

Measurement of Plastisol Gelation and Solution by Infrared Spectroscopy

HARVEY ALTER* and JOHN E. KAUFMAN,† *Harris Research Laboratories, Inc., Washington, D. C.*

Synopsis

The rate and extent of solution of polyvinylchloride in ester plasticizers has been measured using infrared spectroscopy. The measurement is based on shifts in the carbonyl stretching frequency of the ester linkage, similar to the familiar infrared solvent shifts commonly observed for low molecular weight materials. Double beam techniques were necessary to record the shifts. The intensity of the shifted-band increases up to gelation and the rate of increase depends on the temperature of heating. The intensity of the shifted band is directly proportional to the concentration of polymer dissolved in the plasticizer and can be used to measure this concentration at any time during the gelation process. It is estimated that from 17 to 22 per cent of the polymer was dissolved at the gel point after heating at 65°C. and that about 29 per cent of the polymer was dissolved at the gel point after heating at 75°C., for the plastisols used in this study.

Introduction

A plastisol is made by dispersing finely divided poly(vinyl chloride) in a nonvolatile plasticizer to form a pourable mixture. When the plastisol is heated, its viscosity decreases slowly as the plasticizer viscosity decreases, then increases sharply as the resin absorbs plasticizer and rapidly swells to form a friable, gellike solid.¹ The transformation from pourable liquid to gellike solid is an important one and must be controlled in the various applications of plastisols. The transformation is referred to as gelation, and occurs at the so-called gel point or gel temperature. When the plastisol is heated past the gel point it fuses and becomes clear at a second characteristic temperature, termed the clear point or fusion point.^{2,3} After fusion, the resin plasticizer composition is a tough and flexible plastic. An excellent description of the processes has been given by Hoy.⁴

Plastisol gelation can be accomplished by heating the plastisol rapidly from room temperature to the gel point or by heating it for longer periods of time at some intermediate temperatures. The conversions from pourable dispersion to gellike solid and then to clear plastic are not chemical changes

* Present address: Toni Company, Chicago, Ill. 60654.

† Participant in a National Science Foundation sponsored Chemistry-Physics Teacher Institute at American University in cooperation with Harris Research Laboratories. Present address: Tumwater High School, Tumwater, Washington.

in the usual sense but rather involve diffusion, swelling, and solution of the polymer by the plasticizer. The gel point has been associated with the point of maximum resin swelling by Hoy,⁴ but there is no direct experimental measure of the fraction of polymer dissolved or the fraction of plasticizer imbibed at any time during the gel or fusion processes. The results from the spectroscopic technique described here complement Hoy's work by filling this gap in the understanding of plastisol gelation and fusion.

Experimental Methods and Results

The basis for using infrared spectroscopy to detect and measure the physical changes during gelation and fusion is quite simple. When the infrared absorption spectrum of a solvent is compared to the spectrum of the solvent plus a solute, there is a shift in one or more of the infrared absorption frequencies.⁵ These shifts are well documented for a large number of systems.^{6,7} The stretching vibrations are displaced to lower frequencies and the corresponding bending vibrations are shifted to higher frequencies. The reasons for the shift and the extent of the shift involve specific association interactions between the solvent and solute as well as the polarities of each. Before this background could be applied to plastisol gelation, shifted bands in the spectra of plastisols had to be detected and recorded, and the general applicability of the method established.

Plastisols were made by the stir-in method by using a Brookfield high shear mixer. The usual composition was: poly(vinyl chloride) (Geon 121) 100, plasticizer 70, dibutyltin dilaurate (Union Carbide D-22) 2 or 3 parts by weight. Various plasticizers were used. The spectra were recorded on a Perkin-Elmer Model 221G spectrophotometer.

The infrared spectra of several plastisols were scanned before and after heating; the spectra were the same before and after gelation and fusion. However, a "new" band was detected in the carbonyl region of the spectra of the same samples when a double-beam technique was used. Consequently, the double-beam, or differential spectra, technique was adopted for all of the work reported here. The technique was practiced as follows. Plastisol was spread between salt plates by using a 0.1-mm. spacer and mounted in the sample beam. The same sample of plastisol was placed in a variable thickness cell which was then mounted in the reference beam. The thickness of the reference plastisol was adjusted to give flat recording, i.e., zero differential adsorption, over the frequency range from 1650 to 1750 cm^{-1} . The cell containing the plastisol in the sample beam could be removed from the spectrophotometer, heated, cooled, and returned to the spectrophotometer, and spectral differences or changes resulting from the heating recorded. The thickness of the 0.1-mm. layer of plastisol did not change perceptibly after gelation as measured by the adsorption of the 1530 and 1650 cm^{-1} bands. It was found that the difference in absorption at these two frequencies (measured against air in the reference beam) is a linear function of sample thickness in the thickness region of interest.

Thus, a fair check on sample thickness could be made spectrophotometrically.

The differential spectra of six plastisols made with six different ester type plasticizers were recorded before and after gelation against ungelled plastisol in the reference beam. New, sharp adsorption bands were recorded for all of the plastisols. The results are given in Table I, which lists the observed frequencies of the carbonyl stretching of the plasticizers in the plastisol before gelation and of the new, or shifted band, formed after gelation. The shifted bands are very much diminished in intensity compared to the ordinary carbonyl band of the plasticizer, indicating that only a small portion of the carbonyl groups are affected by the resin solute.

TABLE I
Observed Carbonyl Frequency Shifts

Plasticizer	Frequency, cm.^{-1}	
	Before gelation	After gelation
Di(2-ethylhexyl) phthalate	1730	1695
Didecyl phthalate	1730	1690
Di(2-ethylhexyl) isophthalate	1730	1702
Di(2-ethylhexyl) adipate	1740	1690
Didecyl adipate	1740	1705
Butyl benzyl phthalate	1733	1690

The same techniques were applied to a mixture of 2-chlorobutane 100, di(2-ethylhexyl) phthalate 70 parts by weight with the ester in the reference beam. The differential spectrum in the carbonyl region showed a new band at 1700 cm.^{-1} .

The differential infrared technique was used to study the gelation of a plastisol made from PVC and di(2-ethylhexyl) phthalate mixed in the proportion 100:70 parts by weight. The 1530 and 1650 cm.^{-1} bands were recorded for each sample before and after heating as a check of constancy of sample thickness. The plastisol samples, spread between salt plates with a 0.1-mm. spacer, were heated in an oven at 65 and 75°C. for different lengths of time. The gel point of the plastisol is close to 75°C. ,¹ although it can be gelled by longer heating at the lower temperature.⁴ The intensity of the shifted carbonyl band was recorded after each heating interval by the double-beam method. The results are shown in Figure 1 as the shifted band intensity (arbitrary units) as a function of time. Plastisol samples were also heated for 5 and 10 min. at 165 and 175°C. , temperatures well above the clear point^{2,3} to fuse the samples. The band intensities after fusion ranged from 5.5 to 6.5 units, as indicated in Figure 1. However, the sample thickness was not exactly the same before and after fusion, so that this band intensity range must be interpreted with caution.

The intensity of the shifted band was related to the amount of poly(vinyl chloride) dissolved in the plasticizer. Dilute gels were prepared by dis-

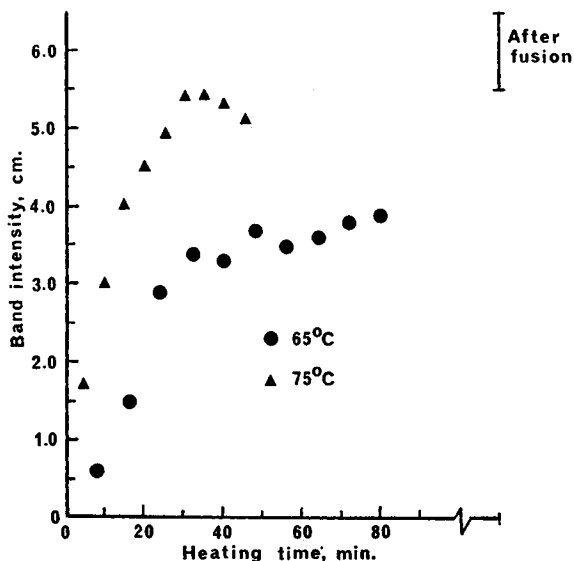


Fig. 1. Changes in shifted band intensity with heating time.

solving known amounts of polymer in a heated mixture of di(2-ethylhexyl) phthalate (DOP) and D-22, 100:2. The dilute gels were spread between salt plates with a 0.1-mm. spacer and their differential spectra were recorded against the mixture of DOP and D-22 in the reference beam of the spectrophotometer. Figure 2 is a plot of shifted band intensity (arbitrary units) as a function of polymer concentration. Gels containing more than 8 g. of polymer were too stiff for convenient quantitative measurement by this technique.

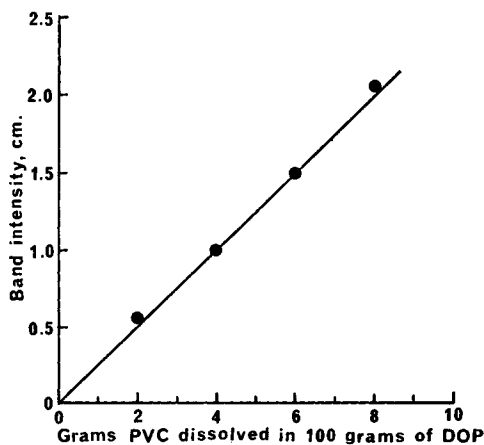


Fig. 2. Changes in shifted band intensity with concentration of dissolved mer.repr.

Discussion

The shifting of an infrared absorption frequency of a solvent by a solute is a familiar phenomenon for low molecular weight compounds. The same phenomenon now has been found to occur in poly(vinyl chloride) plastisols. It seems to be a general effect, occurring in the six ester-type plasticizers tried (Table I), and in the model system, dioctyl phthalate-chlorobutane. Similar shifts could undoubtedly be found with other plasticizers, e.g., phosphates, provided the appropriate frequencies were investigated. This infrared method may have wide applicability for studying polymer solutions.

The intensity of the shifted band was found to be proportional to the amount of polymer dissolved in the plasticizer. Thus, this infrared intensity is a direct measure of the amount of polymer dissolved in the plasticizer at any time during the gelation process. The amount of polymer dissolved increases sharply at short times of heating, as the plastisol gels, then levels off to a near constant value. The samples heated past the leveling-off point were visibly gelled, and the leveling-off point is thought to be the gel point. The rate of polymer solution during gelation was much greater at 75 than at 65°C. as expected, since gelation is faster at the higher temperature. After gelation, the amount of polymer dissolved in the plasticizer at the two temperatures is different. This is consistent with Hoy's finding of lower swellability of PVC in plastisols at lower temperatures.⁴ The shifted band intensity increases again, going from gelation to fusion, indicating that at gelation not all of the polymer is dissolved in the plasticizer, or the equivalent situation, that not all of the plasticizer is dissolved in the resin.

It is an interesting exercise to estimate the amount of polymer dissolved in the plasticizer at gelation. This can be accomplished by extrapolating the line in Figure 2 to much higher band intensities, an admittedly bold procedure. After 65°C. gelation, it is thus estimated that 17–22% of the poly(vinyl chloride) is dissolved in the plasticizer and that after 75°C. gelation about 29% of the polymer is dissolved.

References

1. Alter, H., *J. Appl. Polymer Sci.*, **2**, 312 (1959).
2. Severs, E. T., and G. Smitmans, *Paint Varnish Prod.*, **47** (No. 12), 54 (1957).
3. McKenna, L. A., *Mod. Plastics*, **35**, No. 4, 150 (1958).
4. Hoy, K. L., paper presented to Division of Organic Coatings and Plastics Chemistry, 149th Meeting, American Chemical Society, *Preprints*, **25** (No. 1), 375 (1965).
5. Hallam, H. E., in *Infrared Spectroscopy and Molecular Structure*, M. Davies, Ed., Elsevier, New York, 1963.
6. Archibald, L. B., and A. D. E. Pullin, *Spectrochim. Acta*, **12**, 34 (1958).
7. Bellamy, L. J., and R. L. Williams, *Proc. Roy. Soc. (London)*, **A255**, 22 (1960).

Résumé

La vitesse et le degré de dissolution du chlorure de polyvinyle dans des plastifiants esters ont été mesurés par spectroscopie infra-rouge. La mesure est basée sur le déplacement de la fréquence d'étirement du groupe carbonyle des liens esters de façon semblable au glissement, dû à la présence de solvants des bandes infra-rouge observées pour des matériaux de bas poids moléculaires. Les techniques à double faiseau sont indispensables pour enregistrer les glissements. L'intensité de la bande déplacée croît par gélification et la vitesse de cette augmentation dépend de la température de chauffage. L'intensité de la bande déplacée est directement proportionnelle à la concentration du polymère dissous dans le plastifiant et peut être utilisée pour mesurer cette concentration à n'importe quel moment au cours du processus de gélification. On estime que de 17 à 22% du polymère sont dissous au point de gel après chauffage à 65°C et qu'environ 29% des polymères étaient dissous à ce point de gel après chauffage à 75°C pour les plastifiants utilisés dans cette étude.

Zusammenfassung

Die Geschwindigkeit und das Ausmass der Auflösung von PVC in Esterweichmachern wurde infrarotspektroskopisch gemessen. Die Messung beruht auf Verschiebungen der Karbonylstreckfrequenz der Esterbindung, ähnlich den vertrauten, gewöhnlich an niedermolekularen Stoffen beobachteten Infrarotlösmittelverschiebungen. Zur Aufzeichnung der Verschiebungen waren Doppelstrahlverfahren erforderlich. Die Intensität der verschobenen Bande nimmt bis zur Gelbildung zu, die Geschwindigkeit der Zunahme hängt von der Erhitzungstemperatur ab. Die Intensität der verschobenen Bande ist der Konzentration des im Weichmacher gelösten Polymeren direkt proportional und kann zur Messung dieser Konzentration bei einem beliebigen Zeitpunkt während des Gelbildungsprozesses benützt werden. Es wird geschätzt, dass bei den in der vorliegenden Untersuchung verwendeten Plasticsolen 17-22% des Polymeren beim Gelpunkt nach einer Erhitzung auf 65°C gelöst war und dass etwa 29% des Polymeren beim Gelpunkt nach einer Erhitzung auf 75°C gelöst war.

Received July 15, 1965

Prod. No. 1258