The *in situ* polymerization of vinyl chloride in poly(butyl acrylate)

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The *in situ* polymerization of vinyl chloride with poly(butyl acrylate) has been studied. Vinyl chloride was polymerized using a peroxydicarbonate initiator in sealed ampoules in the presence of various weights of poly(butyl acrylate). The products were examined by dynamic mechanical analysis and electron microscopy. It was found that if about 50% or less vinyl chloride was present in the mixture homogeneous blends were formed. If more than 50% vinyl chloride was present the polymerization passed through a two phase region in the three component phase diagram and inhomogeneous blends were formed. If homogeneous blends prepared as above were reswollen with vinyl chloride and the latter polymerized, then homogeneous blends containing more poly(vinyl chloride) could be prepared, avoiding the two phase region. The interaction parameters between vinyl chloride and both poly(vinyl chloride) and poly(butyl acrylate) were estimated using inverse gas chromatography. Using these and an estimate of the polymer/polymer interaction parameter the three component phase diagram could be qualitatively explained.

Keywords Polymerization; *in situ*; miscibility; compatability; poly(vinyl chloride); poly(butyl acrylate); phase diagram

INTRODUCTION

The miscibility of polymers has received much attention over the last ten or twenty years. A recent book by Olabisi, Robeson and Shaw[1] gives a good background to the subject and lists some of the achievements to date.

Poly(vinyl chloride), (PVC), has been found to be compatible with a wide range of polymers and this has been attributed to its ability to form specific interactions, possibly hydrogen bonds, with polymers containing suitable groups of atoms. One example of this is the mixture with polycaprolactone where a shift in the infra-red carbonyl adsorption has been observed[2]. An interaction has also been shown to exist between a series of haloalkanes and electron donors such as ketones, ethers, esters, tertiary amines and tertiary amides[3].

In a recent paper[4] we showed PVC to be compatible with a wide range of acrylates and methacrylates with ester side chains up to 4 and 6 carbon atoms in length respectively. We explained this by measurements of interaction parameters which were more favourable for the shorter side chains[5]. In the particular case of poly(butyl acrylate), this polymer was found to be compatible with PVC but 50/50 blends phase separated when heated to temperatures above 120°C.

Many compatible polymers have been thought to be immiscible because of the difficulties encountered in mixing. There are three main methods of mixing polymers, mechanical mixing, casting from a common solvent, and *in situ* polymerization (the polymerization of one monomer in the presence of the other polymer). Mechanical mixing cannot always be achieved because of the thermal stability of polymers over the temperatures and times required for mixing. Other polymers, though

compatible at room temperature may be incompatible at the higher temperatures required for mixing. Casting from a common solvent cannot always be achieved because the presence of some solvents causes immiscibility between polymers. For example, in the compatible system polystyrene poly(vinyl methyl ether), when blends are cast from some chlorinated solvents two phase structures are formed[6]. In blends of PVC with polyacrylates, one phase systems were formed when the polymers were cast from butanone, but two phases were produced from THF[4]. *In situ* polymerization can sometimes overcome these problems, but not necessarily in every case. The monomer, during polymerization, acts as a solvent for the polymers and can cause phase separation. When vinyl chloride is polymerized in the presence of chlorinated polyethylene, one phase or two phase products can result depending on the ratio of the starting materials[7]. *In situ* polymerization has been considered a feasible industrial method for producing polymer blends and there are innumerable patents in the literature.

In our previous paper on PVC polyacrylate mixtures, we prepared some blends by *in situ* polymerization of vinyl chloride in the polyacrylates, including poly(butyl acrylate). The products were optically clear and showed a single glass transition but had crosslinked during the polymerization.

In this paper we show that blends of uncrosslinked polymers can be formed by *in situ* polymerization and that the product depends on the ratio of the starting materials, two phase structures sometimes being formed. We have determined the vinyl chloride/PVC/poly(butyl acrylate) three component phase diagram and explained this, and the nature of the products formed during the polymerization in terms of the measured interaction parameters.

Table 1 $\bar{M}_n$ and $\bar{M}_w$ values for PVC, PBA and 50/50 Blend

	PVC	PBA	50/50 Blend
$\bar{M}_n$	31 300	33 000	16 000
$\bar{M}_w$	97 000	119 000	91 051

EXPERIMENTAL

Materials

Poly(butyl acrylate): was supplied as a 20% w/v solution in toluene (Polysciences). Most of the toluene was removed on a rotary evaporator. The remainder was removed on a vacuum line until constant weight was achieved (2 weeks at 10^{-3} mm Hg).

Vinyl Chloride: was obtained in gas cylinders (Cambrian Gas) and was used as supplied.

t-Butyl Cyclohexyl Peroxydicarbonate: (Perkadox 16N, Laporte) was recrystallized from methanol and stored at below 0°C until required.

Preparations

Samples of blends were prepared by *in situ* polymerizations of vinyl chloride with poly(butyl acrylate) using t-butyl cyclohexyl peroxydicarbonate as an initiator, at 0.1% based on vinyl chloride, in sealed ampoules.

The initiator was introduced as a solution in methanol (A.R.) and the solvent removed by evaporation on a vacuum line. Poly(butyl acrylate) was then introduced into the ampoules. The vinyl chloride was then distilled into the ampoules on a vacuum line (in a fume cupboard, N.B. carcinogen). The vacuum line had been previously calibrated by introducing a known weight of dichloromethane and measuring the pressure it achieved using a manometer connected to the vacuum line. We thus knew the volume of the line. Vinyl chloride gas was admitted into the vacuum line from the cylinder until the pressure, read on the manometer, showed that the required weight of monomer was in the line. The cylinder was then isolated from the line and the monomer condensed into the ampoule using liquid nitrogen. The ampoule was then sealed off. The ampoules were then heated for 10 hours in a water bath at 40 C while the ampoules were in a metal gauze container in case of explosion. The product was then removed from the ampoule, and, after allowing residual monomer to evaporate the sample was weighed in order to find the extent conversion. Samples for dynamic mechanical analysis were sectioned from the product using a hand microtome.

In some cases the polymerization was stopped when the contents were observed to go cloudy. The product was then removed and weighed to find the percentage of monomer polymerized. In other cases a sample of a polymer blend previously prepared was used instead of poly(butyl acrylate). Vinyl chloride was then added until free vinyl chloride was present in the ampoule. In this way a rough estimate of the degree of swelling of the blend was obtained. The mixture was then polymerized, and treated and analysed in the usual way.

Characterization

Dynamic mechanical measurements were used to confirm the phase structure of the blends. These were performed using a Rheovibron (Model DDV-II, Toyo Measuring Instrument Co. Ltd.). A strip of the sample was subjected to an imposed oscillatory frequency of 11 Hz. A temperature range of $-180°$C to $120°$C was scanned at $1°$C/min heating rate and a plot of $\tan \delta$ against temperature obtained. A maximum in $\tan \delta$ was taken as a measure of T_g. A single peak suggests a homogeneous blend whereas two separate peaks suggest a two phase structure.

Inverse gas chromatography was used to determine the values of the interaction parameters of the polymers with vinyl chloride. This was carried out using a Pye 104 gas chromatograph equipped with a thermal conductivity detector. The chromatograph was fitted with a 1.5 metre coiled pyrex column which was packed with PTFE 30–60 mesh (Phase Separation) on which the polymer was spread as a thin film The polymers were weighed and dissolved in butanone (A.R.) at 5% w/w. The PTFE beads were added and the solvent evaporated with stirring to produce a powder which was dried in a vacuum oven for 24 hours. The coating weights used were 0.08 g per gram of support.

The columns were installed and heated to 120°C. Nitrogen was then passed through the column for 6 hours in order that the column should come to equilibrium. Helium was finally used as the carrier gas.

A flask, fitted with a serum cap, was filled to atmospheric pressure with vinyl chloride on a vacuum line. From this flask 10 μl samples of vinyl chloride gas were taken with a syringe and injected into the columns. Retention times (t_s) were measured three times each at each of three carrier gas flow rates (25 cm^3/min max). The 'non-interaction' peak elution time (t_A) was obtained by injecting a sample of air.

Electron micrographs were obtained using a J.E.M. 100B transmission electron microscope. Specimens about 900 Å thick were cut using an ultramicrotome (L.K.B.) equipped with a liquid-nitrogen-cooled cold chamber.

Gel permeation chromatography was carried out using a Waters machine with THF as a solvent and molecular weights were determined relative to polystyrene standards (see *Table 1*). Molecular weights for poly(butyl acrylate) and for PVC (as prepared under the conditions of our polymerization) were determined. A sample of the blend was also examined, and although the machine response is not identical for the two polymers $(dn/dc = 0.065$ and 0.11 respectively) this gives an indication of the molecular weight produced in the blend. The PVC might be expected to be of a lower molecular weight due to the effect of dilution.

RESULTS AND DISCUSSION

The three component phase diagram for the system PVC/poly(butyl acrylate) vinyl chloride is shown in *Figure 1*. A polymerization from A to B produces an optically clear product whereas a polymerization from E very soon becomes cloudy. If the polymerization is stopped at this point and the product analysed the point F can be determined. If polymerization is continued to H a cloudy product is formed. As the composition passes point G leaving the postulated two phase region the sample does not become clear presumably due to the size of the phase separated regions and the low diffusion rate. If a blend of composition B is reswollen with vinyl chloride, then there comes a point where free vinyl chloride is visible in the tube. By gauging this point an
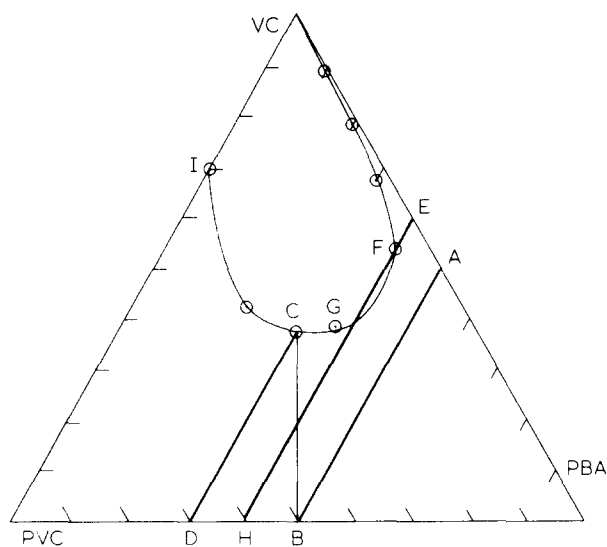
Figure 1 Experimental three component phase diagram for Vinyl Chloride/Poly(butyl acrylate)/Poly(vinyl chloride). The lines within the diagram represent polymerization pathways

estimate of point C can be made. Point I can be estimated from literature values of the degree of swelling of vinyl chloride in PVC though this may not be very reliable due to uncertainty as to how much vinyl chloride is in the PVC and how much is just held within the PVC particle pore structure. This point can also presumably depend on the degree of crystallinity of the PVC. If reswollen material with composition C is polymerized to D a clear product is formed. Thus a one phase or two phase blend of the two polymers at one overall composition can be prepared depending on the polymerization route.

The products obtained by polymerization in this way were examined by dynamic mechanical analysis. The results are shown in *Figure 2*. This shows that the polymerization which avoids the two phase region does indeed produce a homogeneous blend with a single glass transition. The polymerization which goes through the two phase region produces a blend consisting of two phases: one phase has a T_g close to that of pure PVC and the other of a mixture of the two polymers. This gives an indication of the direction of the phase separation tie lines.

Various homogeneous blends were prepared by a one step or two step process as appropriate with different ratios of the two polymers. The values of the glass transition temperature of these blends are shown in *Table 2*. These have been compared with a theoretical value from the Fox equation[8]

$$\frac{1}{T_g} = \frac{m_1}{T_{g_1}} + \frac{m_2}{T_{g_2}}$$

where m_i is the weight fraction of component i with glass transition temperature T_{g_i}. It is apparent that there are large positive deviations from the Fox equation. This has often been associated with strong interactions between polymers[9].

In order to explain the origin of the phase diagram we need estimates of the three interaction parameters χ_{12} (PVC/vinyl chloride), χ_{13}(poly(butyl acrylate)/vinyl chloride), and χ_{23}(poly(butyl acrylate)/PVC). The first two of these were estimated by inverse gas chromatography.

This is not considered to be a reliable quantitative method for reasons discussed elsewhere[10] but it will give a guide to reasonable values of the interaction parameters also bearing in mind how χ may vary between the temperature of measurement and that of polymerization. The detailed aspects of this technique have been reviewed by **Braun** and Guillet[11].

From the measurements we can determine the net retention volume (V_N)

$$V_N = (t_s - t_i)Qj$$

where t_s = sample peak elution time, t_i = non interaction peak elution time, Q = carrier gas flow rate, and j = correction for gas compressibility given by

$$\frac{3}{2} \times \frac{[(P_i/P_0)^2 - 1]}{[(P_i/P_0)^3 - 1]}$$

where P_i is the inlet pressure and P_0 is the outlet pressure.

The peak retention volumes are extrapolated to zero flow rate. At this value

$$V_g = \frac{V_N}{W_L} \times \frac{273.2}{T_E}$$

where V_g is the retention volume per gram of stationary phase corrected to O C at zero flow rate, W_L is the weight of stationary phase and T_E the experimental temperature (K). The interaction parameter χ is given by
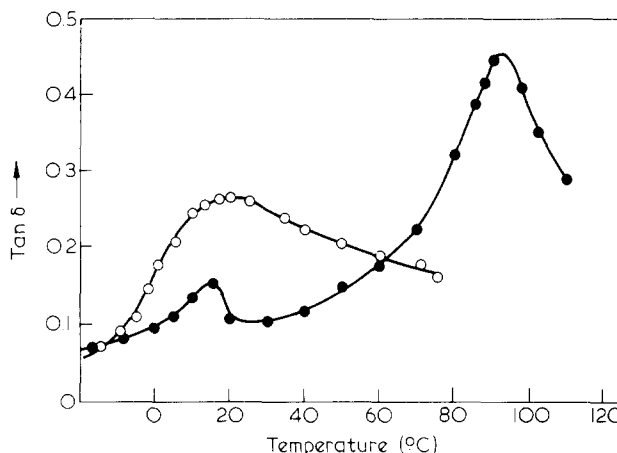

Figure 2 Dynamic mechanical analysis: Plots of tan δ against temperature for a 34 : 66 PBA : PVC blend prepared by a one step polymerization process (●), and a 60 : 40 PBA : PVC blend prepared by a one step polymerization (○)

Table 2 Values of T_g for various blends compared with theoretical values from the Fox equation

Composition of blend PBA : PVC	T_g (°C) (Experimental)	T_g (°C) (Theoretical)
PVC	103	
25 : 75	95	62.6
40 : 60	85	40.5
50 : 50	63	27.3
60 : 40	20	14.35
70 : 30	17	3.73
PBA	−25	

Table 3 Results of inverse gas chromatography

	V_g^0 (cm^3 g^{-1} K^{-1})	χ
PBA/Vinyl chloride	3.34	0.165
PVC/Vinyl chloride	0.695	1.52

$$\chi = \ln\left[\frac{273.2\,R\,v_2}{V_g^\circ\,P_1^\circ\,V_1}\right] - \left[1 - \frac{V_1}{(\bar{M}_2)_n v_2}\right] - \frac{P_1^\circ}{RT}(B_{11} - V_1)$$

where v_2 = specific volume of polymer; V_1 = molar volume of solvent; $(\bar{M}_2)_n$ = number average molecular weight of polymer; P_1° = saturated vapour pressure of solvent; B_{11} = second virial coefficient.

V_1 was estimated for vinyl chloride using the method of Haukinson and Thomson[12] to be 90 cm^3 mol^{-1} under the conditions of the experiment (120°C). This may not be very exact but the value chosen only has a very small effect on the calculated value of χ.

B_{11} was estimated to be -282[13], and P_1° was taken as 29.25 atm[14].

For PVC v_2 was taken as 0.722[15] and $\bar{M}_n$ was measured as 122 000 by g.p.c. relative to polystyrene standards.

For PBA v_2 was taken as 0.893[15] (based on group contributions) and $\bar{M}_n$ was measured as above to 33 000.

The measured values of V_g° and the calculated χ values are shown in *Table 3*.

These values of χ are determined at 120°C whereas polymerization was carried out at 40°C. Unfortunately inverse gas chromatography works best well above the glass transition temperatures of the polymers. We can however use these calculated values as guides to the expected values at the polymerization temperature.

χ_{23} (PVC/PBA) has been calculated before at 120°C as 0.96.[5] This value has not however been normalized for one segment of polymer and would need to be divided by the ratio of molar volumes for polymer and solvent. We therefore predict a small positive value which is consistent with the fact that phase separation occurs around this temperature[4]. At the temperature of polymerization, where the polymers are compatible, we might expect a small negative value for χ_{23} and a reasonable estimate would be -0.1.

Calculating binodals from interaction parameters is very difficult and usually needs solving numerically[16]. However in this case it is much simpler. The critical point is given by[17]

$$\sum \frac{m_i^2 \varphi_i}{(1 - 2\chi_i m_i \varphi_i)^3} = 0 \quad, \quad \sum \frac{m_i \varphi_i}{1 - 2\chi_i m_i \varphi_i} = 0$$

where m_i is the number of segments of species i with volume fraction φ_i and $2\chi_1 = \chi_{12} + \chi_{13} - \chi_{23}$ and χ_2, χ_3 similarly.

As the molecular weights of the two polymers tend to infinity one can see that solutions to this equation can only be found if φ_2 and φ_3 tend to zero. This means that φ_1 tends to 1 and the critical point must be located close to the apex of the three component phase diagram. This means that the tie lines for phase separation must radiate from the apex to be consistent with a tie along the PVC/vinyl chloride axis as shown in *Figure 3*. This is consistent with our observation that phase separation results in one phase which consists of approximately pure

PVC. Because phase separation gives pure vinyl chloride as one component the binodal is approximated to a line joining points where the chemical potential is equal to that of the pure solvent (vinyl chloride) thus since[17]

$$\frac{\Delta\mu_1}{RT} = \ln\varphi_1 + 1 - m_1\sum\frac{\varphi_i}{m_i} + m_1\sum\chi_i\varphi_i - m_1\sum\chi_{ij}\varphi_i\varphi_j$$

$$= \ln\varphi_1 + \left(1 - \frac{m_1}{m_2}\right)\varphi_2 + \left(1 - \frac{m_1}{m_3}\right)\varphi_3$$

$$+ m_1[\chi_1(\varphi_2 + \varphi_3)^2 + \chi_2\varphi_2^2 + \chi_3\varphi_3^2]$$

putting $m_1 = 1$ and letting m_2 and m_3 tend to infinity, simplifying, eliminating φ_3 (since $\varphi_1 + \varphi_2 + \varphi_3 = 1$), and collecting terms we obtain

$$\ln\varphi_1 + 1 + \chi_{13} - (1 + 2\chi_{13})\varphi_1 + \chi_{13}\varphi_1^2$$

$$- 2\chi_3(1 - \varphi_1)\varphi_2 + \chi_{23}\varphi_2^2 = 0$$

This gives a quadratic for φ_2 for any chosen value of φ_1 and the phase boundary can be easily calculated.

The resulting phase diagram for our first chosen values of $\chi_{12} = 1.52$, $\chi_{13} = 0.165$, $\chi_{23} = -0.1$ is shown in *Figure 3*. This is not a very good match to the experimental phase boundary but contains all the main features. A better fit can be obtained by choosing different values. The phase boundary for the case where $\chi_{12} = 0.7$, $\chi_{13} = 0.5$ and $\chi_{23} = -1$ is also shown.

We sould not however expect an accurate match to the phase diagram as our calculations are based on a Flory–Huggins approximation whereas in our system we expect large free volume changes and specific interactions between the components.

The phenomena of phase separation on heating was further investigated. We previously reported phase separation at around 120°C using a 50/50 blend prepared by solvent casting. We have now determined the phase boundary using blends of various compositions prepared by *in situ* polymerization.
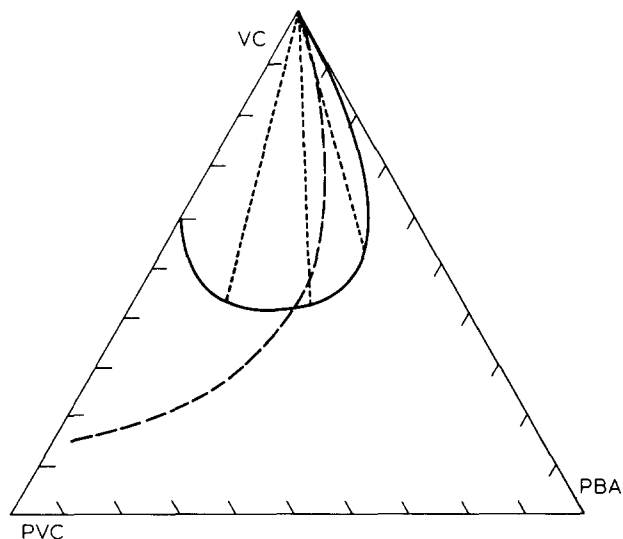

Figure 3 Theoretical phase diagram for vinyl chloride (1)/poly (vinyl chloride) (2)/poly(butyl acrylate) (3) for values of: $\chi_{12} = 1.52$, $\chi_{13} = 0.165$, $\chi_{23} = -0.1$ (broken line), and $\chi_{12} = 0.7$, $\chi_{13} = 0.5$, $\chi_{23} = -1$ (solid line). The broken lines represent the tie lines
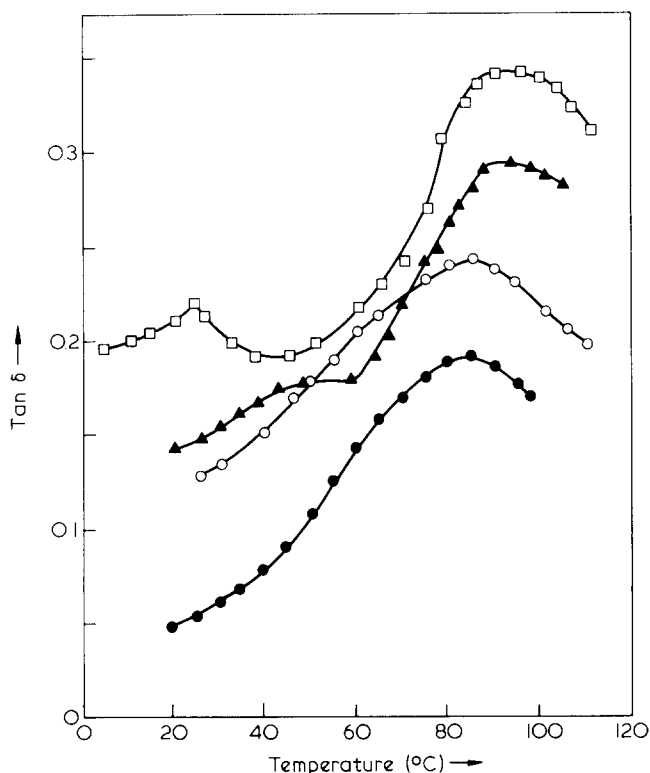
Figure 4 Plots of tan δ against temperature for a 40/60 blend of PBA/PVC (homogeneous, prepared by a two step process) heated to various temperatures; ● = room temperature, ○ = 125°C (tan δ + 0.05), ▲ = 135°C (tan δ + 0.1), □ = 140°C (tan δ + 0.15)
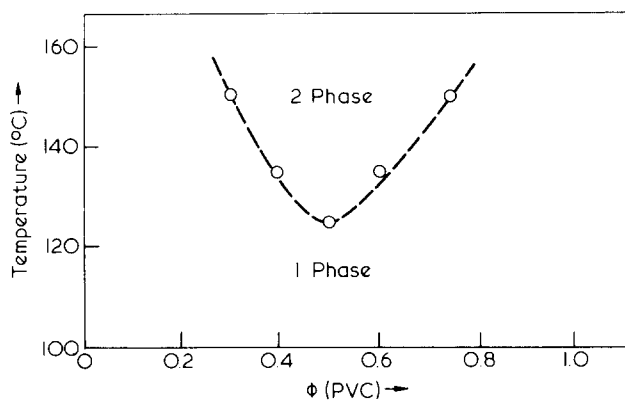

Figure 5 Cloud point diagram for PBA/PVC blends. The points represent the first temperatures at which phase separation was evident

Figure 6 Electron micrographs of: (a) a 40% PBA, 60% PVC blend produced by a one-step polymerization process; (b) a 40% PBA, 60% PVC blend produced by a two-step polymerization process; (c) a sample of (B) which has been heated to 160°C for 20 minutes

Samples were heated for 15 minutes in an oven at ten degree intervals between 110° and 180°C. They were then quenched in liquid nitrogen and examined by dynamic mechanical analysis. The appearance of a second glass transition indicated the phase separation temperature. An example of the plots obtained is shown in *Figure 4* and the phase diagram obtained is shown in *Figure 5*.

The main conclusions of our investigation were further corroborated by electron microscopy. *Figure 6* shows three micrographs of 40% PBA 60% PVC blends. The first was produced by a one step *in situ* polymerization of vinyl chloride in PBA and shows a clear two phase structure. The second was produced by a two step polymerization process as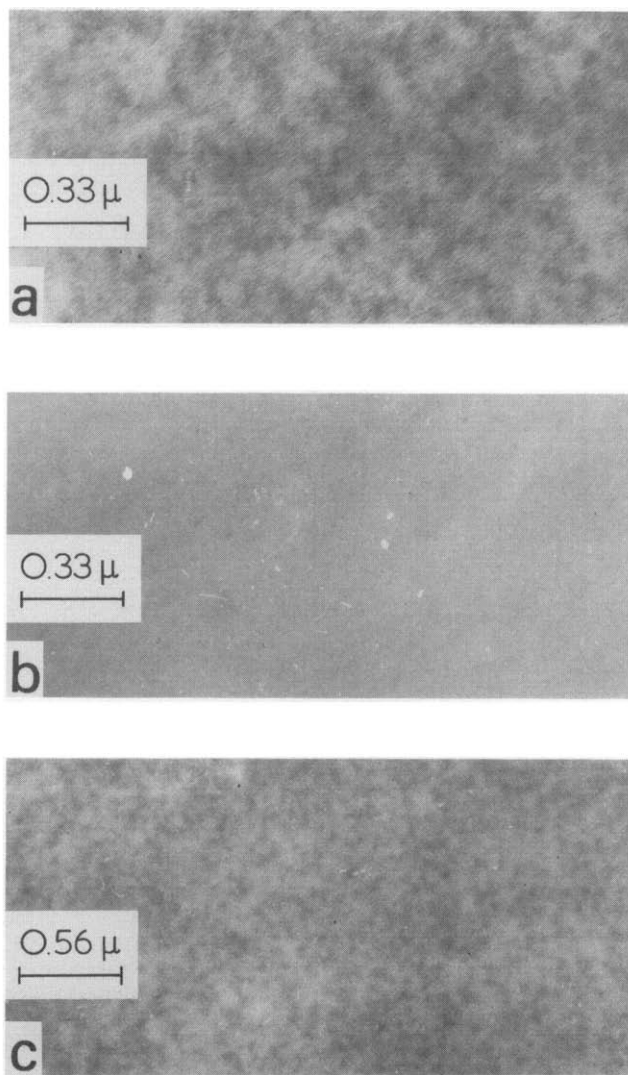 described earlier and shows no observable phase separation. The third shows the structure which developed in the second material when it was heat treated at 160°C for 20 minutes and then quenched.

CONCLUSION

Homogeneous blends of poly(vinyl chloride) and poly(butyl acrylate) can be prepared by the *in situ* polymerization of vinyl chloride with poly(butyl acrylate). If less than 50% vinyl chloride is present in the mixture a homogeneous blend can be formed by direct polymerization. If more than 50% vinyl chloride is present the polymerization route passes through a two-phase region in the vinyl chloride/PVC/PBA three component phase diagram and inhomogeneous blends result. Homogeneous blends within these compositions can be prepared by polymerization with less than 50% vinyl chloride followed by reswelling with vinyl chloride and repolymerization, thus avoiding the two phase region. The three component phase diagram can be qualitatively explained in terms of the interaction parameters between the components.

ACKNOWLEDGEMENTS

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