Studies on poly (hydroxy alkanoates)/(ethylcellulose) blends[†]

VAISHALI SUTHAR, ARUN PRATAP* and HETA RAVAL

Department of Applied Chemistry, *Department of Applied Physics, Faculty of Technology and Engineering, M S University of Baroda, Vadodara 390 001, India

Abstract. Biodegradable polymers represent one of the most significant area of research today. Among these polymers, poly (***b***-hydroxy butyrate co ***b*′**-hydroxy valerate) i.e. PHBV have received special attention because of their unique combination of properties. They are perfectly biocompatible, biodegradable polymers and can be processed by any conventional technique. In the present study an attempt has been made to develop the biodegradable blends of PHBV by blending them with ethyl cellulose (EC). Ethyl cellulose has been selected to monitor the biodegradation rate of PHBV and also for making the blends cost effective. The blends are thoroughly characterized for their compatibility, by the measurement of viscosity of blends and through FT-IR. Various applications of PHBV/EC blend in agriculture and pharmaceutical industries are being explored.

Keywords. Polymer blends; viscosity; ethyl cellulose; PHBV; compatibility.

1. Introduction

Polymer blends have formed a major scientific discipline of research owing to their wide range of applications. Compatibility is an important parameter (Olabishi 1975) in determining the properties of polymer blends. A number of methods has been reported measuring polymer–polymer compatibility in polymer blends. Most of them require highly sophisticated instrumentation like dynamical analysis, thermal analysis and electron microscopy and hence a great amount of technical skill (Bohmer and Florian 1970; Feldman and Rusy 1970; Paul and Newman 1978; Inamura and Jinbo 1991), whereas viscometry is a desirable alternative (Raval and Devi 1993, 1995) for studying interaction of polymers in solution. Many researchers have attempted to correlate viscosity with compatibility for ternary polymer–polymer–solvent systems. It was assumed that repulsion interaction may cause shrinkage of random coils of polymer molecule resulting in reduction in viscosities of the blends when compared with values calculated from the viscosities of the pure components, on the assumption of additivity. On the other hand, in the compatible blends, increase in viscosity due to attraction–interaction is expected. Apart from this, polymer–solvent interaction also plays an important role in changing the viscosity on blending in dilute solution blends. In the present study we have attempted to apply this approach for the study of compatibility of PHBV/EC blend systems by measuring their viscosities. The FT-IR spectroscopy further provides evidence to the result obtained from the measurement of viscosities on the compatibility.

2. Theoretical background

Numerous expressions have been put forward for the prediction of interaction between binary polymer systems through viscosity. But, we have considered the following two approaches for the present purpose.

The viscosity behaviour of an ideally mixed polymer solution (Krigbaum and Wall 1950) can be given by

$$\eta_{sp(mix)} = [\eta_1]C_1 + [\eta_2]C_2 + b_{11}C_1^2 + b_{22}C_2^2 + 2(b_{11}b_{22})^{1/2}C_1C_2, \tag{1}$$

where $\eta_{sp(mix)}$ is the specific viscosity of the mixed polymer solution, η_1 and η_2 are intrinsic viscosities of polymer components 1 and 2, respectively. C_1 and C_2 are concentrations of components 1 and 2 respectively in the mixed polymer solution and b_{11} and b_{22} are specific interaction coefficients of components in single polymer solutions.

On the other hand, a completely empirical equation was developed (Castift and Hewtt 1962).

$$\eta_{sp(mix)} = [C_1(\eta_{sp(1)})_c + C_2(\eta_{sp(2)})_c]/C, \tag{2}$$

where $\eta_{sp(mix)}$ is the specific viscosity of the mixed polymer solution. $(\eta_{sp(1)})_c$ and $(\eta_{sp(2)})_c$ are specific viscosities of polymer components 1 and 2, respectively, at concentration C where $C = C_1 + C_2$ and C_1 and C_2 are concentrations of components 1 and 2, respectively in the blend system. Though this relationship does not have any theoretical justification for definition, ideal behaviour

of many mixed polymer solutions can be quantitatively predicted by using it. In the case of polymers, the solution behaviour is described (Huggins 1942) by equation

$$\boldsymbol{h}_{sp}/c = [\boldsymbol{h}] + K[\boldsymbol{h}]^2 c. \tag{3}$$

If we put $K[\boldsymbol{h}]^2 = b$, a term which arises from polymer interaction at finite concentration, then (2) may be written as

$$\boldsymbol{h}_{sp(mix)} = [\boldsymbol{h}_1]C_1 + [\boldsymbol{h}_2]C_2 + b_{11}C_1^2 + b_{22}C_2^2$$

$$+ ((b_{11}+ b_{22})/2)\, C_1 C_2 . \tag{4}$$

(4) is identical to (1) except for the coefficient of the $C_1 C_2$ term, i.e. polymer–polymer interaction. For the convenience of computation (Krigbaum and Wall 1950), the specific interaction coefficient for the ideal behaviour of mixed polymer solutions is defined as

$$b_{12} = (b_{11}b_{22})^{1/2}. \tag{5}$$

However from (4) the interaction coefficient now becomes

$$b_{12} = (b_{11} + b_{22})/2. \tag{6}$$

In the case when the value of either b_{11} or b_{22} is negative the value of b_{12} according to (5) is imaginary. Thus the Krigbaum's definition of b_{12} becomes unrealistic under these conditions. Therefore, for the present purpose we have used (6) which is modified form of Castift and Hewtt's definition of ideal behaviour, throughout our work inspite of its empirical base.

Further, according to Krigbaum and Wall, information of the interaction between polymers 1 and 2 should be obtained from comparison of experimental b_{12} and theoretical b_{12}^* values. Here b_{12}^* is referred to as the coefficient of interaction between polymers 1 and 2 as computed from (6). The compatibility of polymer mixture is predicted by a parameter

$$\Delta b = b_{12} - b_{12}^* . \tag{7}$$

Negative values of Δb refer to blend solutions containing incompatible polymers while positive values of Δb refer to compatibility of polymers due to attractive-interaction.

Table 1. Composition of various blends.

Code no.	Ethyl cellulose (% w/w)	PHBV (% w/w)
EC	100	–
a_1	90	10
a_2	80	20
a_3	70	30
a_4	60	40
PHBV	–	100

An alternative definition for ideal solutions may be obtained by considering the intrinsic viscosities of mixed polymer solution

$$[\boldsymbol{h}_{sp(mix)}/c]_{c \to 0} = \boldsymbol{h}_1[C_1/C]_{c \to 0} + \boldsymbol{h}_2[C_2/C]_{c \to 0}. \tag{8}$$

The results obtained by this process are independent of the value of b_{12} taken from Krigbaum and Wall or from Castift and Hewtt ((1) and (2)). Hence (2), (7), (8) can be used to predict the compatibility of PHBV/EC blends.

In the present study, attempts are made to correlate the compatibility of PHBV/EC blend systems in terms of their viscosities.

Further the effect of composition of blends on the compatibility of the system is also studied and the blends are characterized through Fourier transform infrared (FT-IR) spectroscopy.

3. Experimental

3.1 *Materials*

Ethyl cellulose (CPS epoxy content = 47·8) (LR) was supplied by National Chemicals, Baroda, India. PHBV was gifted by G.S.F.C. Baroda, India. Dichloromethane (LR grade M.W. 84·93) and chloroform (LR grade) were supplied by Suvidhinath Laboratories, Baroda.

3.2 *Preparation of blends*

PHBV and ethyl cellulose were dissolved in dichloromethane (CH_2Cl_2) separately. The solution of the latter was added to the former with constant stirring. Stirring was continued for 15 min. Total concentration of the polymeric mixture in solvent was kept at 5%. Films of polymer blends were prepared by casting the solution on the glass plate with slow drying at room temperature. Care was taken to control the uniform thickness of the film for
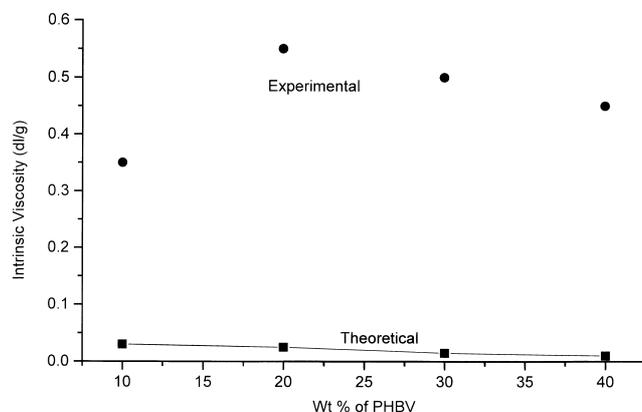
Figure 1. Intrinsic viscosities of EC/PHBV mixture versus composition.
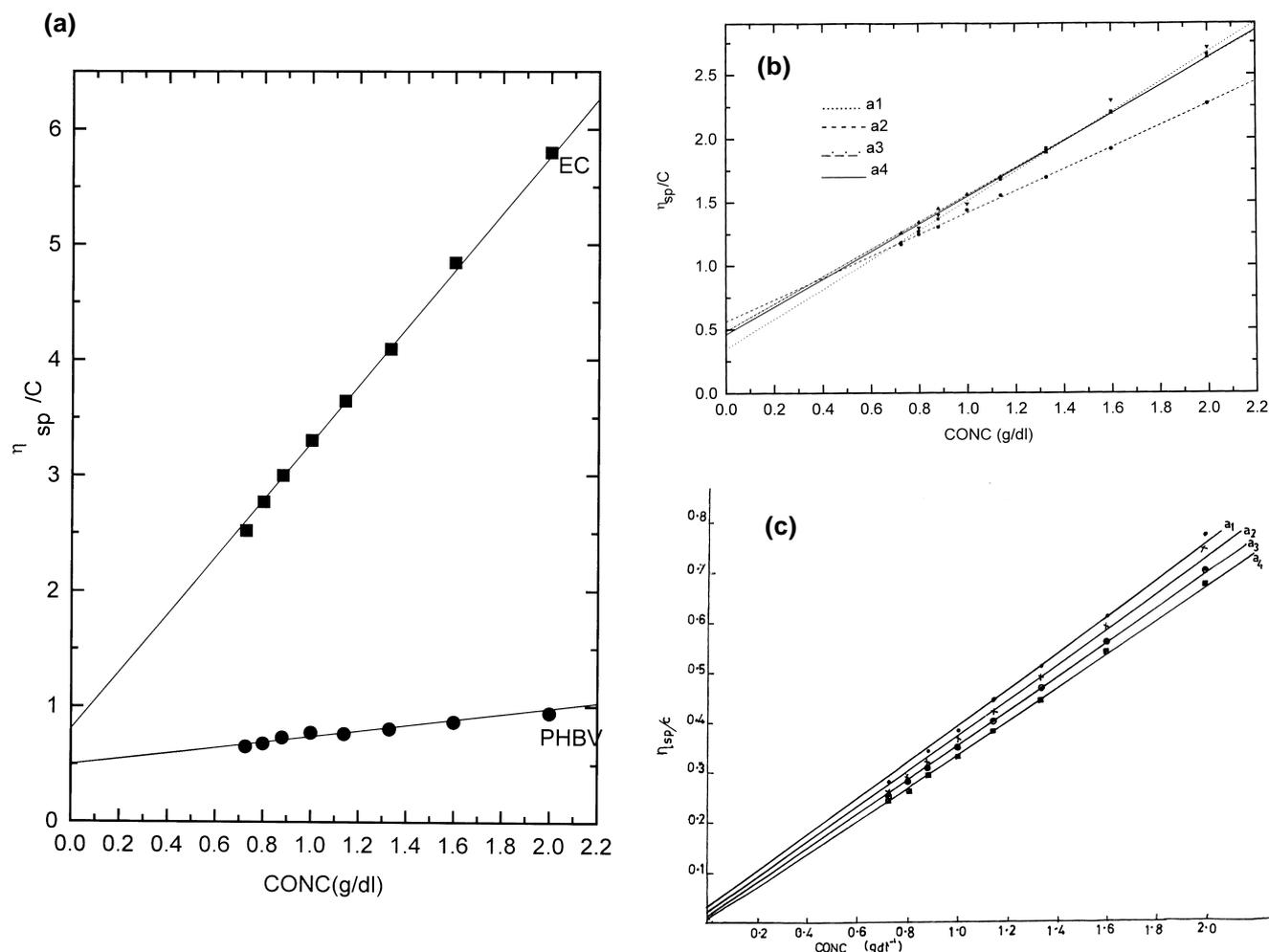
Figure 2. **a**. Reduced viscosity versus polymer concentration of EC and PHBV, **b**. reduced viscosity versus polymer concentration of a_1, a_2, a_3 and a_4 and **c**. theoretically calculated reduced viscosity versus concentration for a_1, a_2, a_3 and a_4.
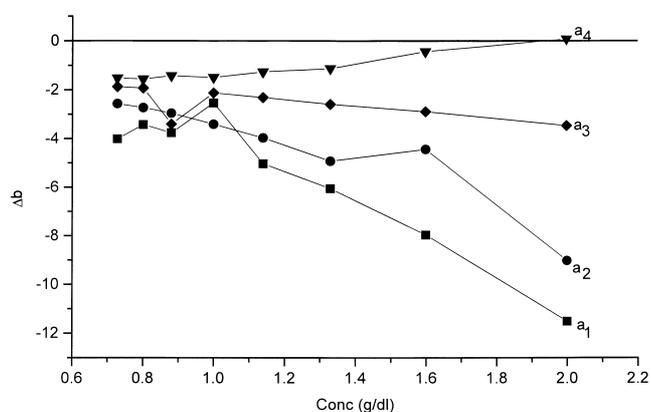
Figure 3. Δb versus concentration for the blends.

all compositions. The composition of the blends is given in table 1.

3.3 *Characterization*

The specific viscosities of the polymers and polymer blend were determined by Ubbelohde viscometer. The measurement was carried out in a closed system at 20°C to minimize solvent evaporation using chloroform as solvent.

IR spectroscopic information was obtained using Nicolet FT-IR and Shimadzu-14,000 Fourier transform infrared (FT-IR) instrument.

4. Results and discussions

The effect of the blend composition on intrinsic viscosities is illustrated in figure 1. The straight line plot of the

(a)

(b)

(c)

(d)

(e)
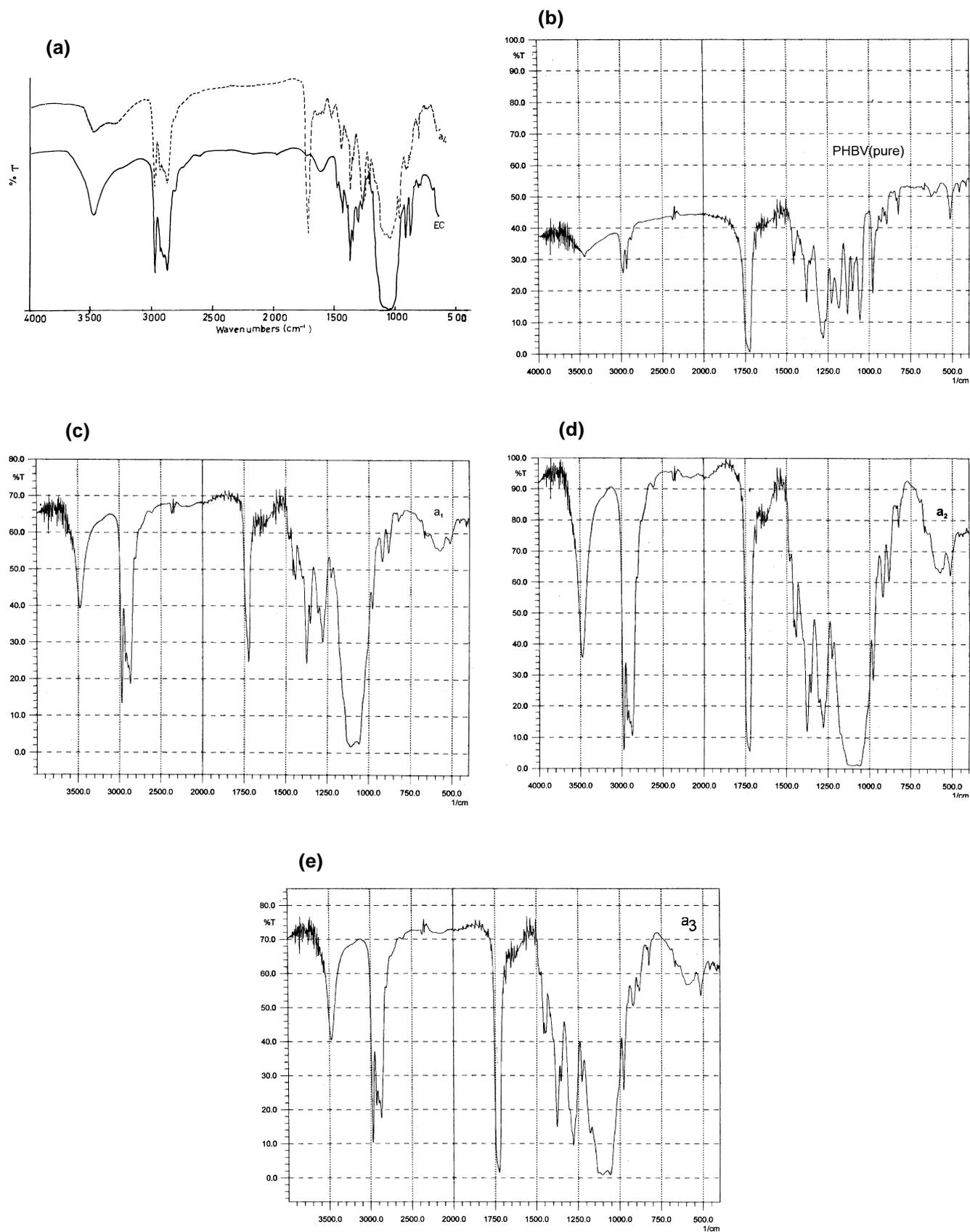
Figure 4. **a**. FT-IR spectra of EC and a_4, **b**. FT-IR spectrum of PHBV, **c**. FT-IR spectrum of a_1, **d**. FT-IR spectrum of a_2 and **e**. FT-IR spectrum of a_3.

intrinsic viscosities represents ideal solution systems. The intrinsic viscosity values obtained experimentally for present system were observed to be higher indicating net attractive interaction in the blends. For the blends with 90% (w/w) PHBV comparatively lesser deviation was observed indicating improved miscibility. However, with the increase of weight of PHBV, there is a sharp decrease in the intrinsic viscosity.

In figure 2a the reduced viscosities of pure PHBV and EC are plotted, whereas in figure 2b, the reduced specific viscosities for the various EC/PHBV blends and of homopolymers are presented. The same for ideally behaving compositions calculated from Castift and Hewtt (1962) (2) has been shown in figure 2c. For all the compositions, the experimentally observed reduced viscosities shown in the single plot in figure 2b and the theoretically calculated values differ in magnitude, but look very similar. The closeness of the results is due to the fact that these blends of EC and PHBV are dilute solution blends.

The plot of Δb versus concentration of the various blends are shown in figure 3. The negative values of Δb for all the blends indicate repulsive interaction between the phases of the blends except 0·6 : 0·4 blends at 2% concentration. However, with increase in concentration a sharp decrease in the Δb value is observed, indicating the existence of poor interaction between the phases of blend, here also exception is for 0·60 : 0·40 blends, in which there is sharp increase in the Δb value as observed at higher concentration indicating existence of attractive-interaction between the phases of the blends. At lower concentration all the blends are observed to deviate from their ideal behaviour.

The negative deviation from the ideal behaviour may be interpreted as a sign of decrease in polymer interaction. However, the overall rise in the viscosity observed experimentally is due to the dominance of polymer solvent attractive interaction over the polymer–polymer repulsion.

Thus, all the results from viscometric studies in terms of intrinsic, reduced specific viscosities and interaction between the polymer phases, indicate the immiscibility of the system except for the one composition (0·60 : 0·40 blend).

5. Spectroscopic studies

Fourier transform infrared (FT-IR) spectroscopy is used to study the formulation (Ferraro and Krishnan 1990) of ethyl-cellulose-PHBV blends. The FT-IR spectra show characteristic bands for ethyl cellulose. A representative FT-IR spectrum for ethyl cellulose is shown in figure 4a along with the corresponding spectra of pure PHBV blended in the ratio of 0·6 : 0·4 respectively. The spectrum of ethyl cellulose shows characteristic absorption

bands for –C–O–C– stretching vibration at 1052 cm^{-1} and C–H stretching bands at 2880 cm^{-1} and 2970 cm^{-1}. The absorption at 1369 cm^{-1} corresponds to C–H bending. The FT-IR spectrum of pure PHBV (figure 4b) shows its own characteristic absorption band from 800 cm^{-1} to 975 cm^{-1} and corresponds to symmetric –C–O–C– stretching vibration. On the other hand, the antisymmetric –C–O–C– stretching leads to bands between 1060 cm^{-1} and 1150 cm^{-1}. The absorption band at 1725 cm^{-1} is due to the C=O stretching in PHBV. The FT-IR spectrum of blend of EC and PHBV (0·6 : 0·4 wt/wt) depicted as a_4 shown in figure 4a exhibits almost all the features of both ethyl cellulose and PHBV as they individually show. The absorption peaks of ethyl cellulose at 1052 cm^{-1} due to C–O–C stretching and at 2880 cm^{-1} and 2970 cm^{-1} corresponding to C–H stretching may be easily observed apart from band at 3500 cm^{-1} owing to O–H stretching. The characteristic absorption bands from 1060 cm^{-1} to 1150 cm^{-1} are clearly visible in the blend. The typical absorption band at 1725 cm^{-1} caused by the C=O stretching of PHBV is also present in the blend. All the other blends i.e. a_1, a_2 and a_3 more or less show the similar observation of absorption bands in the figures 4c, 4d and 4e respectively except for the variation in the intensities of the bands due to difference in their composition. It may also be observed that there is practically no shift in the characteristic absorption bands EC and PHBV after blending showing incompatibility.

6. Conclusion

In general, PHBV shows incompatibility with ethyl cellulose both from viscosity measurements and also from spectroscopic studies. Only for a particular composition EC : PHBV (60 : 40), viscosity studies show attractive interaction indicating improved miscibility.

References

Bohmer B and Florian S 1970 *Eur. Polym. J.* **6** 471
Castift E H and Hewtt W A 1962 *J. Appl. Polym. Sci.* **6** 530, 962
Feldman D and Rusy M 1970 *Eur. Polym. J.* **6** 627
Ferraro J R and Krishnan K (eds) 1990 *Practical Fourier transform infrared spectroscopy* (New York: Academic Press)
Huggins M L 1942 *J. Am. Chem. Soc.* **64** 2716
Inamura I and Jinbo Y 1991 *Polym. J.* **23** 1143
Krigbaum W R and Wall F T 1950 *J. Polym. Sci.* **5** 505
Olabishi O 1975 *Macromolecules* **8** 317
Paul D R and Newman S 1978 *Polymer blends* (New York: Academic Press)
Raval Heta and Devi Surekha 1993 *Polym. J.* **25** 1215
Raval Heta and Devi Surekha 1995 *Die Ang. Makromol. Chem.* **227** 27