight as to what is required for a given application. The known gelation characteristics of various materials, as shown in Figures 7-9 can serve as a guide in formulating a plastisol. A library of gel curves and an understanding of the gel curve requirement for a plastisol in a given application can lead to a rapid and precise way of formulating. The techniques described here for obtaining and interpreting plastisol temperature-rheology characteristics are applicable to any plastisol application.

### References

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2. E. H. Schwenke, U.S. Patent 2,666,036 (1954).
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### Synopsis

A technique is described for the small scale evaluation of plastisol formulations for molding, casting, coating, and foam applications. The technique described rapidly measures and automatically records the viscosity of a plastisol as a function of temperature by means of a Bendix Ultra-Viscoson and thermocouple. The measurements are made under conditions that closely approach process conditions. Small changes are accurately followed and the portion of the curve

in the vicinity of gelation is amplified. The shape and position of the viscosity-temperature plot are dependent on the chemical nature of the plasticizer as well as the intrinsic viscosity and molecular weight distribution of the dispersed polymer. The resulting curves can be used to choose plastisol compositions for a given application. The application of the curves to foam and rotational casting formulations is outlined.

### Résumé

Une technique est décrite pour l'évaluation à petite échelle des plastisols pour les applications au moulage, au therm durcissement, au revêtement, et aux mousses. La technique décrite mesure rapidement et enregistre automatiquement la viscosité d'un plastisol en fonction de la température à l'aide d'un ultra-viscoson Bendix et d'un thermocouple. Les mesures sont faites dans des conditions qui s'approchent de très près des conditions du processus. De petits changements sont suivis fidèlement et la portion de la courbe au voisinage de la gélification est amplifiée. La forme et la position du diagramme viscosité-température dépendent aussi bien de la nature chimique du plastifiant que de la viscosité intrinsèque et de la distribution du poids moléculaire du polymère dispersé. Les courbes résultantes peuvent être employées pour choisir des compositions de plastisol pour une application donnée. On esquisse l'application des courbes aux formules de préparation des mousses et du matériel therm durcissable.

### Zusammenfassung

Eine Methode zur Bestimmung der Brauchbarkeit von Plastisolen in Abhängigkeit von ihrer Zusammensetzung für die Anwendung im Spritzguss, als Giessharz, zum Überziehen und für Schaummassen, mit Verwendung kleiner Mengen, wird beschrieben. Das beschriebene Verfahren erlaubt die rasche Messung und automatische Aufzeichnungen der Viskosität eines Plastisols in Abhängigkeit von der Temperatur mit Hilfe eines Bendix Ultra-Viscoson und eines Thermoelements. Die Messungen werden unter Bedingungen ausgeführt, die sich eng an die Bedingungen in der Praxis halten. Kleine Änderungen können genau gemessen werden und der Kurventeil im Bereiche der Gelierung wird mit Verstärkung aufgenommen. Die Gestalt und Lage des Viskositäts-Temperaturdiagrammes ist sowohl von der chemischen Natur des Weichmachers, als auch von der Viskositätszahl und Molekulargewichtsverteilung des dispergierten Polymeren abhängig. Die erhaltenen Kurven ermöglichen die Auswahl einer geeigneten Plastisolzusammensetzung für eine gegebene Anwendung. Die Anwendung der Kurven auf Schaum und Rotaionsguss wird erläutert.

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