

# Miscibility and the Specific Interaction of Polyhydroxybutyrate Blended with Polyvinylacetate and Poly(vinyl acetate-co-vinyl alcohol) with Some Biological Applications

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Received 23 February 2001; accepted 13 February 2002

**ABSTRACT:** Bacterially produced polyhydroxybutyrate (PHB) polymer has a lot of potential as an application for environmentally degradable plastics. We aimed in this study to blend PHB with the semicrystalline polymers poly(vinyl acetate) (PVAc) and poly(vinyl acetate-co-vinyl alcohol) (PACA) to obtain material with better physical properties. We investigated compatibility over a wide composition range using different techniques. Viscosity measurements were used to study polymer–polymer miscibility in dilute solutions with chloroform as cosolvent. The data is discussed according to the viscosity interaction parameters, which are treated as excess properties by similarity with those of real solutions. Dielectric investigations were carried out at different frequencies ranging from 100 Hz to 50 kHz. The obtained data indicated that more than one relaxation mechanism was present, which were ascribed to the rotation of the main chain and its related motions. A glass-transition

temperature composition diagram, IR spectroscopy, and a morphological investigation were also used to give more information about the compatibility of such blends. The results of this study indicate that PHB/PVAc is semicompatible, whereas PHB/PACA is compatible at least in the assayed composition range of hydrolysis. We also extended the study to carry out some biological activity investigations, which were tested against the representative number of pathogenic organisms with the disk diffusion method. The different compositions of the investigated blend were biologically active when compared with the individual polymers. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2363–2374, 2002

**Key words:** biopolymers; blends; compatibility; dielectric properties; DSC

## INTRODUCTION

Bacterially synthesized poly( $\beta$ -hydroxybutyrate) (PHB) has attracted much attention because it is a truly biodegradable and highly biocompatible polyester.<sup>1–4</sup> It has potential uses as environmentally degradable plastics. However, it has some disadvantages, such as brittleness and a narrow processability. The blending of PHB with amorphous polymers is considered to be an interesting way to achieve good properties. Extensive work has recently been carried out in the field of polymer blends.<sup>5–7</sup> This new and interesting field of research has allowed for a great deal of progress in the commercial exploitation of polymer blending as an approach for the preparation of materials with newly

described properties absent in the component polymers.<sup>8–12</sup>

Blending PHB with other polymers may offer opportunities to modify the physical properties, improve the processability, and lower the cost.<sup>10</sup> Many blends containing PHB have been studied, including binary blends with polyethylene oxide (PEO),<sup>11</sup> ethylene propylene rubber,<sup>12</sup> polyvinylidene fluoride (PVDF),<sup>13</sup> polyvinyl acetate (PVAc),<sup>14</sup> and many other synthetic compounds,<sup>15</sup> to investigate the resultant morphology of the blends, with factors such as phase behavior, glass-transition temperature ( $T_g$ ), and percentage crystallinity dominating the degradability. Also, biodegradable natural composites containing PHB–cellulose fiber<sup>16</sup> and PHB–straw fiber<sup>17</sup> have been investigated.

The miscibility, crystallinity, and melting behavior of PHB and ethyl cellulose (EC) blends prepared by casting films have been studied with differential scanning calorimetry (DSC), Fourier transform infrared

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(FTIR) spectroscopy, scanning electron microscopy, and polarizing optical microscopy. The casting films of these blends showed composition-dependent glass transition, which increased with increases in EC content.<sup>11</sup>

This work presents a study of PHB blended with polyvinyl acetate (PVAc) and poly(vinyl acetate-co-vinyl alcohol) (PACA) to establish a miscibility map for these blends and to analyze the types of interactions that were expected to take place between the blend components, with different tools and techniques including viscosity, dielectric measurements, DSC, and IR. This study was extended to carry out some biological investigations.

## EXPERIMENTAL

### Materials

PHB, which was a kind gift from Ulm University (Ulm, Germany), was prepared via bacterial fermentation with methanol as a carbon source by methylotrophic strain 8502-3. The crude product was dissolved in chloroform, filtered, and then precipitated into methanol. The precipitate was filtered and dried under vacuum. The average molecular weight was  $2.3 \times 10^5$ , determined by intrinsic viscosity  $[\eta]$  measurement with the relationship  $[\eta] = 1.18 \times 10^{-4} \times (\text{Molecular Weight})^{0.78}$  in chloroform at 30°C.

PVAc was a commercial product and was purified by dissolution in methanol and precipitation in water. Its average molecular weight was  $2.7 \times 10^5$ , also determined by intrinsic viscosity measurements in chloroform at 25°C.

PACA copolymer was synthesized by hydrolysis-methanolysis of PVAc at 50°C in an acid medium. We controlled the degree of hydrolysis by varying the time of reaction and determined it by titration of residual acetate groups.

### Preparation of blends

We prepared thin films of PHB/PVAc and PHB/PACA blends with different weight ratios (100/0, 90/10, 80/20, . . . , 0/100) by casting from 1% (w/v) solutions of the two components in chloroform, allowing the solvent to evaporate at room temperature overnight and then keeping them at 40°C under vacuum for 48 h.

### Viscosity measurements

All measurements were performed at  $20 \pm 0.1^\circ\text{C}$  with an Avs 350 automatic Ubbelohde-type capillary viscometer from Schott-Gerate (Hofheim, Germany), which allowed reproduction of the flow times with an

accuracy of 0.03 s. The instrument was also equipped with a thermostated bath (model CT 1450).

We prepared the solution of binary system by dissolving the polymer blend in chloroform up to concentration of 1 g/100 mL. We made dilutions to yield at least five lower concentrations by adding the appropriate aliquots of solvent. The elution time of each solution was then determined as the average of four readings. The intrinsic viscosity was determined from the Huggin's plots of the relative viscosity versus concentration by the extrapolation to infinite dilution (zero solute concentration).

### Dielectric measurements

The permittivity ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ) measurements were carried out with a microcapacitor consisting of two glass plates ( $d = 0.05$  mm,  $A = 1$  cm<sup>2</sup>), and a frequency range from 100 Hz to 100 kHz was covered with an LCR meter (type AG-4311B, Ando Electric Ltd., Tokyo). The glass plates were coated on one side with gold. The cell was calibrated with standard materials of known permittivity. The capacitance and the loss tangent were obtained directly from the bridge from which  $\epsilon'$  and  $\epsilon''$  were calculated.

### DSC

We performed DSC to study the miscibility and thermal behavior of the blends on a Shimadzu DSC-50 (Tokyo). The apparatus was calibrated with an indium standard, and a nitrogen atmosphere was used throughout. Samples as casting films were first heated from  $-50$  to  $200^\circ\text{C}$  at a heating rate of  $20^\circ\text{C}/\text{min}$ , quenched to  $-40^\circ\text{C}$  (second run), and then reheated at a heating rate of  $20^\circ\text{C}/\text{min}$ . The melting temperature ( $T_m$ ) and apparent enthalpy of fusion ( $\Delta H_f$ ) were determined from DSC endothermal peaks.

### FTIR

IR spectra of the pure polymers and its blends were obtained with a Jasco FTIR-300E spectrometer (Tokyo) at room temperature.

### Biological activity

The activity of the prepared blends were tested by the minimum inhibitory concentration (MIC) method. We determined the MIC by diluting the agent where the filter paper discs were impregnated with the diluted samples. The antibiotic assay media were sterilized at temperature ( $40$ – $50^\circ\text{C}$ ) and were divided into 20-mL portions among sterile petri dishes 15 cm in diameter. A suspension (1 mL) of the test microorganism spores was seeded in the medium of each petri dish. The

TABLE I  
Experimental and Theoretical Viscometric Data for the Ternary Mixture PHB/PVAc/CHCl<sub>3</sub>

PHB content (%)	$[\eta]_m^{\text{exp}}$ (mL/g)	$[\eta]_m^{\text{id}}$ (mL/g)	$\Delta[\eta]$ mL/g	$b_m^{\text{exp}}$ (mL/g) <sup>2</sup>	$b_m^{\text{id}}$ (mL/g) <sup>2</sup>	$\Delta b$ (mL/g) <sup>2</sup>	$b'_m$ (mL/g) <sup>2</sup>	$\Delta b'$ (mL/g) <sup>2</sup>
PHB	1.166	—	—	1.744	—	—	—	—
90	1.179	1.275	-0.096	0.689	1.655	-0.966	1.422	-0.733
80	1.432	1.439	-0.007	0.672	1.569	-0.896	1.155	-0.482
70	1.509	1.575	-0.066	1.144	1.484	-0.340	0.941	-0.263
60	1.570	1.711	-0.142	1.280	1.402	-0.123	0.781	-0.498
50	1.210	1.848	-0.637	1.665	1.323	-0.342	0.676	-0.988
40	1.446	1.984	-0.488	0.644	1.244	-0.599	0.624	-0.020
30	1.704	2.120	-0.416	0.202	1.170	-0.968	0.627	-0.424
20	2.153	2.256	-0.103	0.704	1.098	-0.391	0.684	0.023
10	2.367	2.393	-0.025	1.224	1.027	-0.196	0.794	0.429
PVAc	2.529	—	—	0.959	—	—	—	—

media were allowed to solidify. Sterilized Whatmann No. 1 filter paper discs were impregnated with 100  $\mu\text{g}$ /disc of the test compounds, which dissolved in chloroform. The impregnated discs were placed in the medium, suitably spaced apart with forceps, and pressed gently to ensure even contact with the medium. The petri dishes were first incubated at (5–7°C) for 1 h and then transferred to the incubator at 28–30°C overnight (at least 24 h). After 24 h of incubation, each antimicrobial agent had diffused into the medium. The antimicrobial agent (polymer) that inhibited microbial growth produced a clear zone around the disc in which no growth was obtained. The diameters of the obtained zones were measured with a caliper, and according to these diameters, the MICs were determined by the extrapolation of the plot of diameter against the concentration.

The microorganisms used were *Escherichia coli* (1357), *Bacillus subtilis* (1020), *Bacillus cereus* (1080), *Pseudomonas aeruginosa* (1259), *Aspergillus niger* (147), and *Candida albicans* (22); these were obtained from Microbiological Resource Center, Ain Shams University, Cairo, Egypt.

## RESULTS AND DISCUSSION

### Viscosity measurements

The viscometric technique was applied to investigate the homogeneity of polymeric blends in solution. The nature of the viscosity of dilute polymer solutions is based on analysis of their hydrodynamic properties, that is, properties related to the movement of macromolecules in solution. The two-phase structures of polymer mixtures and the deformation of the drops in flow may affect the value of viscosity. For this reason, the effective viscosity of a polymer mixture depends not only on the component ratio but also on the value of viscosity. The principle of using dilute solution viscosity to measure the miscibility characterization is

based on the fact that, while in solution, molecules of both components may exist in a molecularly dispersed state, and they undergo a natural attraction or repulsion that will influence the viscosity.

For a ternary system formed by polymer 1, polymer 2, and solvent 3, the intrinsic viscosity of the mixture

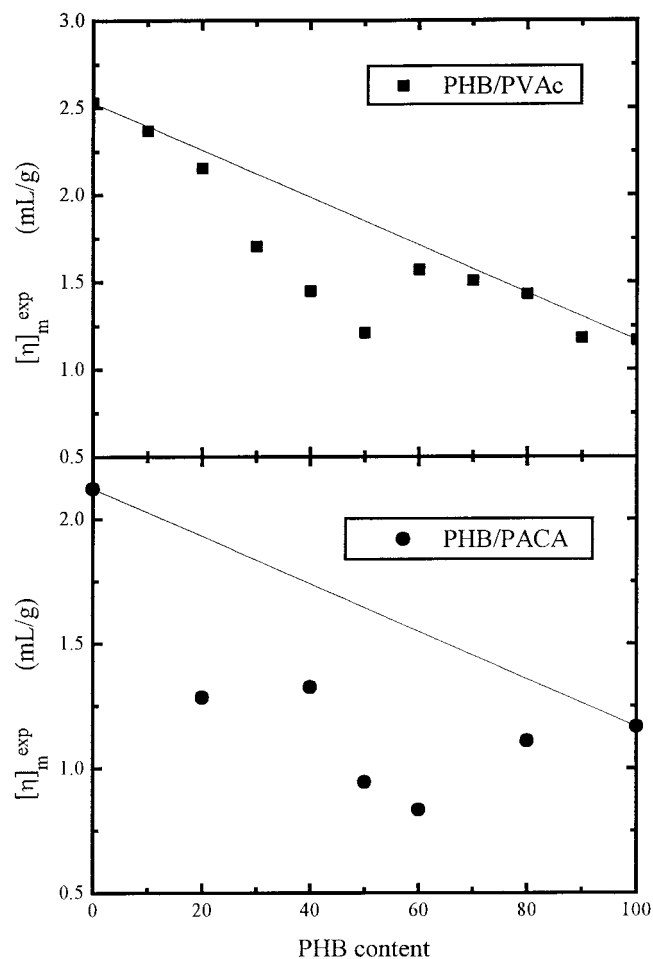


Figure 1 Intrinsic viscosity dependence on blend content.

TABLE II  
Experimental and Theoretical Viscometric Data for the Ternary Mixture PHB/PACA/CHCl<sub>3</sub>

PHB content (%)	$[\eta]_m^{\text{exp}}$ (mL/g)	$[\eta]_m^{\text{id}}$ (mL/g)	$\Delta[\eta]$ (mL/g)	$b_m^{\text{exp}}$ (mL/g) <sup>2</sup>	$b_m^{\text{id}}$ (mL/g) <sup>2</sup>	$\Delta b$ (mL/g) <sup>2</sup>	$b'_m$ (mL/g) <sup>2</sup>	$\Delta b'$ (mL/g) <sup>2</sup>
PHB	1.166	—	—	1.744	—	—	—	—
80	1.109	1.358	-0.249	1.670	1.415	0.255	1.134	0.536
60	0.833	1.549	-0.716	2.172	1.120	1.052	0.699	1.474
50	0.945	1.645	-0.700	1.589	0.986	0.603	0.547	1.042
40	1.325	1.741	-0.416	1.568	0.860	0.768	0.438	1.130
20	1.283	1.932	-0.650	1.744	0.634	1.110	0.353	1.391
PACA	2.123	—	—	0.442	—	—	—	—

( $[\eta]_m$ ) denotes the coil dimensions, which can be altered by contraction or expansion of the coil, whether the interactions between unlike polymer segments are attractive or not. Likewise, the viscometric interaction parameter ( $b_m$ ) characterizes the overall interaction between like chains of both polymers and can be used to determine polymer–polymer compatibility.

With the previous assumption, these two criteria of polymer–polymer compatibility are based on the classical Huggin's equation<sup>13</sup>:

$$\eta_{\text{sp}} = [\eta]C + k[\eta]^2C^2 \quad (1)$$

where the specific viscosity  $\eta_{\text{sp}}$  of the single solute solution was expressed as a function of the concentration  $C$ , and  $[\eta]$  is the intrinsic viscosity, with the assumption that  $K[\eta]^2 = b$ , where  $b$  reflects the binary interaction between polymer segments.<sup>14</sup> Equation (1) can be adapted and expressed in a weight-average form because the reduced viscosity is an additive property:

$$(\eta_{\text{sp}})_m/C_m = \sum(\eta_{\text{sp},i}w_i/C_i) \quad (2)$$

where  $w_i = C_i/C_m$  is the weight fraction of polymer  $i$  by the combination of eqs. (1) and (2).

$$\begin{aligned} (\eta_{\text{sp}})_m/C_m &= \sum([\eta]_i + b_iC_i)w_i \\ &= \sum[\eta]_iw_i + C_m(\sum b^{1/2}w_i)^2 \end{aligned} \quad (3)$$

comparing eqs. (1) and (3)

$$[\eta]_m = \sum[\eta]_iw_i \text{ and } b_m = (\sum b^{1/2}w_i)^2$$

The intrinsic viscosities for the ternary system (PHB/PVAc/CHCl<sub>3</sub>) measured at 20°C were obtained from extrapolation of the Huggin's equation for all the investigated compositions of the blends and are listed in Table I. From this table, one can see that the intrinsic viscosities of the polymer mixtures were between those of the pure polymers. The intrinsic viscosities of

this system with different compositions are illustrated graphically in Figure 1. From this figure, it is clear that the intrinsic viscosities of the different compositions

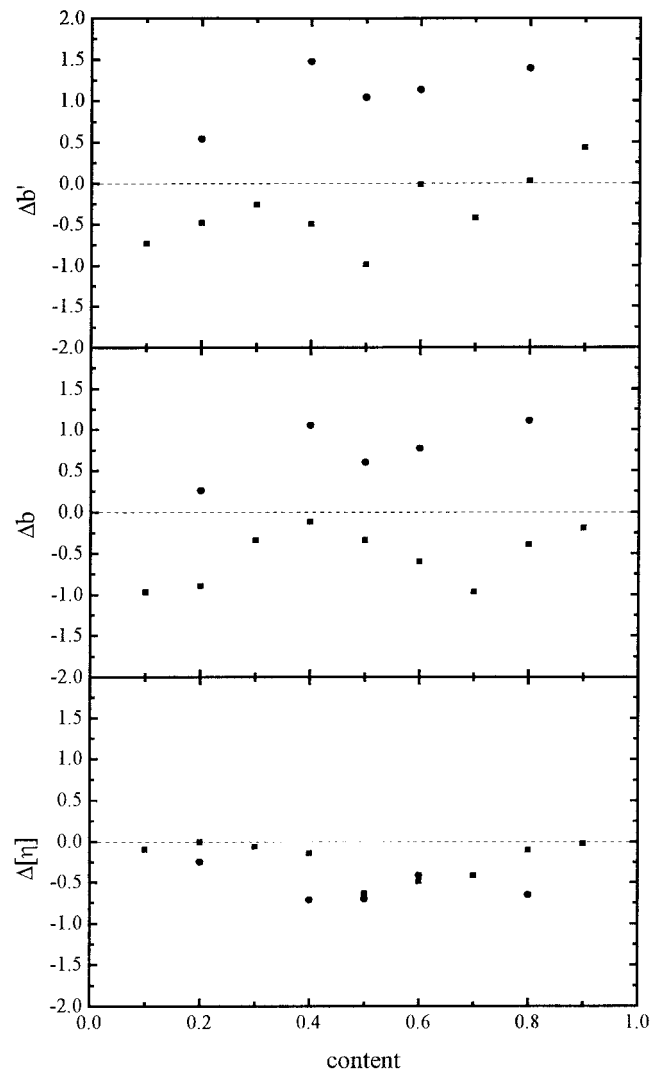


Figure 2 Different compatibility magnitudes ( $\Delta s$ ) as a function of mixture composition for the polymer pairs: (■) PHB/PVAc and (●) PHB/PACA.

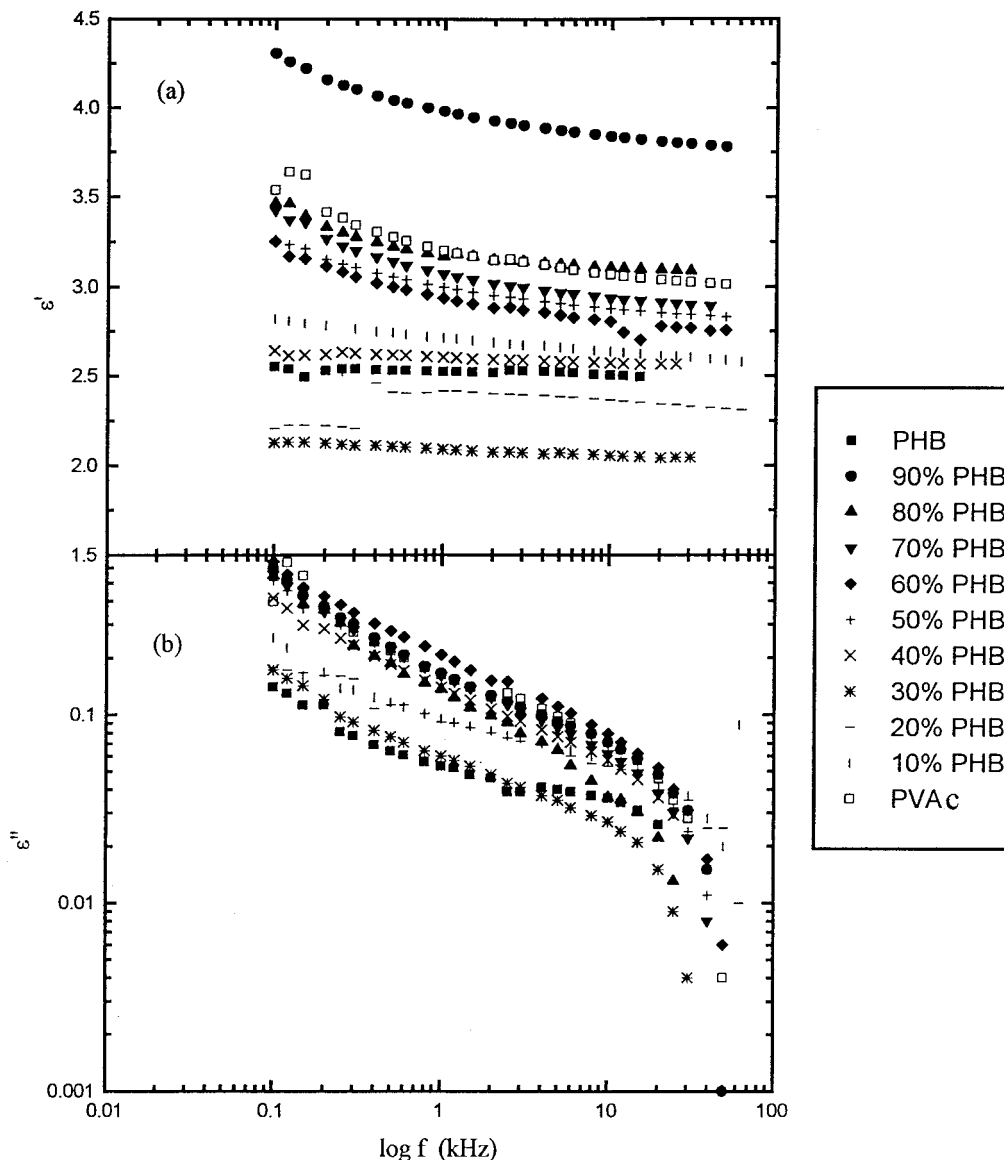


Figure 3  $\epsilon'$  and  $\epsilon''$  dependence on  $\log f$  for the PHB/PVAc blend with different compositions.

reflect the change in the molecular dimensions of PHB and PVAc because of interactions between unlike chains when mixed together.<sup>5</sup>

Moreover, the slopes of the lines from the Huggin's plot that predict the interaction parameter  $b_m$  are listed in Table I. From this data, a noticeable change on the values of these slopes was observed, which reflected the interaction between the polymer-polymer compositions.

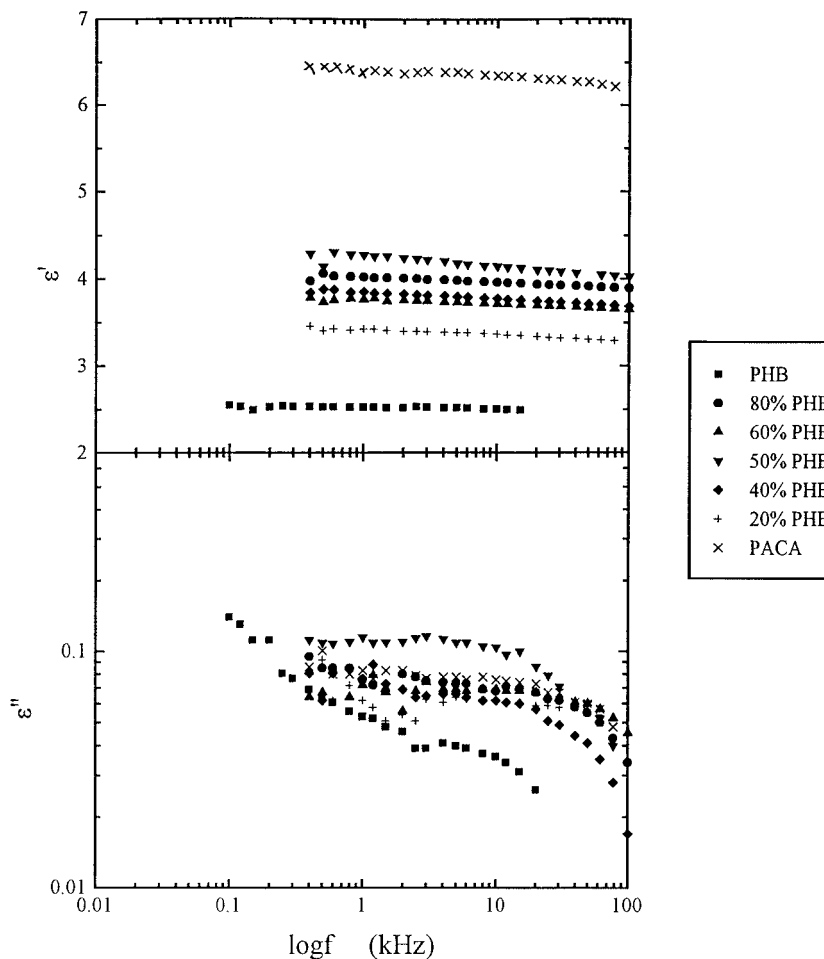
To study the interaction between both polymers in the system and to give useful sight into the attractive and repulsive molecular interactions, three different criteria were used. These criteria were based on the difference between the experimental and ideal values of either the intrinsic viscosity or the interaction parameter:

$$\Delta[\eta]_m = [\eta]_m^{\text{exp}} - [\eta]_m^{\text{id}}$$

where  $[\eta]_m^{\text{exp}}$  is determined from the extrapolation of the Huggin's equation and  $[\eta]_m^{\text{id}}$  is obtained from the data of the individual polymers:

$$[\eta]^{\text{id}} = [\eta]_1 w_1 + [\eta]_2 w_2$$

where  $w_1$  and  $w_2$  are the weight fractions of polymer 1 and polymer 2, respectively. The difference between the experimental and the ideal values of the interaction parameter ( $\Delta b_m = b_m^{\text{exp}} - b_m^{\text{id}}$ ) can be used to discuss the miscibility of the polymer blend solutions. The ideal value of the global viscometric interaction parameter ( $b_m^{\text{id}}$ ) is calculated from



**Figure 4**  $\varepsilon'$  and  $\varepsilon''$  dependence on  $\log f$  for the PHB/PACA blend with different compositions.

$$b_m^{\text{id}} = b_1 w_1^2 + b_2 w_2^2 + 2(b_1 b_2)^{1/2} w_1 w_2$$

where  $b_m^{\text{exp}}$  is obtained from the Huggin's plots as indicated previously. The summation in eq. (3) is a mathematical mistake, which exists by development of the summation of the second term:

$$\sum b_i w_i^2 = \sum (b_i^{1/2} w_i)^2$$

For this reason, a new viscometric interaction parameter ( $b_m^{\text{id}}$ ) was developed and is given by

$$b_m^{\text{id}} = b_1 w_1^2 + b_2 w_2^2$$

This new parameter can be used in addition to  $b_m$ .

These three different parameters ( $\Delta[\eta]$ ,  $\Delta b$ , and  $\Delta b'$ ) were calculated for the investigated system, and the data obtained are listed in Table I. From this table, the values of three  $\Delta$  parameters ( $\Delta[\eta]$ ,  $\Delta b$ , and  $\Delta b'$ ) for the different compositions changed from positive to negative signs, which reflected the degree of compatibility of the system. When these data were compared with

those found by Garcia and colleagues<sup>15,16</sup> for polyethylene sulphoxide (PES)/polyvinylidene fluoride (PVDF), it was interesting to find that PHB/PVAc/CHCl<sub>3</sub> was semicompatible, as the system was compatible when  $[\eta]_m^{\text{exp}} < [\eta]_m^{\text{id}}$  and  $b_m^{\text{exp}} < b_m^{\text{id}}$ , whereas it was considered incompatible when  $[\eta]_m^{\text{exp}} > [\eta]_m^{\text{id}}$  and  $b_m^{\text{exp}} > b_m^{\text{id}}$ . It was considered semicompatible when the parameter changed signs.

Viscosity behavior was studied for the other ternary system, PHB/PACA/CHCl<sub>3</sub>. The reduced viscosity for both individual polymers and their compositions were calculated, and their plots against the concentration of the mixture were fitted through the Huggin's equation. The intrinsic viscosities and the viscometric interaction parameters for this system and their assayed compositions at 20°C are compiled in Table II. From these data, it is important to notice that the PHB/PACA/CHCl<sub>3</sub> system in the whole composition range had a negative deviation from the theoretical or ideal line formed between both individual polymers (PHB and PACA). Figure 1, relating intrinsic viscosity and the composition for the PHB/PACA system,

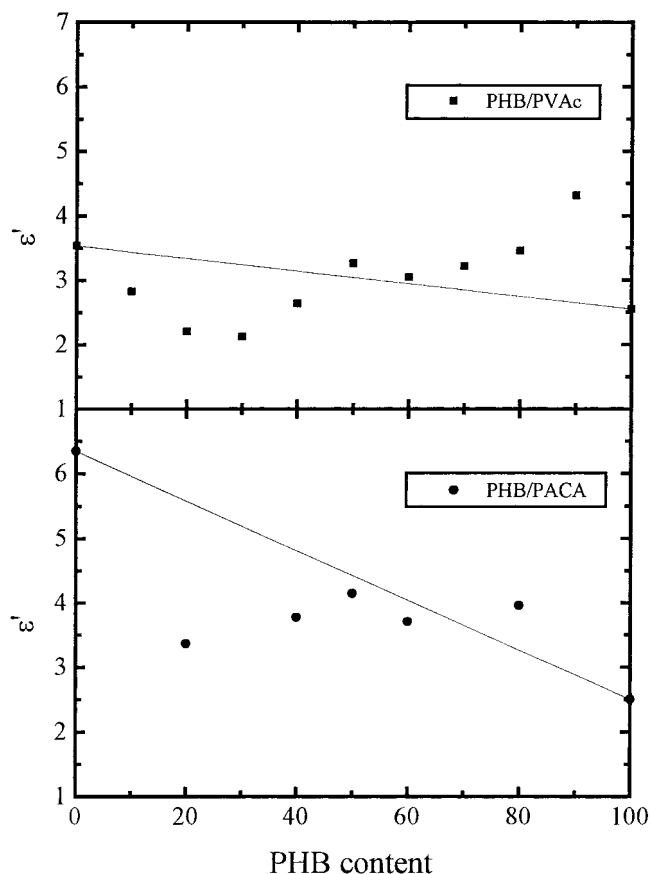


Figure 5  $\epsilon'$  dependence on the blend content.

shows that in all cases, the intrinsic viscosity of the blend was lower than the average intrinsic viscosity of the pure polymers. The deviation seen in this figure could be attributed to deviation from linearity of the free volume in the system. Free volume changes are related to the interactions between polymer chains that reflect orientation effects. On the other hand, the negative deviation of intrinsic viscosity from linearity given in the case of PHB/PACA was found to be higher when compared with that of the PHB/PVAc system (Fig. 1), which could be considered evidence for the existence of specific interactions between hydroxyl groups and carbonyl groups in polymer blends. To investigate the degree of compatibility in this system, we calculated the three criteria that have been applied before to the case of PHB/PVAc/CHCl<sub>3</sub>; these are listed in Table II and illustrated graphically in Figure 2 as a function of polymer-polymer content. According to these data and to the assumption given by Garcia, it was interesting to find that this system (PHB/PACA/CHCl<sub>3</sub>) was compatible as  $[\eta]_m^{\text{exp}} < [\eta]_m^{\text{id}}$  and  $b_m^{\text{exp}} < b_m^{\text{id}}$ .

#### Dielectric measurements

$\epsilon'$  and  $\epsilon''$  of PHB/PVAc and PHB/PACA blends with different compositions were carried out at different

frequencies ranging from 100 Hz to 100 kHz and at room temperature (25°C). The data obtained for the two systems are illustrated graphically in Figures 3 and 4. From Figure 3(a), it is clear that the values of  $\epsilon'$  decreased the applied frequency increased, and, they showed anomalous dispersion.

The absorption curves given in Figure 3(b) relating  $\epsilon''$  and log frequency were broad, indicating that more than one relaxation mechanism was present. These expected mechanisms were ascribed to the orientation of the main chain and its related motions. From this figure, it is clear that the values of  $\epsilon''$  in the case of the PHB/PVAc system increased when the PVAc content increased. When the data of  $\epsilon'$  and  $\epsilon''$  for PHB/PACA given in Figure 4 were compared with those for PHB/PVAc, it was interesting to find that  $\epsilon'$  values were higher, whereas  $\epsilon''$  were lower, than for the individual homopolymers.

For the PHB/PVAc blend,  $\epsilon'$  is plotted graphically versus the content of PVAc in the blend at different frequencies (1, 5, 10, and 20 kHz), which gave the S shape. As an example, Figure 5 shows the dependence of  $\epsilon'$  on the blend content at 10 kHz.

According to the phase theory<sup>18</sup> in relation to the obtained shape, there was a fairly equivalent ratio

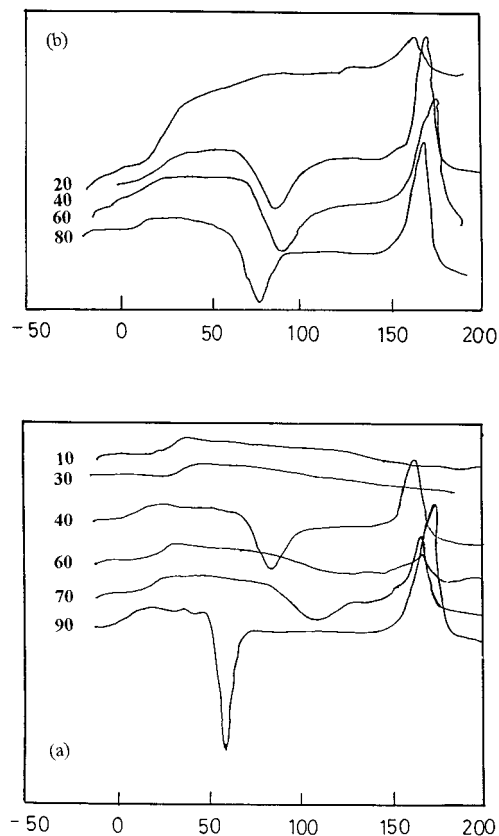


Figure 6 DSC thermograms of casting samples: (a) PHB/PVAc and (b) PHB/PACA.

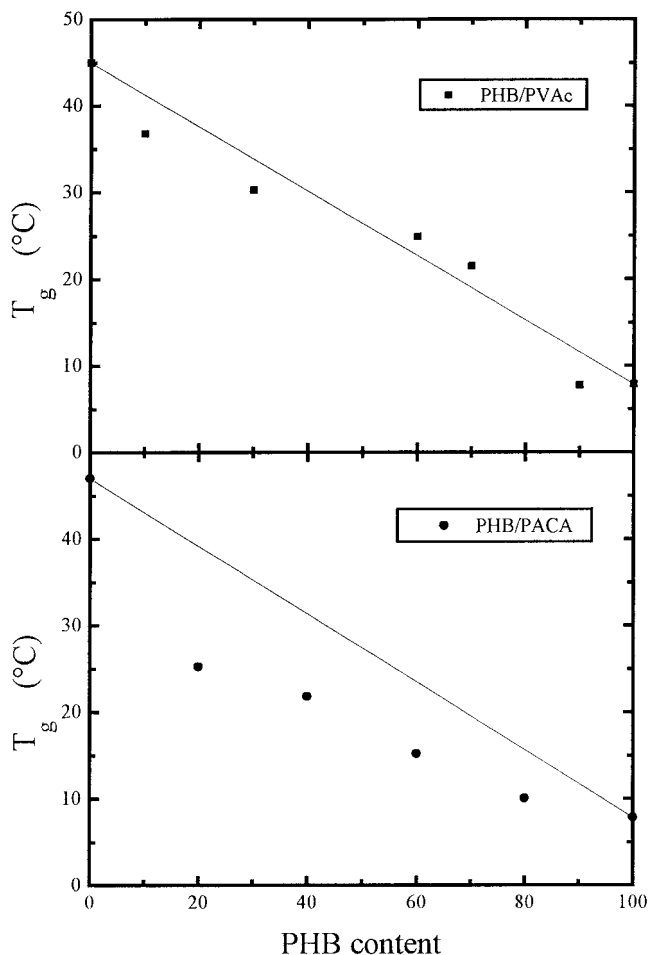


Figure 7  $T_g$  dependence on blend content.

from PHB and PVAc in the blend at which a rapid change in the properties from one plateau to the other happened. This shape is generally taken as typical evidence of the system to be semicompatible.

On the other hand, the relation between  $\varepsilon'$  against the blend content in PHB/PACA is also plotted graphically in Figure 5. From this figure, it is seen that the values of  $\varepsilon'$  for all of the investigated compositions of the blend were somewhat far from the line connecting the values of PHB and PACA (the ideal line). There-

fore, the negative deviation with respect to linearity was greater when the specific interaction between blend composites was smaller. In other words, the mobility of polymer chains diminished due to the presence of more hydroxyl groups in PACA, which formed hydrogen bonds that acted as effective crosslinks.<sup>16</sup>

## DSC

Figure 6 shows the thermograms of investigated blend films with different compositions. The curves show  $T_g$ , crystallinity (exotherm), and melting (endotherm). Only one  $T_g$  was apparent in all the investigated samples, indicating the compatibility of the blends in the used composition range.  $T_g$  values were calculated from the curves and are plotted against composition in Figure 7. The negative deviation of  $T_g$  from the ideal lines in the PHB/PACA system was consistent with the data obtained from the viscosity and dielectric measurements. The hydrogen-bond formation after hydrolysis increased the chance of hydrogen-bond formation and facilitated the miscibility of the blend. This result was comparable with that found in the case of PACA when it was blended with poly-*N,N*-dimethylacrylamide<sup>16</sup> and PEO,<sup>17</sup> where the negative deviation from the average line depended on the degree of hydrolysis.

For both of the investigated systems,  $T_m$  and the apparent enthalpy of fusion ( $\Delta H_m$ ) were determined from DSC endothermal peaks (see Tables III and IV). The crystallization temperatures ( $T_c$ 's) and the heat of crystallization ( $\Delta H_c$ ) were determined from DSC exothermal peaks. As seen in Tables III and IV,  $\Delta H_m$  and  $\Delta H_c$  decreased by increasing either PVAc or PACA content as an indication for the decrease of crystallinity, whereas a small change was noticed in the case of  $T_m$  and  $T_c$ .

## IR spectroscopy

IR spectroscopy can be used to detect the existence of specific interactions in polymer blends and also re-

TABLE III  
Experimental Results for the Thermal Analysis of PHB/PVAc

PHB content (%)	$T_m$ (°C)	$\Delta H_m$ (mJ/mg)	$T_c$ (°C)	$\Delta H_c$ (mJ/mg)	$T_g$ (°C)
PHB	174.94	65.95	61.00	24.48	7.84
90	172.49	66.00	60.00	37.08	7.71
70	166.68	24.40	109.07	17.14	21.46
40	166.80	9.38	118.60	4.28	24.87
30	162.95	0.38	—	—	30.28
10	—	—	—	—	36.76
PVAc	—	—	—	—	44.95



TABLE IV  
Experimental Results for the Thermal Analysis of PHB/PACA

PHB content (%)	$T_m$ (°C)	$\Delta H_m$ (mJ/mg)	$T_c$ (°C)	$\Delta H_c$ (mJ/mg)	$T_g$ (°C)
PHB	174.94	65.95	61.00	24.48	7.84
80	172.15	45.10	—	—	10.03
60	172.93	39.34	88.25	34.30	15.17
40	172.98	33.22	86.54	27.51	21.78
20	162.95	—	—	—	34.50
PACA	—	—	—	—	46.00

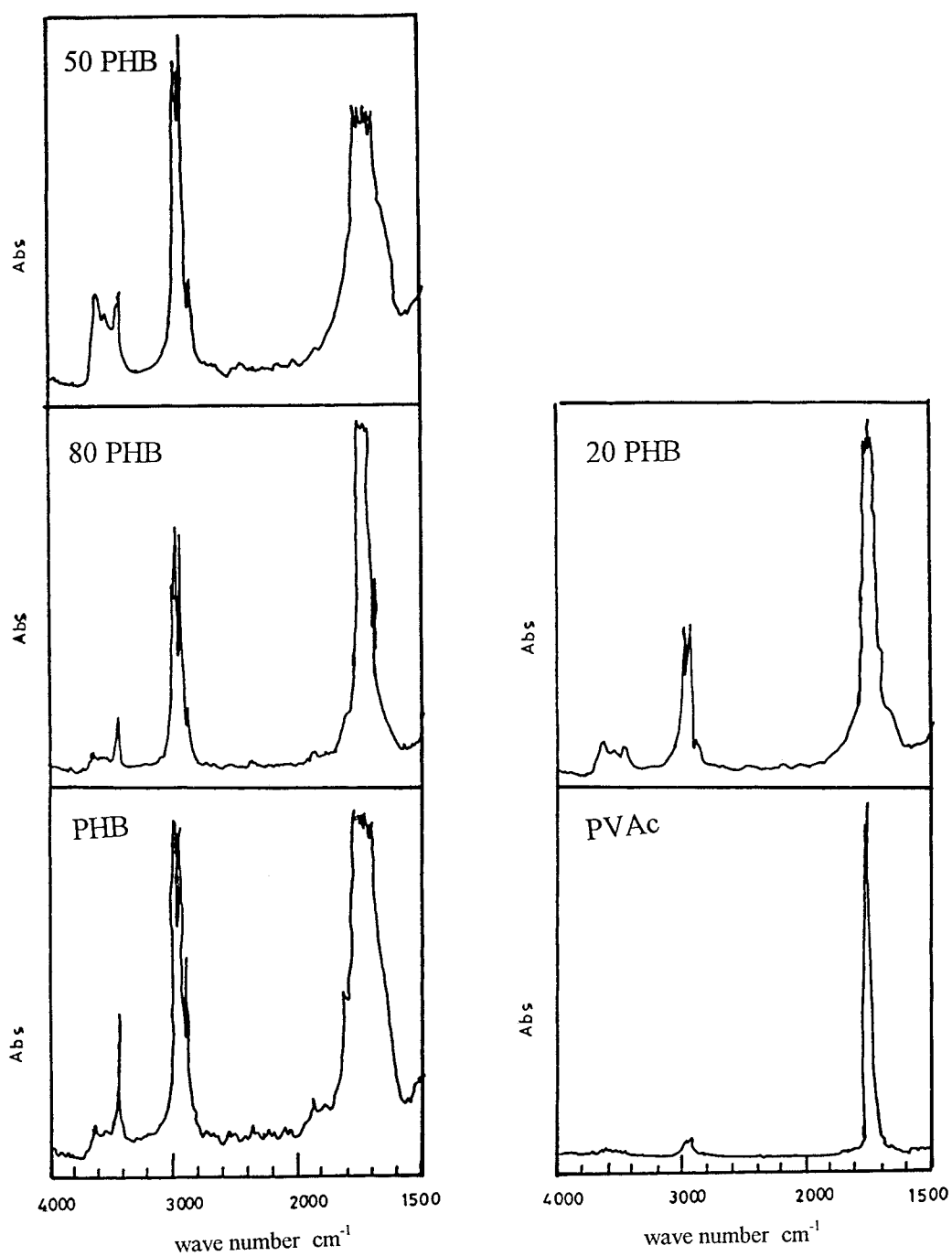


Figure 8 FTIR spectra in the region of 4000–1500  $\text{cm}^{-1}$  for PHB/PVAc casting samples.

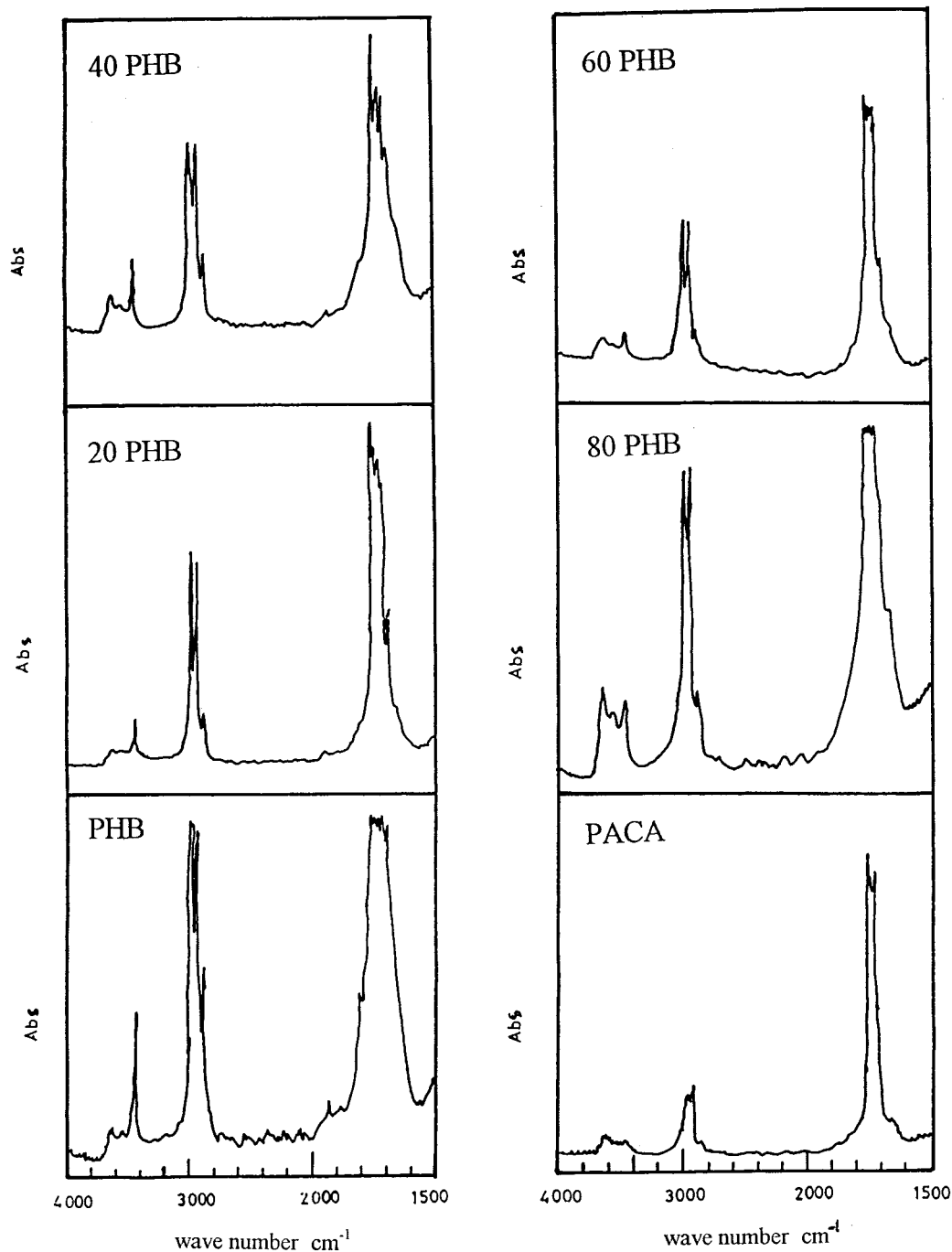


Figure 9 FTIR spectra in the region of 4000–1500  $\text{cm}^{-1}$  for PHB/PACA casting samples.

flects the specific groups, which are found in all components. In PHB/PVAc blends, the carbonyl region at  $1750\text{ cm}^{-1}$  showed a more broad spectrum at the ratio 50/50 than the other contents, which reflected the interaction between the two components through hydrogen-bond formation. On the other hand, the PHB/PACA blend gave a possible interaction between its components due to the hydrogen bonding of hydroxyls bearing on the backbone of the semicrystalline polymer PACA. The absorption of hydroxyl in PACA

was broad, strong, and symmetrical, centered at  $3470\text{ cm}^{-1}$ . In PHB/PACA blends, the O—H stretching bands of PACA shifted to a lower frequency, whereas the carbonyl region showed that C=O stretching bands of PHB at  $1720\text{ cm}^{-1}$  were independent of PACA content.

Figures 8 and 9 show the IR spectra of polymer blends with different compositions and of the pure homopolymer. No apparent band shift was noticed. However, the ratio of the band intensities of the experimental ratios of the C=O and O—H intensities

TABLE V  
MIC ( $\mu\text{g/mL}$ ) of the Highly Sensitive Compositions of PHB/PVAc in (1) *Escherichia coli*, (2) *Bacillus subtilis*, (3) *Bacillus cereus*, (4) *Pseudomonas aeruginosa*, (5) *Aspergillus niger*, and (6) *Candida albians*

PHB content (%)	1	2	3	4	5	6
PHB	—	—	—	—	—	—
90	$6.65 \times 10^{-3}$	—	$6.50 \times 10^{-3}$	—	—	$6.50 \times 10^{-3}$
80	$6.90 \times 10^{-4}$	—	$6.90 \times 10^{-4}$	—	—	$6.90 \times 10^{-4}$
70	$8.70 \times 10^{-5}$	—	$8.70 \times 10^{-5}$	—	—	$8.70 \times 10^{-5}$
60	$8.70 \times 10^{-5}$	$8.70 \times 10^{-5}$	$8.70 \times 10^{-5}$	$8.70 \times 10^{-5}$	$8.70 \times 10^{-5}$	$8.70 \times 10^{-5}$
50	$9.87 \times 10^{-6}$	$9.87 \times 10^{-6}$	$9.80 \times 10^{-6}$	$9.80 \times 10^{-6}$	$9.80 \times 10^{-6}$	$9.80 \times 10^{-6}$
40	$6.50 \times 10^{-7}$	$6.50 \times 10^{-7}$	$6.50 \times 10^{-7}$	—	—	$6.50 \times 10^{-7}$
30	$6.90 \times 10^{-4}$	—	$6.90 \times 10^{-4}$	—	—	$6.90 \times 10^{-4}$
20	$8.74 \times 10^{-5}$	—	$8.74 \times 10^{-5}$	—	—	$8.70 \times 10^{-5}$
10	$6.90 \times 10^{-4}$	—	$6.90 \times 10^{-4}$	—	—	$6.90 \times 10^{-4}$
PVAc	—	—	—	—	—	—

with that of C—H reflected the presence of some sort of interaction between the blend contents.

In summary, IR data clearly proved that the involvement of PACA hydroxyl groups in the specific intermolecular interactions was responsible for the miscibility of the blends.

#### Biological activity measurements

The biological activity of the two investigated systems were tested against a representative number of pathogenic organisms (given in the Experimental section), and the data obtained are given in Tables V and VI. The monitoring of antimicrobial activity is usually performed by determination of the MIC, the smallest amount of the agent that inhibits the multiplication of the pathogen. The actual antimicrobial concentration is represented by the diameter of the zone of inhibition formed around the discs impregnated with the polymer in different composition ratios. Therefore, from Tables V and VI, it is interesting to notice that the different compositions of both blends were biologically active against the representative organisms when compared with the individual polymers but with dif-

ferent degrees. This could be attributed to the formation of specific interactions between the blend compositions.

#### CONCLUSIONS

The results obtained with the different tools and techniques indicated that the PHB/PACA system was compatible, whereas the other system, PHB/PVAc, was semicompatible. The compatibility behavior of the PHB/PACA system was not a surprising result, when the chemical structure of the blend component was taken into consideration. The formation of hydrogen bonds between carbonyl and hydroxyl groups of the polymer blend was detected with IR spectroscopy and confirmed by viscosity and dielectric measurements. Viscosity measurements of the blends allowed us to determine the presence of specific interactions through hydrogen bonding, which were responsible for the miscibility behavior of this system. Also, we concluded that the degree of compatibility depended on the blend composition and the degree of hydrolysis of the copolymer.

TABLE VI  
MIC ( $\mu\text{g/mL}$ ) of the Highly Sensitive Compositions of PHB/PACA in (1) *Escherichia coli*, (2) *Bacillus subtilis*, (3) *Bacillus cereus*, (4) *Pseudomonas aeruginosa*, (5) *Aspergillus niger*, and (6) *Candida albians*

PHB content (%)	1	2	3	4	5	6
PHB	—	—	—	—	—	—
80	$6.90 \times 10^{-4}$	$4.28 \times 10^{-4}$	$6.90 \times 10^{-4}$	$4.28 \times 10^{-4}$	$4.28 \times 10^{-4}$	$6.90 \times 10^{-4}$
60	$8.70 \times 10^{-5}$	$8.70 \times 10^{-5}$	$8.70 \times 10^{-5}$	$8.70 \times 10^{-5}$	$8.70 \times 10^{-5}$	$8.70 \times 10^{-5}$
50	$9.87 \times 10^{-6}$	$9.87 \times 10^{-6}$	$9.80 \times 10^{-6}$	$9.80 \times 10^{-6}$	$9.80 \times 10^{-6}$	$9.80 \times 10^{-6}$
40	$6.50 \times 10^{-7}$	$6.50 \times 10^{-7}$	$6.50 \times 10^{-7}$	$6.50 \times 10^{-7}$	$6.50 \times 10^{-7}$	$6.50 \times 10^{-7}$
20	$8.74 \times 10^{-5}$	$8.70 \times 10^{-5}$	$8.74 \times 10^{-5}$	$8.70 \times 10^{-5}$	$8.70 \times 10^{-5}$	$8.70 \times 10^{-5}$
PACA	—	—	—	—	—	—

It was highly interesting to find that the different compositions of the blend were biologically active against different microorganisms, contrary to the results found for homopolymers.

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