Automated Microscopic Technique for Evaluating Poly(Vinyl Chloride)-Plasticizer Compatibility

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SYNOPSIS

An automated microtechnique has been developed that permits a rapid, reproducible determination of the Flory–Huggins χ interaction parameters for poly(vinyl chloride)-plasticizer systems. It is a modification of the Anagnostopoulos method of determining an apparent melting temperature of a poly(vinyl chloride) (PVC) particle in excess plasticizer. A microscope equipped with a photodiode sensor is used to measure changes in the light transmitted through a plasticizer sample containing a PVC particle as the temperature is increased at a fixed rate, either 0.2 or 1.0°C/min. Data acquisition is done by computer so that minimal operator assistance is required. The apparent melting region is characterized by a sigmoidal change in the light transmitted through a fixed sample area. This curve allows an accurate, reproducible definition of the apparent melting temperature from which the χ parameter is easily derived. The values obtained for the interaction parameter of PVC with four plasticizers chosen from the phthalate and phosphate families are in good agreement with general trends of solvent quality. Separate experiments demonstrated that the overall transmittance profile reflects changes in both the size and the optical clarity of the PVC particle during heating. This leads to added features in the profile that reflect important diffusion and swelling characteristics for a given system. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

A large portion of commercial poly(vinyl chloride) (PVC) consumption relies on the use of liquid plasticizers that, in the main, are added to lower its flow temperature during processing and to achieve greater flexibility in the end product.[1] Such flexible compounds exhibit a wide range of properties depending on the type and concentration of plasticizer. Although commercial plasticization of PVC has been practiced for over half a century, the fundamental aspects of the phenomenon are still incompletely understood. Consequently, the determination of PVC–plasticizer interactions is a problem of considerable academic as well as industrial importance.

In the past few decades, much effort has been devoted toward the development of methods for determining the type[2-11] and degree of these interactions.[12-14] Because it is simple and rapid and requires relatively low cost equipment, a method that has received considerable attention is the microtechnique of Anagnostopoulos et al.[15] It involves the determination of the temperature range, referred to as an apparent melting temperature, at which a single PVC particle in the presence of excess plasticizer undergoes a characteristic change, which has also been described as a transformation from the gel-to-sol state. Using Flory's statistical thermodynamic theory for the melting point depression in a polymer–diluent system, the apparent melting temperature can be related to the Flory–Huggins χ parameter. According to the Anagnostopoulos method, this temperature is determined visually by noting the point at which the particle changes from a "seemingly firm gel with distinct contours to a smooth-edged drop." Since it is based on visual observations, this procedure is highly subjective and only with some practice can the data be reproduced at best to

within $\pm 2°C$, depending on the width of the transition.

In this work we describe a modification to the Anagnostopoulos et al.[15] technique that involves the use of a microscope equipped with a photo sensor, thus eliminating the subjective, visual detection of the transition region. This allows a better determination of the melting region, yielding highly reproducible transition temperatures with minimal operator assistance. Furthermore, the method allows the observation of an additional transition, which is found to occur at a lower temperature than the apparent melting transition and is characteristic of the plasticizer.

EXPERIMENTAL

Chemicals

The PVC used in this study was an Esso 366 industrial resin for which the following characteristics were quoted: $\bar{M}_n$ = 46,000; $\bar{M}_w$ = 83,000; density = 1.39 g/cm^3, and [η] = 0.98 dL/g at 25°C in chlorobenzene. The plasticizers, di-2-ethyl hexyl phthalate (DOP), di-n-butyl phthalate (DBP), dimethyl phthalate (DMP), and tri-n-butyl phosphate (TBP) were purchased from Aldrich Co. and were used without further treatment.

Apparatus

The apparatus used in this study was a modified version of that described previously.[12,13] The viewing apparatus consisted of a Leitz HM-LUX binocular light microscope equipped with a polarizer/analyzer accessory that was used at 250× magnification. A DC-powered fiber optic light source was used for transmittance illumination. In addition, the optical microscope was equipped with a high-speed response silicon photodiode with a photosensitive effective surface area of 1.6 mm^2 and a spectral response range between 320 and 730 nm (peak wavelength at 560 $\pm$ 20 nm). The photodiode analog signal was conditioned using a noninverting operational amplifier circuit, converted to digital format via a Techmar A/D board, and the data were acquired with an AT computer using a Turbo Pascal program specifically written for this application. A Mettler FP52 hot stage with the FP5 temperature controller was used to heat the samples, at a constant heating rate, in the temperature range between 30 and 120°C. Temperature calibration was performed using thermometric standards.

Method

The method employed to study the interaction of PVC with plasticizers is a variation of the technique described by Anagnostopoulos et al.[15] and involves the determination of the temperature at which a PVC particle in excess plasticizer undergoes an apparent phase change. The particle was observed through the microscope, with the polars positioned at ca. 15° from cross polarization, while the temperature was raised from 30°C, at a constant heating rate of either 0.2 or 1°C/min, until an apparent phase change occurred. Within this temperature region, the photodiode detected the total light transmitted through a fixed viewing area that included a single PVC particle in excess plasticizer. An AT computer recorded all changes in total light transmitted, thus allowing a reproducible determination of the temperature range in which the phase change occurred. The observed change was always gradual, occurring over several degrees. In this method, it is important that no foreign particle, even another PVC particle, dust, or air bubble, intrude into the viewing area because this disrupts the photodiode signal rendering the experiment a failure.

Video Analysis System

To study the overall light transmittance profile, independent analyses of particle size and light intensity as a function of temperature were performed using a video analysis system that allows frame-by-frame analysis of a previously recorded video image. The PVC particle in excess plasticizer was viewed through a Nikon Optiphot polarizing microscope equipped with a Cohu video camera and the images were recorded on a Mitsubishi U80 VCR. The video image was displayed on a secondary monitor by means of a frame grabber board (PCVision Plus) located on an AT computer that translated the video signal to digital format by defining light intensity intervals on a 256 gray level scale through the use of a software program (Java, purchased from Jandel Scientific). The software allowed measurement of the area and the average light intensity within a selected region of a frozen image. Area calibration was performed using a prerecorded scale of known size while intensity measurements were performed in arbitrary units.

RESULTS AND DISCUSSION

General Considerations

A typical photodiode response curve of the light transmitted through a fixed viewing area that includes a PVC particle in DBP is presented in Figure 1. Superimposed on it are photomicrographs of a PVC particle that show the physical changes that occur as the temperature is raised from 30 to 95°C, at a heating rate of 1.0°C/min. A sharp increase in light transmission is observed in the region between 70 and 85°C. It is apparent from photographs D and

E that this change reflects an expansion, as well as an increase in the clarity, of the PVC particle. However, it still retains its distinct outline and contours.

The sigmoidal shape in the light transmission curve suggests the occurrence of a phase change that can be characterized by three temperatures: the onset (T_0), the midpoint (T_m), and the final (T_f) temperatures. Since this curve of transmitted light corresponds to a change in the volume of the PVC particle as the plasticizer is imbibed, this transition region represents a *better* basis for the approximation to the apparent melting temperature than the visual determination of the temperature at which
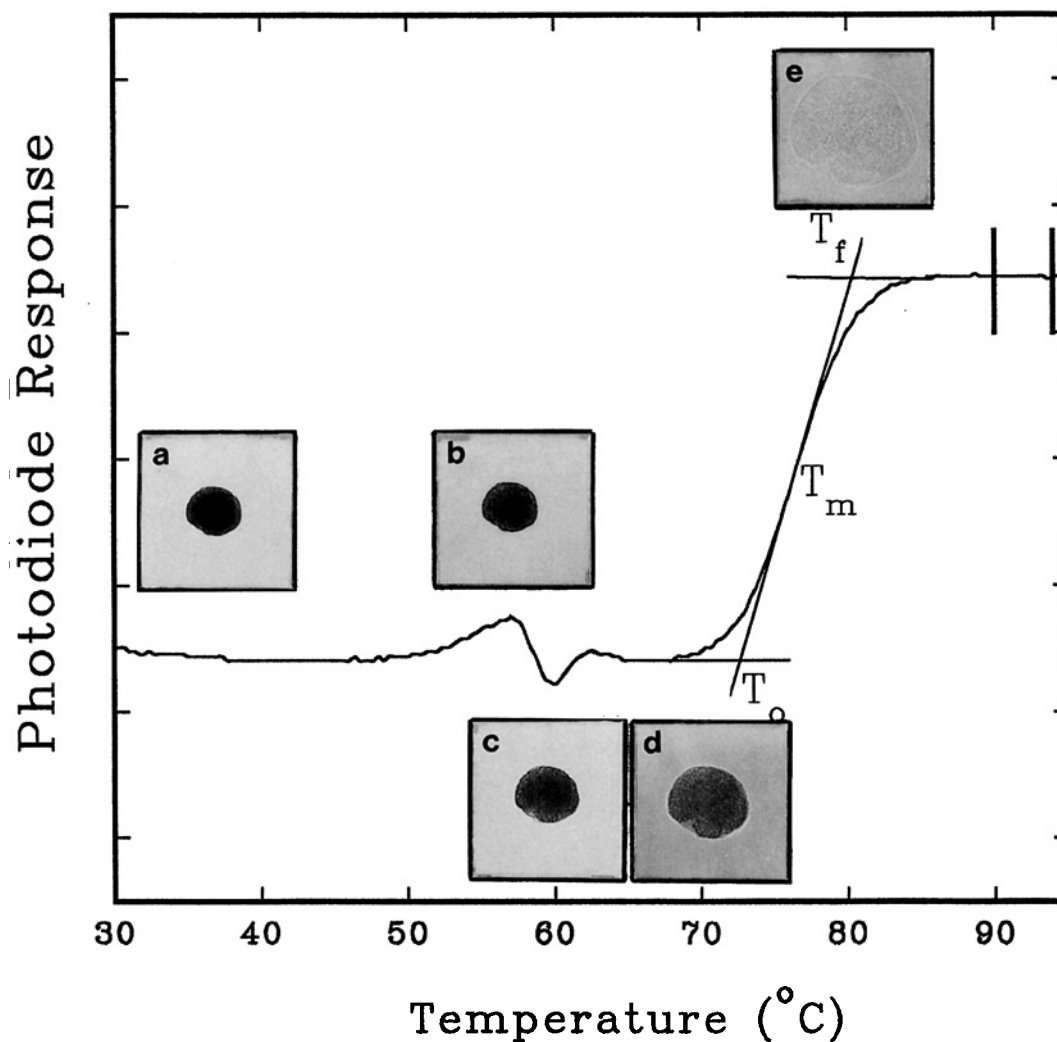

Figure 1 A typical photodiode light transmission curve for a single PVC particle in DBP recorded at a heating rate of 1°C/min. Superimposed are photomicrographs of the PVC particle at selected temperatures of (a) 35, (b) 57, (c) 60, (d) 70, and (e) 81°C. The apparent melting temperatures T_o (onset), T_m (midpoint), and T_f (final) are defined and the transition region reported by Anagnostopoulos et al.[15] for this system identified by two vertical lines between 90 and 94°C.

the surface contours disappear, as proposed by Anagnostopoulos et al.[15] Indeed, this transition region is well defined and reproducible for a given heating rate.

The derivation of a χ parameter from the plot requires that a transition temperature be defined. The final temperature, T_f, was chosen since it describes the point where the PVC particle has essentially swollen to a maximum detectable value. It may be noted that, in addition, the quantity $T_f - T_0$ can be used to describe the width of the transition, which should also be related to the solvent quality.

By the Anagnostopoulos visual method, this transition region could not be identified, and consequently the appropriate transition temperatures could not be defined. Instead, for practical reasons the apparent melting temperature was defined as the temperature at which "the distinct contours of the swollen particle became smooth" as manifested by the disappearance of the interface. As depicted by the photomicrographs in Figure 1, the interface between the PVC particle and DBP has essentially disappeared by 82°C, i.e., at a temperature slightly higher than T_f (ca. 1°C). It is of note that Anagnostopoulos et al. report that it occurs between 90 and 94°C, for a heating rate of 0.5°C/min.[16] Since photographs D and E depict changes in the appearance of the particle that are similar to those used by Anagnostopoulos et al. in defining the apparent phase change, it would appear that this discrepancy is not due to the different definitions of the transition temperature, but rather reflects other effects, e.g., differences in particle morphology.

In addition to the large change in light transmission at the high temperatures, a second feature is evident in the region between 50 and 65°C. Initially, the light transmitted through the PVC particle increases, as is evident from a comparison of photographs A and B. This is followed by an expansion of the particle in going from photographs B to C with a concomitant increase in particle clarity. These physical changes suggest the occurrence of partial swelling of the PVC particle in this temperature region as the plasticizer is imbibed and probably reflect an expected solid-to-gel transformation. A more detailed description of the changes in particle area and clarity during this phase change will be presented later.

Determination of Interaction Parameter

The calculation of the Flory–Huggins interaction parameter, χ, for the PVC–plasticizer systems is based on Flory's[17] theory of the melting point depression for a polymer–diluent system that was adapted to the microtechnique by Anagnostopoulos et al.[15] From Flory's theory,

$$\frac{1}{T_m} = \frac{1}{T_m^0} + \frac{RV_u(\phi_1 - \chi\phi_1^2)}{\Delta H_u V_1} \tag{1}$$

where T_m^0 is the melting temperature of the pure polymer, T_m is the melting temperature of the mixture, ΔH_u is the molar heat of fusion of a polymer repeat unit, V_u and V_1 are the molar volumes at T_m of the polymer repeat unit and diluent, respectively, and ϕ_1 is the volume fraction of the diluent. With the assumption that the volume fraction of polymer in excess plasticizer is negligible, i.e., $\phi_1 = 1$, and substitution of the values for ΔH_u, V_u, and T_m^0, 656 cal/mol, 44.6 cm^3, and 449 K, respectively, into Eq. (1) yields the following simplified form:

$$\frac{1}{T_m} = 0.002226 + \frac{0.1351(1 - \chi)}{V_1} \tag{2}$$

To calculate the Flory–Huggins interaction parameter, χ, from a single measurement of T_m, the molar volume of the plasticizer at that temperature must be known. This quantity can be calculated using the following relation:

$$V_1 = \frac{M}{\rho_{25°C}}[1 + \alpha(T_m - 25)] \tag{3}$$
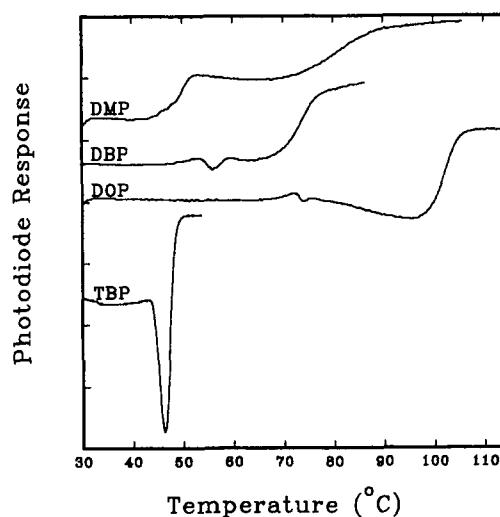

Figure 2 Typical photodiode light transmission curves for a single PVC particle in different plasticizers recorded at a heating rate of 0.2°C/min.

Table I Apparent Melting Temperatures and χ Values for Various PVC–Plasticizer Systems at Different Heating Rates

Plasticizer	V_1 (cm^3)	T_f (°C)	χ	$T_f - T_0$
	Heating Rate of 0.2°/min			
DMP	171.7	91	0.34	18
DMP	277	77	−0.30	7.0
DOP	422.5	105	−0.31	5.7
TBP	278.9	48	−0.83	2.0
	Heating Rate of 1°/min			
DMP	171.8	92	0.35	16.4
DBP	277.9	81	−0.23	6.7
DOP	423.7	109	−0.23	5.5
TBP	280.9	57	−0.67	1.8

where α is the coefficient of thermal expansion, M is the molecular weight, and ρ is the density, at 25°C, for the plasticizer.

As seen in Figure 2, in the region of the apparent melting temperature all of the plasticizers considered in this study showed a similar pattern of transmitted light as a function of temperature thus allowing a precise determination of the three transition temperatures. Multiple experiments revealed no appreciable differences in the transition temperatures and width of the transitions. For example, in the PVC–DBP system, T_f values ranging between 76.0 and 77.5°C were obtained that correspond to a standard deviation of 0.8 (1.0%). For all of the plasticizers studied, these temperatures, for a given heating rate, are reproducible to within ±1%. Using the final temperature, T_f, as the apparent melting temperature, in conjunction with the molar volumes deter-

mined from Eq. (3), the χ parameters for various PVC–plasticizer systems were calculated using Eq. (2) and are summarized in Table I. Comparison of the values obtained at heating rates of 0.2 and 1°C/min, shows that the faster heating rate causes the end point to shift to a higher temperature by an amount that is dependent on the temperature of the phase transition. In keeping with the observations of Anagnostopoulos, the transitions occurring at higher temperatures, i.e., transition temperatures greater than about 80°C seem to be less sensitive to the sample heating rate. The width of the transitions, as described by the difference between the final and onset temperatures, are also given in Table I. As expected, a decrease in the χ parameter is accompanied by a decrease in the width of the apparent melting transition for all plasticizers. For example, DMP, which has the highest χ parameter (0.34), also shows the largest width in the apparent melting transition (18°C), indicating that it is a poorer solvent than TBP, which has the lowest value for these parameters, exhibiting the highest solvating power.

The χ values obtained by other workers from melting point depression[12,13,15,18,19] or swelling[14] studies for the various plasticizers investigated in the present work, where available, are listed for comparison in Table II. With the exception of those reported by Tomaselli et al.,[12,13] the interaction parameters derived by the present method are consistently lower than those obtained by other workers. The higher χ values reported by Anagnostopoulos et al. are a direct reflection of a higher transition temperature. As discussed previously for the PVC–DBP system, since similar morphological changes were observed visually as the temperature was raised, it is unlikely that the discrepancies are due to differences in the method. A dependence of the transition temperature on other factors, such as particle morphology, molecular weight, and purity

Table II Literature Values for the Flory–Huggins Interaction Parameters χ for Various PVC–Plasticizer Systems

Plasticizer	χ				
	Anagnostopoulos et al.[15]	Tomaselli et al.[12,13]	Jasse[19]	Bigg[18]	Doty and Zable[14]
DMP	0.52	—	0.55	—	0.56
DBP	−0.05	−0.22	−0.11	0.05	−0.04
DOP	−0.03	−0.24	—	0.04	0.01
TBP	−0.53	−0.44	−0.55	—	−0.65

as well as plasticizer purity, may be responsible. Indeed, for DBP and DOP the derived χ values are identical with those reported by Tomaselli et al.[12,13] who used the same polymer resin (Esso 366) heated at a rate of 1°C/min. There remains an apparent contradiction in the case of the PVC–TBP system for which the χ value reported by Tomaselli et al. is higher than that determined in the present study. Various attempts to reproduce their transition temperature of 71°C, visually and by the present method, using TBP samples from different sources, were unsuccessful. Transition temperatures between 56 and 59°C were obtained consistently.

When trends, rather than the absolute values, of χ are considered, the results are in very good agreement concerning the solvent quality for PVC. For example, for the di-alkyl phthalate series (Table I), the χ parameter decreases as the molecular weight is increased, indicating an improved polymer–plasticizer compatibility. This is in keeping with the work of Doty and Zable[14] who, in a study of the variation of χ with plasticizer molecular weight, noted a decrease in χ parameter with increase in molecular weight up to dihexylphthalate, whereafter an increase was observed. Further work by Sears and Darby[20] indicated a much broader minimum in the χ value ranging from DBP to DOP, which is more consistent with the present study.

Analysis of the Photodiode Curve

As seen in Figure 2, in addition to the apparent melting transition (gel-to-sol), a second, smaller change in transmitted light is clearly evident at lower temperatures for all plasticizers. The photodiode signal indicates a sequential increase and decrease in transmitted light. These low temperature transitions, which probably reflect an expected solid-to-gel transition, are reproducible and also occur at temperatures characteristic of the plasticizer. To assess the nature of both of the observed transitions more completely, independent analyses of particle size and light intensity as a function of temperature were performed for all PVC–plasticizer systems, using the video analysis system.

When PVC in DBP is heated at a rate of 0.2°C/min, there is no change in size or optical clarity of the PVC particle in the temperature range from 30 to 47°C, as shown in Figure 3(a). However, further heating to about 55°C causes an increase in particle clarity, reported as a light intensity, with no appreciable change in its size. This corresponds with the visual observation that the particle loses its dark
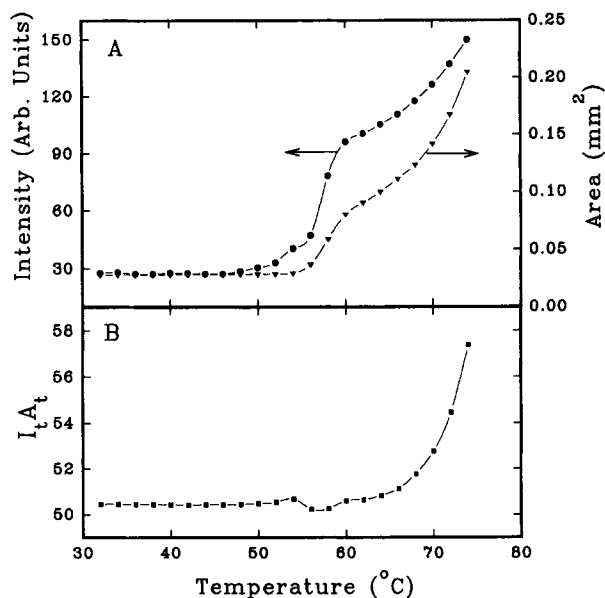

Figure 3 (a) Independent analysis of particle optical clarity (circle) and size (triangle) as a function of temperature for PVC in DBP at a heating rate of 0.2°C/min. (b) Reproduction of the photodiode transmitted light profile from the recombination of particle size and clarity as described by Eq. (4).

appearance and becomes more translucent as it imbibes the diluent. At 55°C, the particle begins to swell, in a two-step fashion, with a concomitant increase in optical clarity. Thus, the signal changes registered by the photodiode as the temperature is raised reflect variations in particle size and clarity.

Assuming these two effects are the only factors that control the changes in the photodiode output, the following approach was taken to reproduce the transmitted light profile. The changes to the particle noted in Figure 3(a) were recombined taking into account the intensity of light transmitted through the surrounding plasticizer, I_b, and the total viewing area, A_t, using the following relation:

$$I_t A_t = I_p A_p + I_b (A_t - A_p) \qquad (4)$$

where $I_t A_t$ is the total light transmitted as registered by the photodiode and I_p and A_p are the average intensity of the light transmitted through the particle and area of the particle, respectively. The total transmitted light as calculated by this recombination method, shown in Figure 3(b), is in excellent agreement with the photodiode light response curve shown in Figure 2. Therefore, the physical changes that occur prior to the apparent melting transition
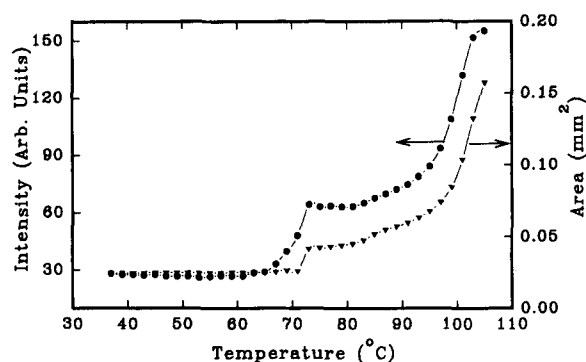
Figure 4 Independent analysis of particle optical clarity (circle) and size (triangle) as a function of temperature for PVC in DOP at a heating rate of 0.2°C/min.

involve a swelling of the PVC particle as a result of the penetration of the plasticizer. This transition at lower temperatures corresponds well with an expected solid-to-gel transformation. Beyond this point, a region of moderate stability, i.e., minimal changes in particle size and clarity, is observed, whereafter sudden increases in these quantities reflect the gel-to-sol transition.

Similar results were obtained with respect to particle clarity and size as function of temperature for a PVC particle in DOP (Fig. 4) and DMP (Fig. 5). Prior to particle swelling, which is inherent to the solid-to-gel transformation, both systems show an increase in the amount of light transmitted through the particle, as with PVC in DBP. However, the region of moderate stability in optical clarity and size between the solid-to-gel and gel-to-sol transitions is prolonged relative to that for PVC in DBP and results in a larger separation between the two transitions, as is apparent in Figure 2. Although not
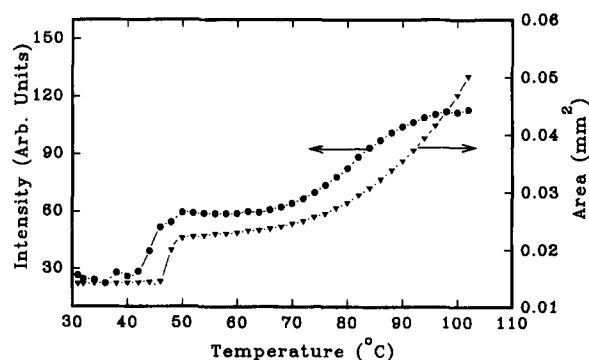
shown, recombination of these two effects using the method described by Eq. (4) yielded a curve identical to that obtained experimentally; indeed, this is true for all of the plasticizers studied.

For PVC in TBP a somewhat different behavior was observed; with heating the boundaries of the particle became more translucent, while the center remained dark. There was an immediate swelling of the boundary region, with loss of its distinguishable form, similar to that seen in the gel-to-sol transition, that continued in an inward fashion. It appears that plasticizer diffusion into the PVC particle is accompanied by a concurrent solvation. Hence the solid-to-gel and gel-to-sol transitions occur simultaneously. Independent analyses of the changes in clarity and size that accompany these physical changes, shown in Figure 6, are consistent with the above-mentioned observations. Indeed, the increase in particle size predominates over the change in the average light intensity resulting in a decrease in the photodiode signal, as seen in Figure 2. These changes occur almost simultaneously with the gel-to-sol transition as evidenced from the sudden increase in the signal from the photodiode.

It has been demonstrated that, for all of the PVC–plasticizer systems studied, the changes in the photodiode signal can be attributed to morphological changes occurring to the PVC particle, i.e., size and optical clarity. An increase in the optical clarity of the PVC particle without a change in area results in an increased photodiode output while a decreased signal results when the optical clarity of the particle remains constant while the area increases. Simultaneous changes in particle clarity and size will result in a photodiode response that is dependent on the relative magnitude of the two changes. If the change
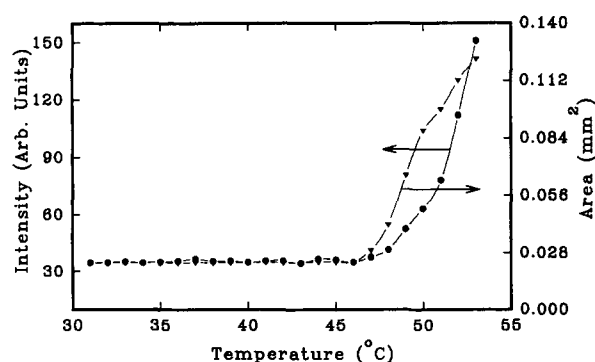

Figure 5 Independent analysis of particle optical clarity (circle) and size (triangle) as a function of temperature for PVC in DMP at a heating rate of 0.2°C/min.

Figure 6 Independent analysis of particle optical clarity (circle) and size (triangle) as a function of temperature for PVC in TBP at a heating rate of 0.2°C/min.

in clarity of the particle is larger than the change in particle size, the photodiode signal will increase while the reverse will result in a decreased signal.

The various regions of the photodiode response curve are in keeping with most of the steps described by Sears and Darby[21] for the plasticization of PVC. The initial increase in light intensity without change in particle volume is consistent with solvation and/or penetration of the particle surface. This change is followed by partial swelling of the particle, which reflects absorption and diffusion of the plasticizer into the particle. Disassociation and freeing of polar groups, i.e., dissolution in the amorphous region, is reflected by the region of partial stability that lies between the two transitions observed by the photodiode. Structure breakdown with dissolution of some of the crystalline regions is observed as the final increase in light intensity and described here as the final gel-to-sol transition. Therefore, this technique not only allows the evaluation of the PVC–plasticizer interaction parameter but also allows the investigation of the effects of plasticizer type on any of the observable steps in the overall plasticization process.

CONCLUSIONS

An automated microscopic technique has been developed for the evaluation of PVC–plasticizer compatibility. It involves measurement of the temperature at which a PVC particle in excess plasticizer undergoes a gel-to-sol transition. This temperature is used to determine the Flory–Huggins interaction parameter, χ. It is demonstrated that the technique is simple and reproducible with minimal operator assistance. Although the interaction parameters obtained from this method are lower than those found in the literature, the general trends in solvent quality are in agreement. A direct relation is also found to exist between the interaction parameter and the width of the transition, i.e., as the χ value increases, the width of the transition also increases.

This method also allows the observation of a second transition that occurs at a lower temperature, which is attributed to an expected solid-to-gel transition or initial steps in the plasticization process, i.e., solvation and/or penetration of the particle surface, absorption, and diffusion of the plasticizer into the particle, and dissolution into the amorphous regions. As with the gel-to-sol transition, the phase change that occurs at lower temperatures also occurs at a temperature characteristic of the plasticizer. This suggests that as more plasticizers are examined, this technique may be used as a means of studying the effects of plasticizer type on the overall plasticization process.

The changes in light intensity as observed by the photodiode were reproduced by taking into account independent measurements of particle size and optical clarity. By this means, it is possible to correlate the behavior of the particle in terms of the physical changes as it undergoes various transitions until the final apparent melting transition. For the gel-to-sol transition, similar changes in particle size and light intensity were observed for all plasticizers, i.e., as the particle size increased, the light intensity increased. For the solid-to-gel transition, in the dialkyl phthalates, the PVC particle light intensity increases prior to swelling and the formation of a gel state whereas in the case of TBP swelling occurs prior and at a faster rate than changes in optical clarity.

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