Binary Blends of Poly(vinyl chloride) Stabilized by Lithium Acetate-Thermal Studies

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ABSTRACT: A series of blends of poly(vinyl chloride) (PVC) with (1) poly(methyl methacrylate) (PMMA) or (2) polyoxymethylene (POM), with lithium acetate as a stabilizing agent, was investigated by differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA), either alone or coupled with Fourier transform infrared (FTIR) spectroscopy. It was found that lithium acetate has a significant effect on the thermal properties of blends under investigation. It causes the initial decomposition temperatures to increase by about 60–150°C for PVC–POM blends, a substantial suppression of the volatile products evolution for PVC/PMMA blends, and an improvement in the surface morphology for both polymer systems by lowering the degree of roughness. The origin of these effects was discussed by analysis of the intermolecular complexation between metal salt and PVC structural arrangements in the blends. Such interactions may lead to the formation of long-range, directional-specific structural regularities, which in turn thermally stabilize the whole system (strong interactions model). © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2576–2587, 1999

Key words: poly(vinyl chloride); blends; stabilization; thermal studies

INTRODUCTION

Poly(vinyl chloride) (PVC) is one the most important thermoplastics and is often blended with other polymers to produce materials with a number of improved end properties over the individual component polymers. For instance, PVC is known to be miscible with a wide range of polymethacrylates.[1–6] The miscibility of these systems is attributed to the exothermic mixing arising from the formation of weak hydrogen bonds between the carbonyl groups of the esters and the methine protons of PVC.[7–9] Studies on the heats of mixing of various oligomeric polymethacrylates with PVC reveal the existence of a maximum interaction for the lower alkyl methacrylates. The higher

concentration of carbonyl groups in the lower methacrylates is responsible for the better miscibility with PVC, leading to lower critical solution temperatures that are higher in these blends.[10] The presence of additional functional moieties like carbonyls, ether oxygens, pendent hydroxyl groups, or any specific interactions (e.g. complexation) can have a significant effect on miscibility behavior with PVC.[11,12]

On the other hand, most pairs of chemically different polymer–PVC systems are immiscible because of the negligible entropy of mixing and the normally positive enthalpy of mixing. It is usually considered that miscibility requires the existence of a favorable interaction between the units of the dissimilar polymers. The development of strong specific interactions by complexation is therefore a subject that has attracted considerable interest over the past decade.[13–18] These interactions not only provide a viable

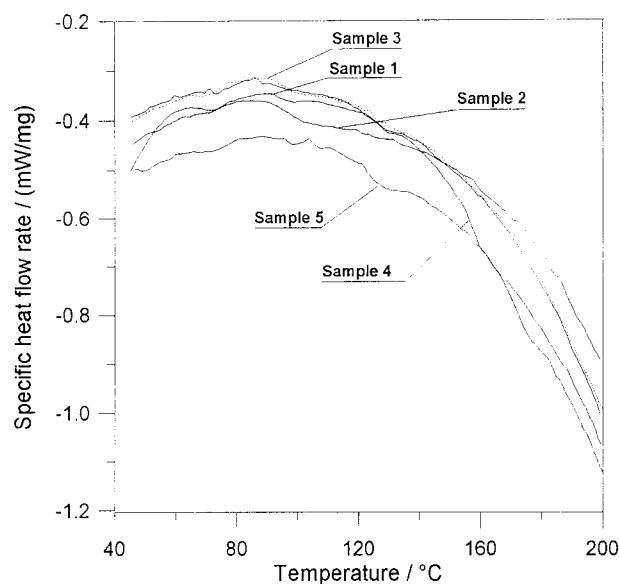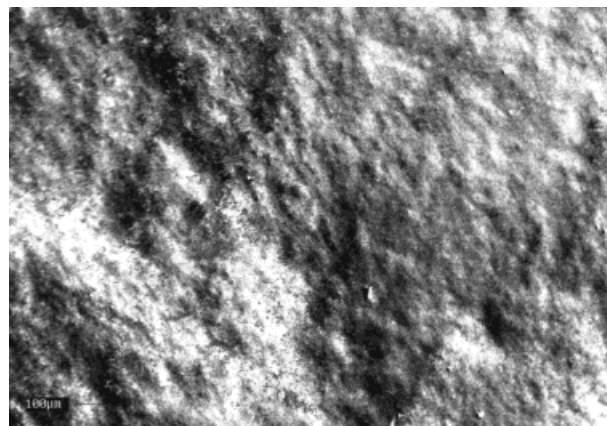**Table I   Characteristics of the Samples Used in This Work**

Sample No.	PVC/PMMA Blend (by Weight)	Sample No.	PVC/PMMA (1 : 1) + Lithium Acetate (wt %)
1	1 : 1	6	0.5
2	4 : 1	7	2.0
3	3 : 2	8	5.0
4	2 : 3	9	10.0
5	1 : 4		

Sample No.	PVC/POM Blend (by Weight)	Sample No.	PVC/POM (1 : 1) + Lithium Acetate (wt %)
10	1 : 1	15	0.5
11	4 : 1	16	2.0
12	3 : 2	17	5.0
13	2 : 3	18	10.0
14	1 : 4		

method for making compatible multicomponent polymer mixtures to attain tailored properties, but they also offer new challenges for fundamental studies of interfacial phenomena. Interfacial mixing in polymer blends results from interdiffusion of the different components, which governs the interfacial width and composition profile at the interface. The amount of interfacial mixing that occurs in a blend influences the morphology and interfacial adhesion, which ultimately control

**Figure 2**   SEM microphotograph of sample 1.

the physical (thermal) and mechanical properties of the blend.

The present investigation studied the thermal behavior of the two PVC systems—namely (1) miscible PVC–poly(methyl methacrylate) (PMMA) blends and (2) virtually immiscible PVC–polyoxymethylene (POM) blends—in the presence of lithium acetate as a stabilizing agent.

EXPERIMENTAL

Materials

The samples were prepared by dilution of PVC-S (Zaklady Azotowe w Tarnowie-Moscicach S.A.; $M_w = 154,200$) with PMMA (ICI, Runcorn, UK; $M_w = 108,000$) or POM (a copolymer of trioxane and dioxolane from ZA Tarnów-Moscice S.A.) in dimethylformamide. Transparent polymer films were obtained in a reproducible way by solution

Figure 1   DSC scans of samples 1–5.
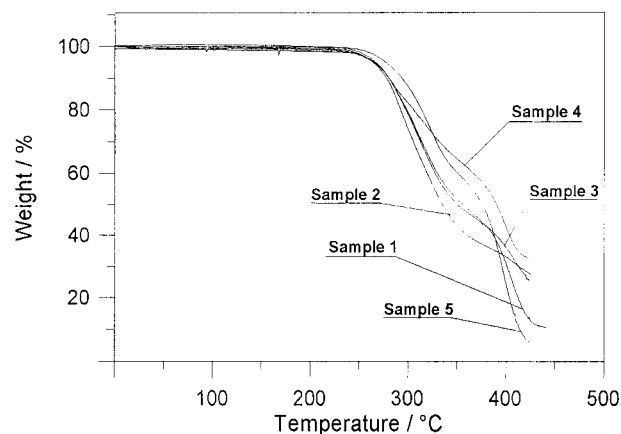
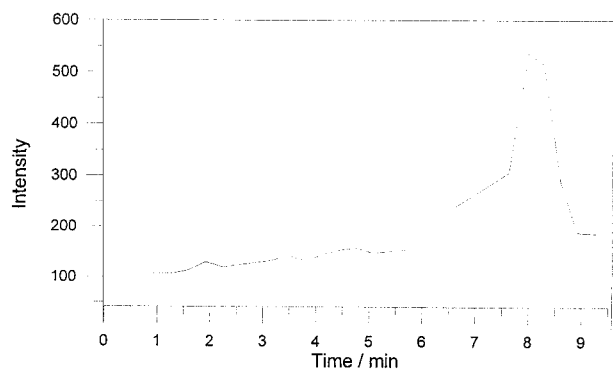**Figure 3**   TGA curves of samples 1–5

Figure 4 A Gram–Schmidt chromatogram of sample 1.

casting and were then dried *in vacuo* for several days and stored in closed containers. Lithium acetate was a product of POCh (Gliwice, Poland). Descriptions of the samples are given in Table I.

Techniques

Differential Scanning Calorimetry

For the DSC measurements a Netzsch DSC 200, operating in dynamic mode, was employed on a first scan. Samples of ~5 mg weight were placed in a sealed aluminum pan. A heating rate of 10 K/min was applied to ensure high resolution of the DSC curves. Prior to use, the calorimeter was calibrated with an indium standard; an empty aluminum pan was used as a reference.

Thermogravimetric Analysis

Thermogravimetric analysis was performed on a Netzsch TG-209 thermogravimetric analyzer, operating in dynamic mode at heating rate of 10 K/min. The conditions were: sample weight of ~5 mg, atmosphere of argon, flow rate of 30 cm^3/min, and a temperature range of 30–450°C.

Thermogravimetric Analysis Coupled with Fourier Transform Infrared Spectroscopy

Thermogravimetric analysis coupled with Fourier transform infrared (FTIR) spectroscopy was carried out using a Perkin-Elmer 7 thermogravimetric analyzer (heating rate = 50 K/min, sample weight ~5 mg, nitrogen flow = 50 cm^3/min) and a Perkin-Elmer 1725X FTIR spectrometer. The thermogravimetric analyzer and spectrometer were suitably coupled to enable the passage of evolved products (molecular weight fragments) from the furnace to the gas cell over a short path in order to minimize secondary reaction or condensation on the cell walls.

Electron Microscopy Investigation

A variable-pressure scanning electron microscope (LEO 435 VP, Germany) was used to investigate the surface morphology of the blends. The samples were used directly for examination, and the apparatus operated in the variable pressure mode. The pressure in the specimen chamber was
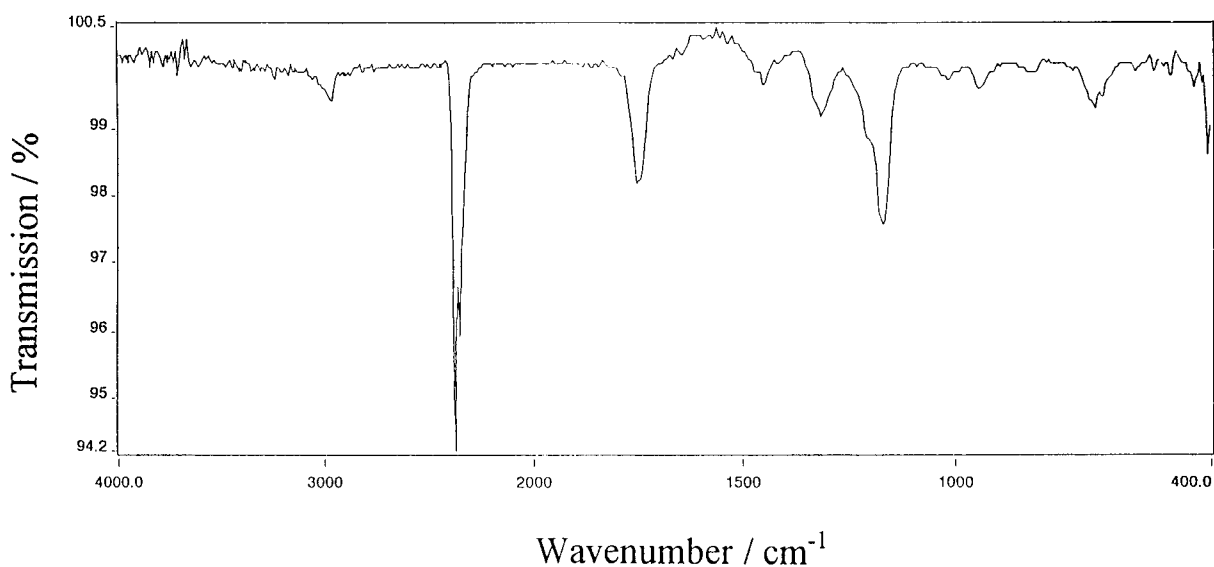

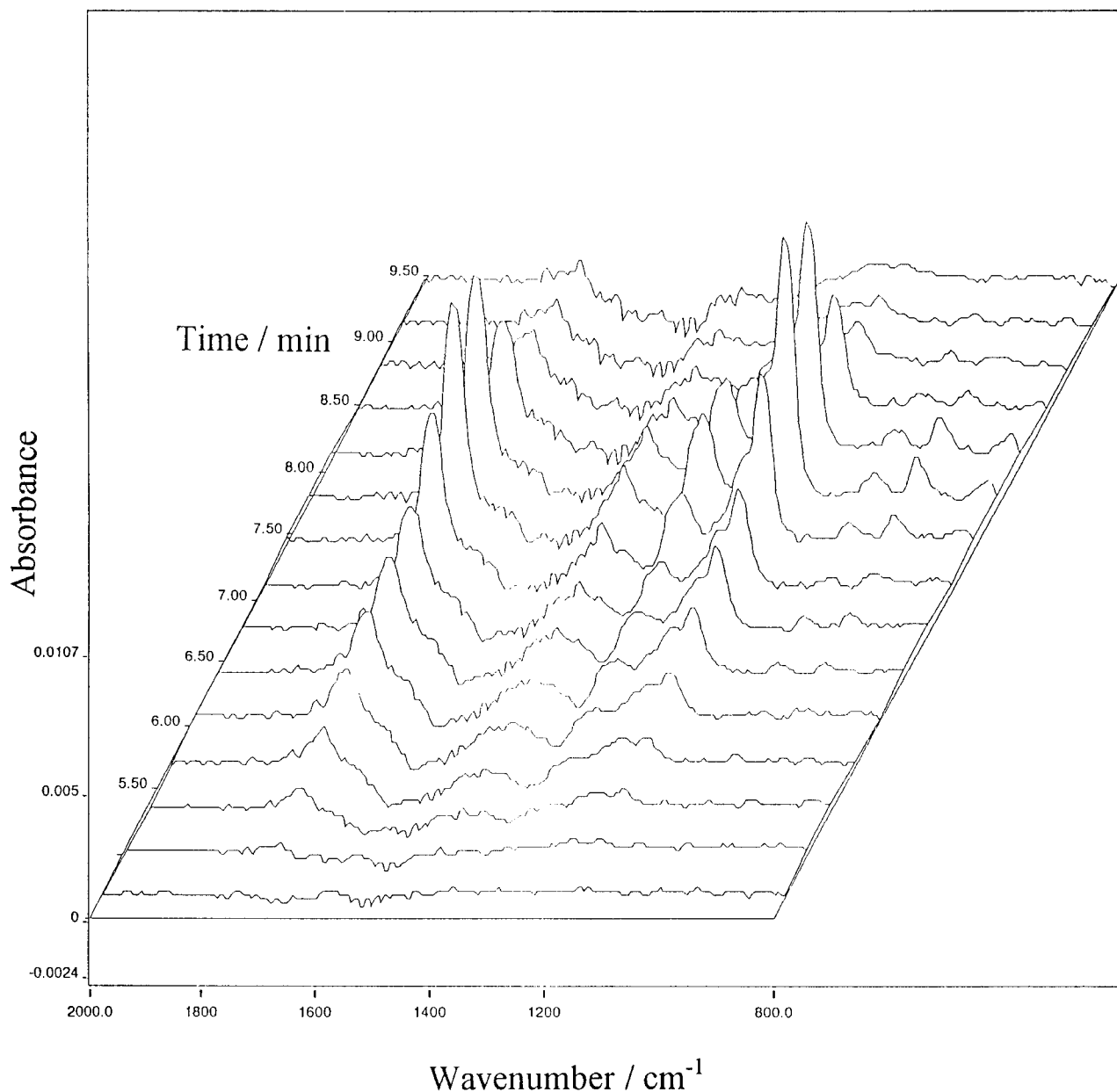**Figure 5** FTIR spectrum of sample 1 after 7.88 min.

Figure 6   Stacked plots of FTIR spectra of sample 1 from 4.50 to 9.50 min.

adjusted to 36 Pa, while maintaining a high vacuum in the region of the gun. The energy of the electron beam was 20 kV, the electron probe current was ~300 pA, and a four-quadrant backscattered detector was used for analysis.

RESULTS AND DISCUSSION

PVC–PMMA Blends

First, the blends of PVC–PMMA were investigated. DSC traces reveal similar thermal behavior, with an onset temperature of initial internal structural rearrangements commencing at $\approx 150°C$, as can be seen in Figure 1.

The morphology investigation indicates on-surface inhomogeneity due to irregular domains distribution, as shown in Figure 2.

Thermogravimetric analysis shows no mass loss up to 250°C, as presented in Figure 3; above this temperature a two-step degradation occurs. From the slope of the *TG* curves, different decomposition rates are to be expected; values of the char residue at 450°C differ substantially, from 4 to 32%.
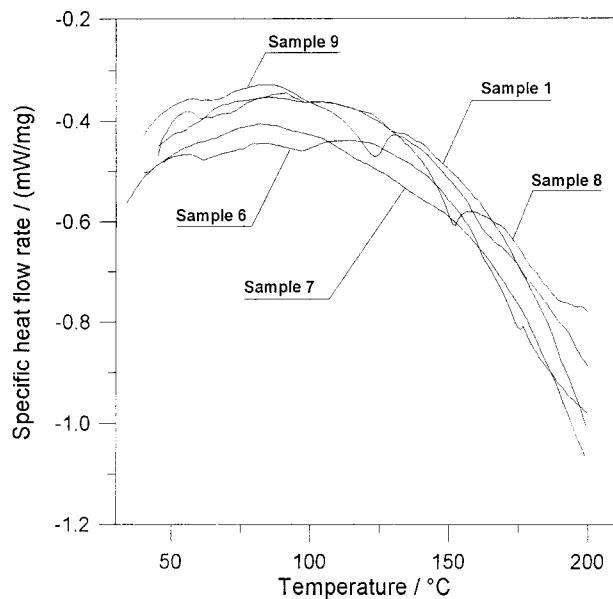
Figure 7   DSC scans of samples 1 and 6–9.

Figure 9   TGA curves of samples 1 and 6–9.

Some more information concerning evolution of the decomposition products yields thermogravimetric analysis coupled with Fourier transform infrared spectroscopy (*TG*–FTIR). Analysis of the Gram-Schmidt chromatograms shows that emission of volatile products essentially starts at ~310°C (Fig. 4).

It should be noted that for the heating rate of 50 K/min, all the thermal events are shifted toward higher temperatures. Such a high heating rate was necessary, however, to produce volatiles at concentrations high enough to be detected online in the FTIR measuring cell.

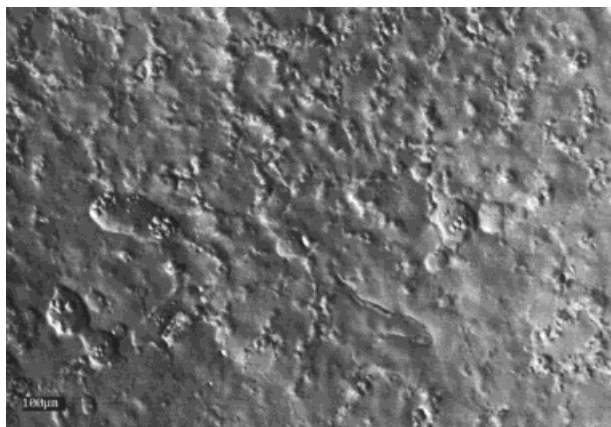The FTIR spectrum taken at the maximum gas-products evolution profile reveals several

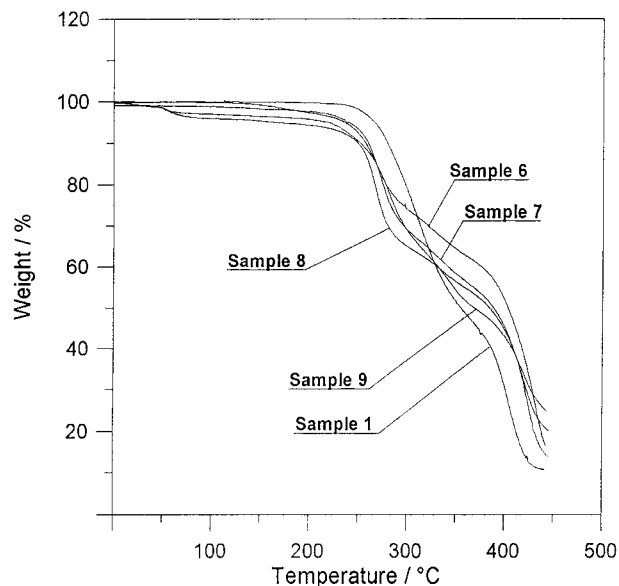characteristic absorption bands at ~2470, ~1750 and ~1200 cm^{-1}, which correspond to the vibrational frequencies of the CO_2, C$=$O, and C—O groups, respectively (Fig. 5).

Their change versus time in the region 800–2000 cm^{-1} can conveniently be observed using stacked plots, depicted in Figure 6.

A unique feature of the *TG*–FTIR system is its ability to provide continuous monitoring of the IR spectra of evolving products as well as quantitative analysis of gases.[19–23] In contrast to pyrolysis GC, in which all the gases produced by heating to a given temperature are separated and analyzed as a batch, *TG*–FTIR offers the great advantage of sequentially identifying the gases for a comprehensive vapor–phase analysis.
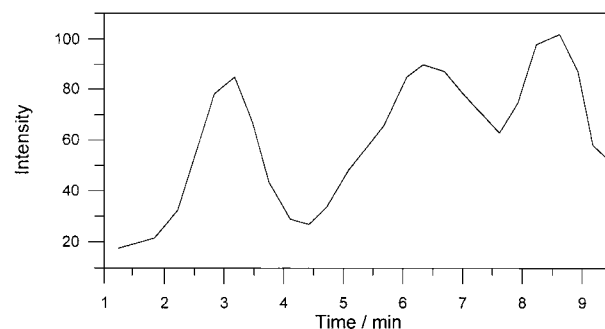

Figure 8   SEM microphotograph of sample 7.

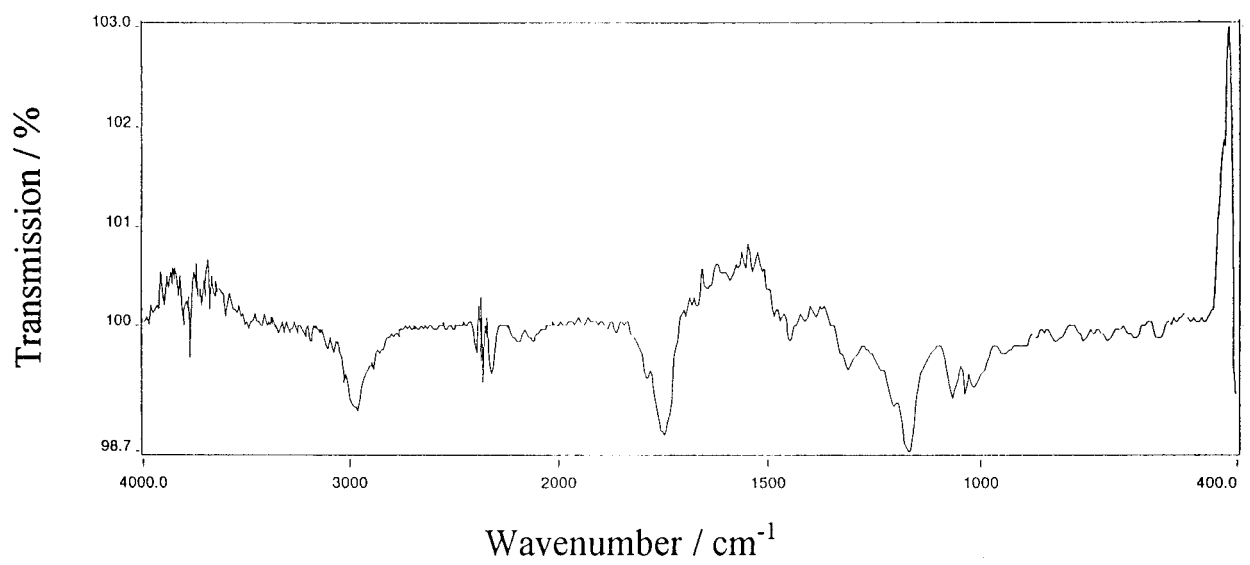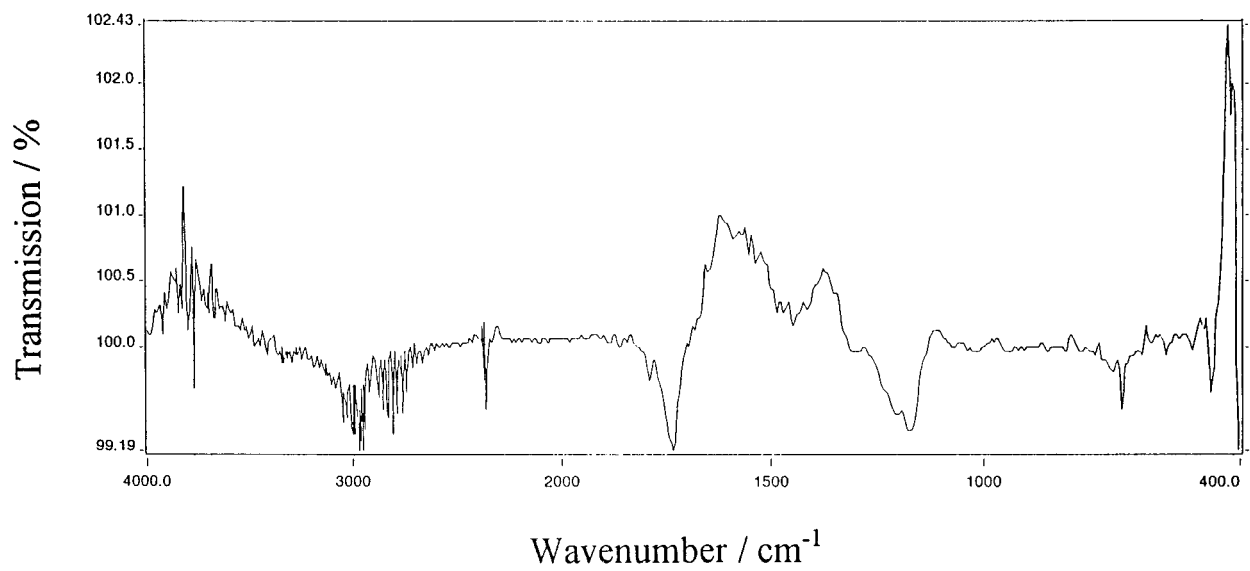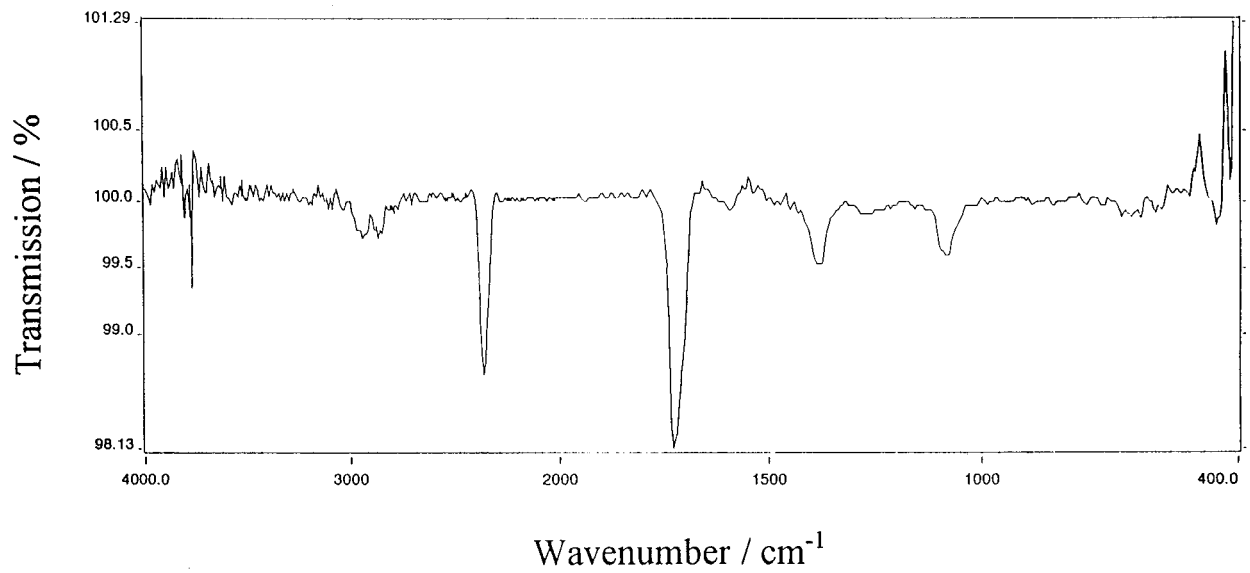**Figure 10**   A Gram–Schmidt chromatogram of sample 8.

Figure 11 (a) FTIR spectrum of sample 8 after 3.04 min. (b) FTIR spectrum of sample 8 after 6.07 min. (c) FTIR spectrum of sample 8 after 8.44 min.

PVC–PMMA Blends Made Compatible by Lithium Acetate

Making compatible polymer blends by the introduction of metal salts has been studied in many laboratories.[24–28] Among alkalimetal cations, lithium provides substantial improvement of miscibility, while sodium, for example, does not.[29] In the literature there are conflicting explanations of the chemistry of metal ion–polymer functional group complexes. For instance, for polyamides some studies have concluded that metal ions coordinate to amides via the carbonyl oxygen[30,31]; others attribute the results to the formation of a metal–nitrogen ligand.[32,33]

DSC results show that there is no substantial deviation in the course of thermal events of modified PVC–PMMA blends as compared to the pure PVC–PMMA blend, as shown in Figure 7.

From the SEM microphotograph (Fig. 8) it can be seen that the surface is smoother compared to the rough surface of the pure PVC–PMMA blend; this was also observed in the bulk since the modified blends were substantially more rigid than the pure ones. Differences between degradation of blends studied by thermogravimetry are minimal (Fig. 9). The same type of decomposition curves indicates on similar degradation mechanism, but this observation should be confirmed by detailed kinetic analysis - such studies are underway.

On the basis of the Gram-Schmidt chromatogram (Fig. 10), it is possible to observe various stages of decomposition: the maximum of the first peak corresponds exactly to a reference spectrum of DMF[34] [Fig. 11(a)], the FTIR spectrum at the maximum of the second peak reveals characteristic absorption bands of HCl at ≈ 2970 cm^{-1} (Fig. 11b), and the third one taken at the maximum of the last peak shows that evolution of hydrogen chloride has been completed [Fig. 11(c)].

A very distinct suppression action of lithium acetate on volatile products emission can be observed compared to the pure PVC–PMMA blend; this effect (secondary stabilization action) may further be utilized for multicomponent PVC systems containing primary stabilizers. A possible explanation can be done by analysis of specific interactions or complexation in the presence of lithium salts, as it has been documented for a variety of metal salt adducts with secondary and tertiary amide compounds.[35]
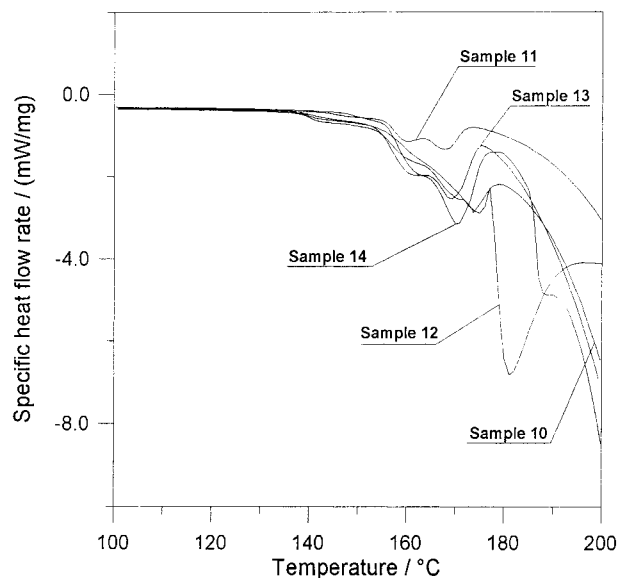

Figure 12 DSC scans of samples 10–14.

PVC–POM Blends

PVC–POM blend is an interesting example of a blend of poorly crystalline polymer (PVC) with a semicrystalline polymer (POM). Considering that by virtue of the nucleation and growth mechanism and spinodal decomposition mechanism the phase separation may lead to different morphologies that will be reflected in the morphology of amorphous and crystalline phases, it is apparent that the phase separation in binary blends can be rather complex.[36]

DSC traces of PVC–POM blends show two thermal transitions, namely glass point in the region of 80–85°C, originated from PVC, and melting transition in the range of 170°C, coming from POM. Then, above 180°C, a gradual decomposition follows (Fig. 12). SEM investigations show that the surface of the blend is not smooth, but the irregularities are located in a rather uniform way, as presented in Figure 13. The PVC–POM blends were thermally stable, as found on the basis of TG measurements, up to the temperature of 150°C (Fig. 14). Then they underwent a two-step decomposition reaction whose rate and degree of extent were controlled by the composition of the blend. Evolution of volatile products proceeds in two steps as well (Fig. 15); first fragments of POM macromolecules appear [Fig. 16(a)], then traces of HCl due to the dehydrochlorination reaction of PVC were detected, as shown in Figure 16(b). In general, POM blends are prospective candidates for many technical applica-
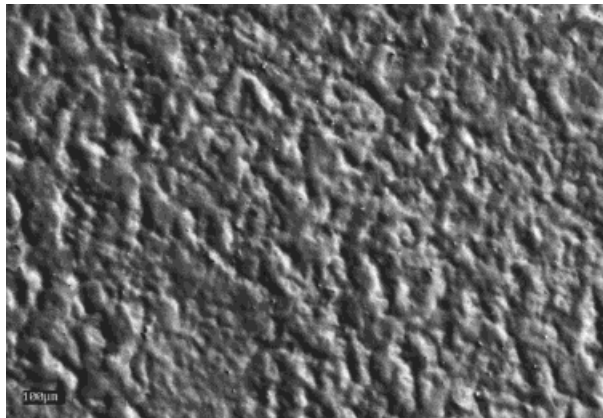
Figure 13 SEM microphotograph of sample 10.

Figure 15 A Gram–Schmidt chromatogram of sample 10.

tions due to mechanical properties of this polymer. However, the simplicity of the POM macromolecular chain does not provide any particular variety of specific interactions; therefore advantageous processing methods, such as reactive processing with or without of a third component, are applied.

PVC–POM Blends Complexed by Lithium Acetate

From the DSC studies it can be seen that lithium acetate stabilizes the thermal behavior in the region of higher temperatures—there is no substantial deviation of the baseline observed above 170°C, except of the sample with the lowest content of lithium acetate (0.5%), as shown in Figure 17.
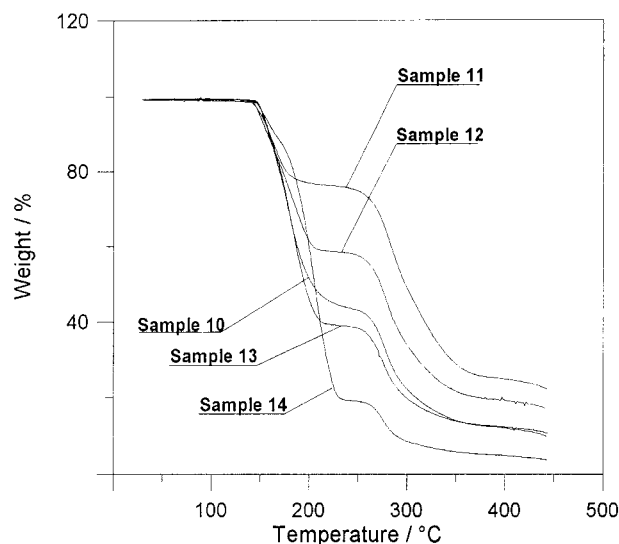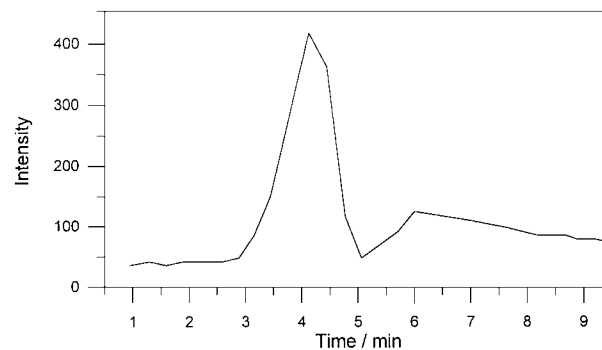

Figure 14 TGA curves of samples 10–14.

The surface morphology, presented in Figure 18 and compared with that of the pure blend, reveals that the degree of roughness of both blends is different; blends modified by the lithium salts have a finer distribution of surface inhomogeneities.

The *TG* data confirm conclusions from the previous observations: lithium acetate as an additive for PVC–POM blends causes an increase of the initial decomposition temperature by about 60–150°C, as shown in Figure 19. It can be also found on the basis of Figure 19 that the initial decomposition temperature of PVC–POM blends depends on the concentration of LiOAc. This effect may be attributed to its action on the polymers' interfaces via intermolecular complexation and, as such, depends on the stabilizer's concentration.

The explanation of this phenomenon can be done by analysis of the influence of lithium acetate on PVC and the PVC–POM blend, rather than on POM alone, although a synergistic action cannot be excluded.

In the literature, two main classes of stabilizers have been intensively studied in the thermal stabilization of PVC: the metal carboxylates and the organotin compounds. Two principal functions of such stabilizers have been thought to be HCl scavenging and, in many cases, the replacement of labile chlorine by the more stable thiolate (mercaptide) or carboxylate (Y).[37–40] The latter mode of stabilization was first proposed by Frye and Horst, who demonstrated the attachment of Y moieties to the polymer upon heating.[41,42] Since the retention of moieties as well as the shorter average length of the polyene sequence in the backbone of stabilized PVC could not be easily explained except by the substitution of labile sites in PVC, such as allylic chlorine or tertiary chlorine atoms, which stopped the zipperlike elimina-
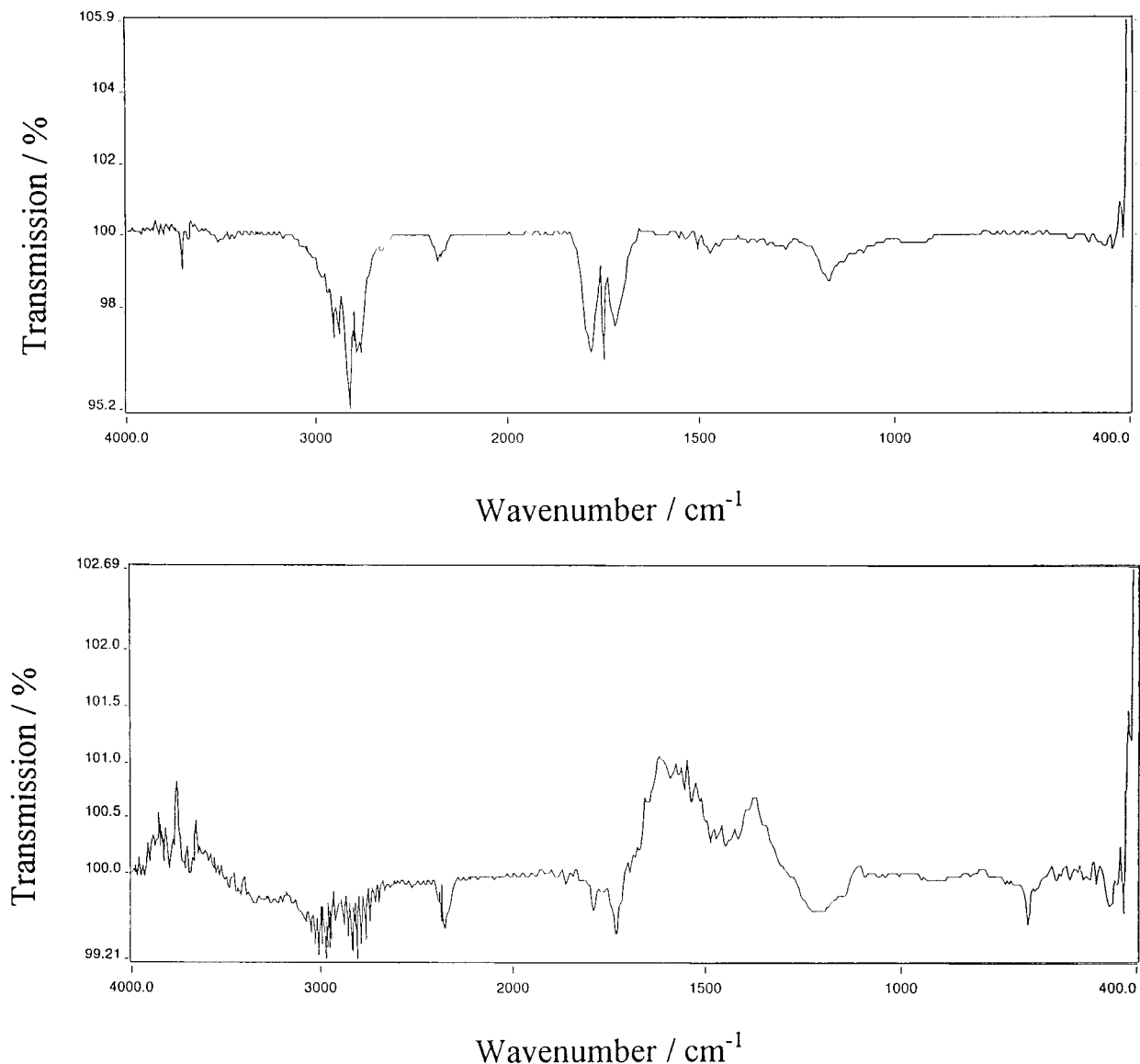
Figure 16 (a) FTIR spectrum of sample 10 after 4.10 min.(b) FTIR spectrum of sample 10 after 5.97 min.

tion of HCl,[43] the Frye and Horst theory seems to be widely accepted. While the mechanisms of thermal degradation of PVC are still being discussed in terms of different basic mechanisms—ionic, radical and molecular—those of thermal stabilization of PVC are in a different situation because the supporters of a radical mechanisms are in the minority. Accordingly, the stabilization mechanisms are widely believed to be ionic in nature—ion-pair mechanism or an analogous quasi-ionic concerted route[44−47]—and they should be supported in the presence of lithium acetate, which is known for its ability to form

complexes. For a lithium acetate action on higher microstructural level, one needs to consider another important factor. Low molecular weight metal–labile PVC structures may form complexes in form of crystals, and the long-range structural regularity of a crystal requires every metal cation to form a fixed number of ligands coordinated to a functional group, since two crystal populations, denoted as *A* and *B*, occur in solution-cast films of PVC.[48,49] Type A crystals are hypothesized to represent folded-chain lamellar crystals formed by arrangement of syndiotactic sequences. Type A crystals are the more perfect and hence have
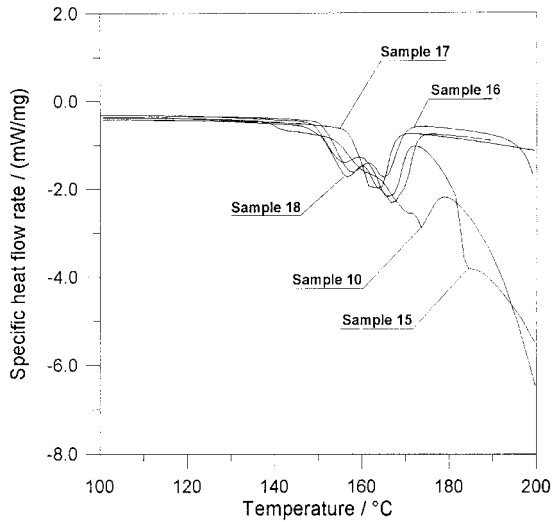
Figure 17 DSC scans of samples 15–18.

Figure 19 TGA curves of samples 10 and 15–18.

slightly smaller *d*-spacings and lattice parameters. They also tend to align, not with the stretch directions as the micellar Type B crystals do, but rather with their chains perpendicular to the drawing direction. Type B crystals are thought to correspond to fringed micelle crystals, formed by the bounding of adjacent chains with short stereoregular segments.[50] If strain is applied (Fig. 20), different behavior of A and B crystallites can be observed.

Crystal formation may not be true for polymer–polymer complexes because of steric hindrance due to the polymer chains and the lack of long-range order in the chain conformations. As a result, the electron density distributions in low molecular weight and high molecular weight complexes are likely to be very different. Moreover,
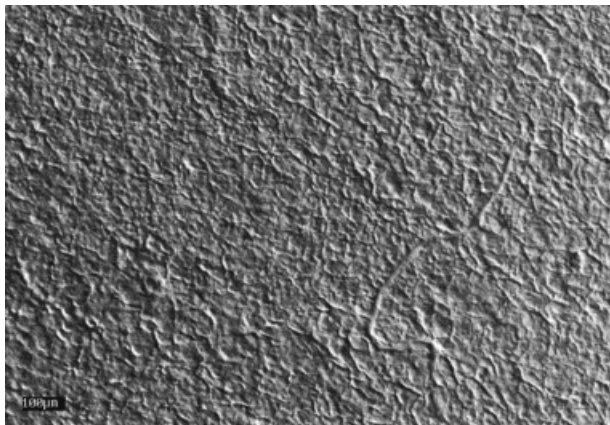
when two polymer surfaces are in contact, different crystal structures strongly influence interfacial mixing,[51] and the extent and rate of interdiffusion depend on the interactions between the two polymers.[52] Diffusion of low molecular compounds is usually Fickian with a constant diffusion coefficient,[53] but in glassy regions of a polymer, it cannot generally be described by Fickian diffusion.[54] In that case, diffusion is influenced by

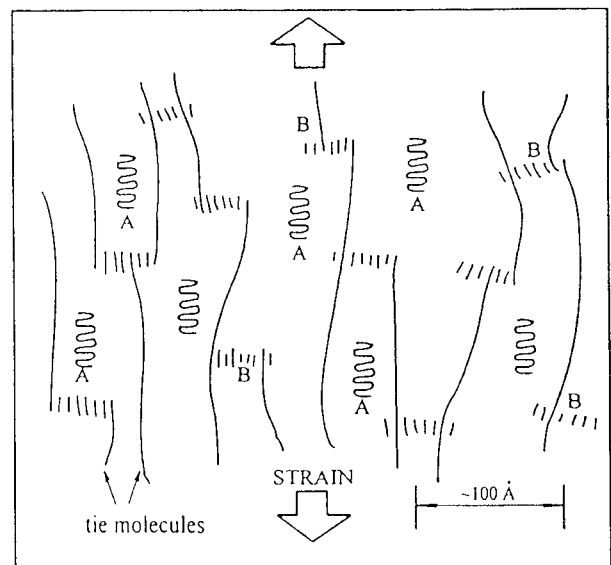**Figure 18** SEM microphotograph of sample 16.

Figure 20 Microdomain model of crystallinity in PVC, showing the behavior of type A and B crystallites in a uniaxial strain model.[58]

the relaxation times of the glassy polymer, and the combined process of molecular relaxation and diffusion is called anomalous diffusion. In the limiting case, when the transport rate is dominated by polymer relaxation, the process is designated as Case II diffusion.[55] A characteristic feature of Case II diffusion is that as the mobile species penetrates into the glassy polymer, a sharp advancing boundary separating the inner glassy core from the outer rubbery shell moves at constant velocity toward the glassy polymer. Case II diffusion has been generally observed for the sorption of organic compounds into polymer glasses,[56,57] and that also may be the case for lithium salts since they are able to influence the polymer structure via intermolecular complexation. Such interaction may lead to the formation of long-range, directional-specific structural regularities, which in turn stabilize the whole system (the strong interactions model).

CONCLUSIONS

Lithium acetate was successfully applied to PVC–PMMA and PVC–POM blends to improve the thermal properties of those systems containing polymers of commercial importance. As it was assumed through analysis of possibly interactions between metal salt and PVC structures on different microstructural levels, a stabilization effect leading to an improvement of surface morphology, increase of initial decomposition temperature by about 60–150°C, and suppression of low molecular volatile products emission for PVC blends was observed. These observations may further be utilized for multicomponent PVC systems in order to enhance their heat performance.

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