Optics and Spectroscopy, 2024, Vol. 132, No. 9

02

Temperature transitions in the polyvinyl chloride–polyvinyl butyral binary polymer system according to the data of IR spectroscopy

© D.I. Kamalova, O.A. Kochurova, M.K. Salakhov

Kazan Federal University,
Kazan, Russia

e-mail: dina.kamalova@kpfu.ru

Received August 27, 2023
Revised July 03, 2024
Accepted July 04, 2024

The crystallinity and glass transition of the polymer system based on polyvinyl chloride and polyvinyl butyral at different percentage of components were investigated by FTIR spectroscopy. Complex spectral contours were decomposed, and the temperature behavior of the structurally sensitive spectral components in the region of $500-800\,\mathrm{cm}^{-1}$ in the temperature range of $100-500\,\mathrm{K}$ was analyzed. The glass transition temperatures of the blends were determined from the temperature dependences of the optical densities of absorption bands of order for polyvinyl chloride. The compatibility of the blend components under study was shown by IR spectroscopy method, and the degree of crystallinity of the blends was determined.

Keywords: FTIR spectroscopy, polymer blend, glass transition, polyvinyl chloride, polyvinyl butyral, degree of crystallinity.

DOI: 10.61011/EOS.2024.09.60038.5520-24

Introduction

Ultrafiltration separating membranes are widely used for cleaning and desalinization of water; the major raw material for their fabrication are polymers, in particular, polyvinylchloride (PVC) [1–3]. However, PVC is a hydrophobic material, and its membranes are susceptible to serious contamination on the surface and in pores because of deposition and absorption of foreign substances. The use of PVC and polyvinyl butyral (PVB) mixtures is considered an efficient and cost-effective solution, since the material becomes hydrophilic and this allows obtaining products with better characteristics [4].

The quality of ultrafiltration membranes directly depends on physical and chemical properties of polymers from which they are made. The portion of the crystalline phase impacts mechanical properties, heat capacity, density of finished products, permeability of gases and liquids. Thus, in the ultrafiltration membranes made from a binary mixture of semi-crystalline PVC and amorphous PVB, the crystallites are themselves impermeable inclusions, and diffusion occurs through the amorphous regions [5]. Thus, the quality of membrane separation and the rate of diffusion depend on the degree of crystallinity.

There are no completely crystalline polymers, since there are always some defects and other inclusions in the crystalline lattice that impair the ordered structure of the material. Semi-crystalline polymers combine both, amorphous (disordered), and crystalline (ordered) regions. The degree of crystallinity (degree of ordering) indicates the content of crystalline regions in the polymer — the so-called crystallites. The fraction of crystalline regions depends on the structure and flexibility of the molecular chain, regularity of its structure, and is determined by the crystallization of the high-molecular compound [6–8]. The structure of semi-crystalline polymers is characterized by the presence of absorption bands in IR Fourier spectra, the spectral characteristics of which change with temperature variations. The dependence of intensity of the semi-crystalline polymer absorption bands on temperature varies: for some bands, the intensity increases with the growth of temperature, while for others, the intensity decreases until it disappears at a temperature of polymer melting. This makes it possible to attribute the structurally sensitive absorption bands to the amorphous and crystalline regions of the polymer.

Absorption bands where optical density grows with higher degree of crystallinity are called ordering bands, and bands with decreasing optical density are called disordering bands [9].

Another characteristic of polymers, which also affects the mechanical and transport properties of the membrane material, is the glass transition temperature. It sets a thermal interval within which the product becomes the most wear-resistant, durable and long-living product due to its ability to sustain large reversible deformations.

Three physical states of polymers are known: viscous-flow, highly elastic, and glassy, which depend on thermal transitions of various structural units in polymers. In the viscous-flow state an intense thermal motion of both, the segments and the macromolecules themselves occurs, which results in a disordering of the atomic groups arrangement; deformation in such polymers is irreversible. In a highly elastic state, only intense thermal motion of individual segments is possible, while the macromolecule remains stationary. Such state is distinguished by high values of reversible deformations. In the glassy state, neither motion of segments nor motion of the macromolecule itself occurs, however, there is a local molecular transition of fragments of the polymer chain. Such polymers are featuring a very slow deformation. The temperature when transition from the glassy state to the highly elastic one occurs is defined as a glass transition temperature T_g.

One of the ways to change the glass transition temperature is to add a foreign substance, e.g. another polymer, to the high-molecular compound. The glass transition temperature of the obtained binary mixture may be found using Fox equation [10]:

$$\frac{1}{T_{gb}} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}},$$

where T_{gb} — calculated glass transition temperature of the mixture, T_{g1} and T_{g2} — values T_g of individual compounds, W_1 and W_2 — corresponding mass fractions of polymers. It should be emphasized that Fox equation is applicable to fully compatible polymer components and, therefore, may be used to confirm the single-phase nature of the mixture.

Although most polymer pairs do not mix or mix only partially, some combinations, called compatible, have good mechanical, thermal, or other properties. To evaluate miscibility in different polymer–polymer systems the concept of Hildebrand solubility parameter is used [11–13]. According to this approach, compatibility will be observed if the difference in solubility parameters is small. Evaluation of PVC and PVB solubility parameters according to group contributions method [14] gives values 19.7 and 19.4 $(\mathrm{J/cm^3})^{1/2}$, respectively. If the difference between solubility parameters doesn't exceed 0.5 $(\mathrm{kal/cm^3})^{1/2}$, the polymers are considered fully compatible [14]. Since the difference in solubility parameters for PVC and PVB is about 0.15 $(\mathrm{kal/cm^3})^{1/2}$, thus, in theory they are considered as fully compatible.

The most common experimental criterion for polymer compatibility is the presence of a single glass transition temperature, which is between the glass transition temperatures of the components. If resolution of the glass transition temperature measurement is high enough, then, presence of a single glass transition temperature indicates the uniformity of the mixture at a molecular level. A different pattern is observed for mixtures of incompatible polymers, where phase separation is observed. In this study, the capabilities of FTIR spectroscopy method are used to study the crystallinity and compatibility of PVC and PVB mixtures with a different percentage ratio.

Experiment

Powder PVC with a molecular mass of $M_n = 4.7 \cdot 10^4$ and $M_w = 8 \cdot 10^4$ by SigmaAldrich and powder PVB (Butvar B-98) by SigmaAldrich were used for the study. Polymer film samples were obtained by dissolving PVC and PVB mixtures in various ratios in tetrahydrofuran. Binary mixtures of PVC and PVB were obtained by physically mixing the polymers. Mixtures with the following ratios were used: 80/20, 60/40, 50/50, 40/60, 20/80. The films were fabricated on KBr substrate. Polymer films were dried at 343 K for several hours to remove the solvent, as indicated by the absence of solvent absorption bands in the spectrum.

IR spectra were registered using Fourier transform spectrometer Frontier by Perkin Elmer within 4000–400 cm^{-1}. Specac thermostat is used to study the effect of temperature (higher than room temperature) on the structure of pure PVC and PVC/PVB mixture in the range of 303–523 K. In the range of 223–303 K the same nitrogen-cooled cryostat by Specac was used. We changed the temperature with an increment of 10 K, and in the range 323–373 K — with an increment of 5 K to define the glass transition temperature more precisely. The temperature measurement error was ±1 K.

Results and discussion

Fig. 1 illustrates the FTIR spectrum for the PVC/PVB mixture in the ratio 50/50. Structurally sensitive absorption bands of stretch vibrations C–Cl within the spectral range 500–800 cm^{-1} were used to analyze the crystallinity and glass transition of polymers [15]. Since the absorption bands strongly overlap in this spectral region, it was necessary to decompose all complex spectral contours into components, which was carried out using the least squares method. Using the first and second derivatives of the spectral function, the number and position of elementary contours were determined. This information was taken a priori. It should be noted that in the spectral range 500–800 cm^{-1}, in addition to the absorption bands of PVC, very weak absorption bands of PVB 743 and 578 cm^{-1}, lying on the wings of the main components of the contour, fall into the spectral range. Thus, in the FTIR spectrum of PVC/PVB mixture within the region of 500–800 cm^{-1} the following elementary components were found: positions of maxima

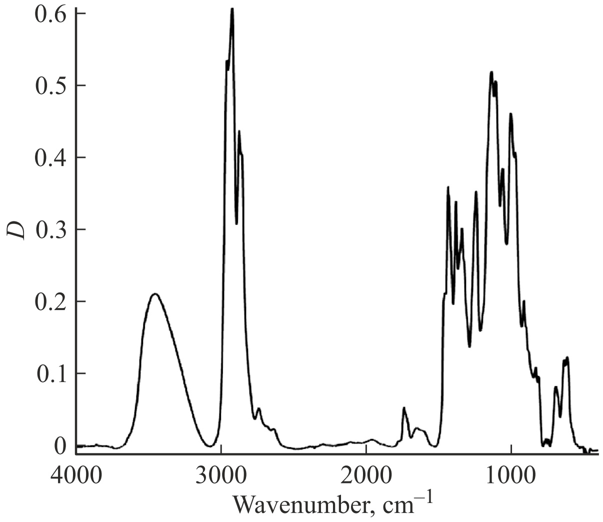

Figure 1. FTIR spectrum of 50/50 PVC and PVB mixture film fabricated from tetrahydrofuran solution.

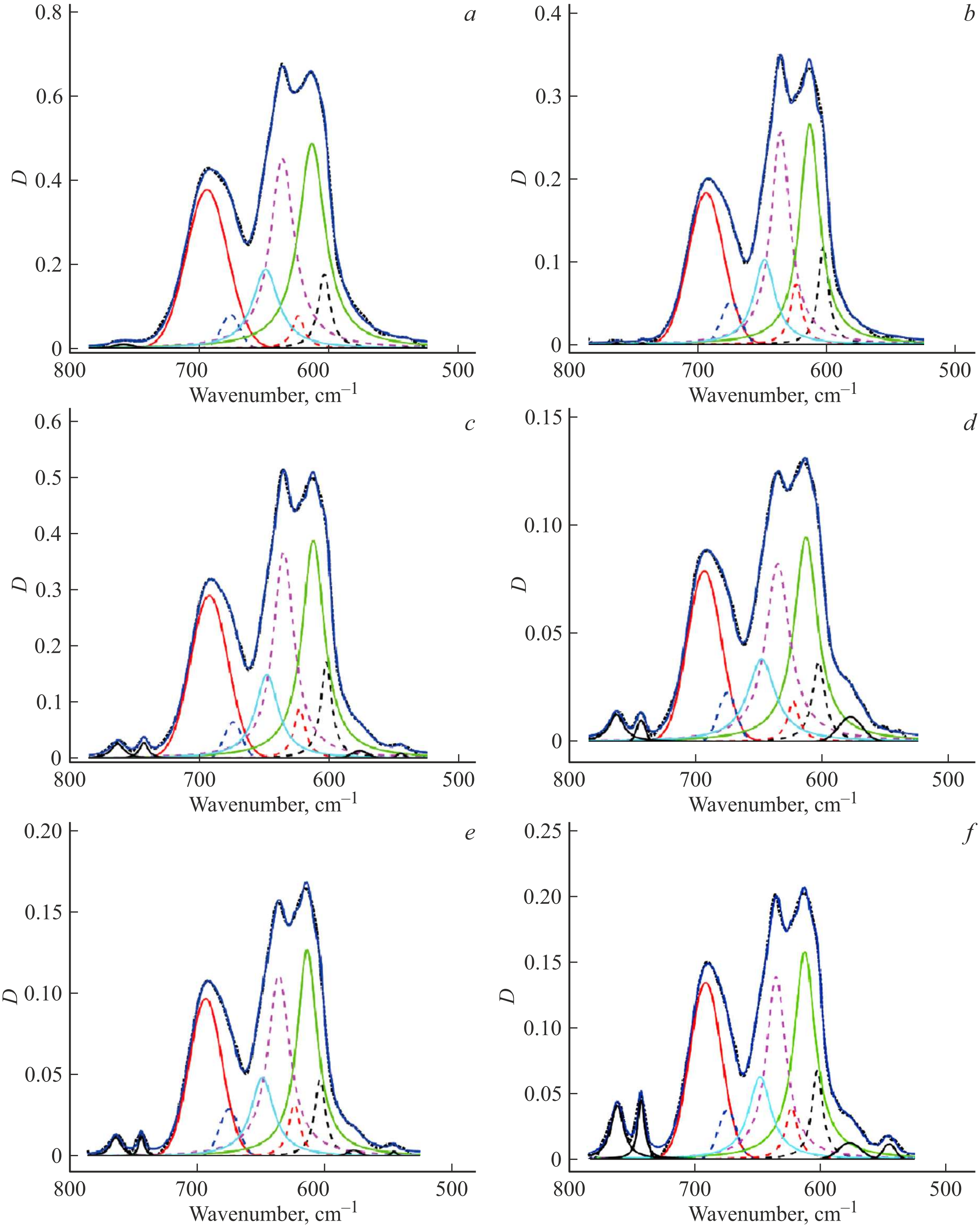

Figure 2. Fragments of FTIR spectra in 500–800 cm^{-1} region for PVC/PVB polymer mixtures: 100 : 0 (*a*), 80 : 20 (*b*), 60 : 40 (*c*), 50 : 50 (*d*), 40 : 60 (*e*), 20 : 80 (*f*) at 303 K.

at 540, 578, 603, 613, 623, 636, 649, 676, 693, 743, 758 cm^{-1}. The contribution of low-intensity components at 540, 578, 743, and 758 cm^{-1} located on the wings of the main components is very small, although they were taken into account during decomposition.

Various combinations of Gaussian and Lorentz components were considered, and the optimal combination of Gaussian and Lorentz elementary contours was selected, where almost an exact match of the original experimental and reconstructed contours was achieved. It should be

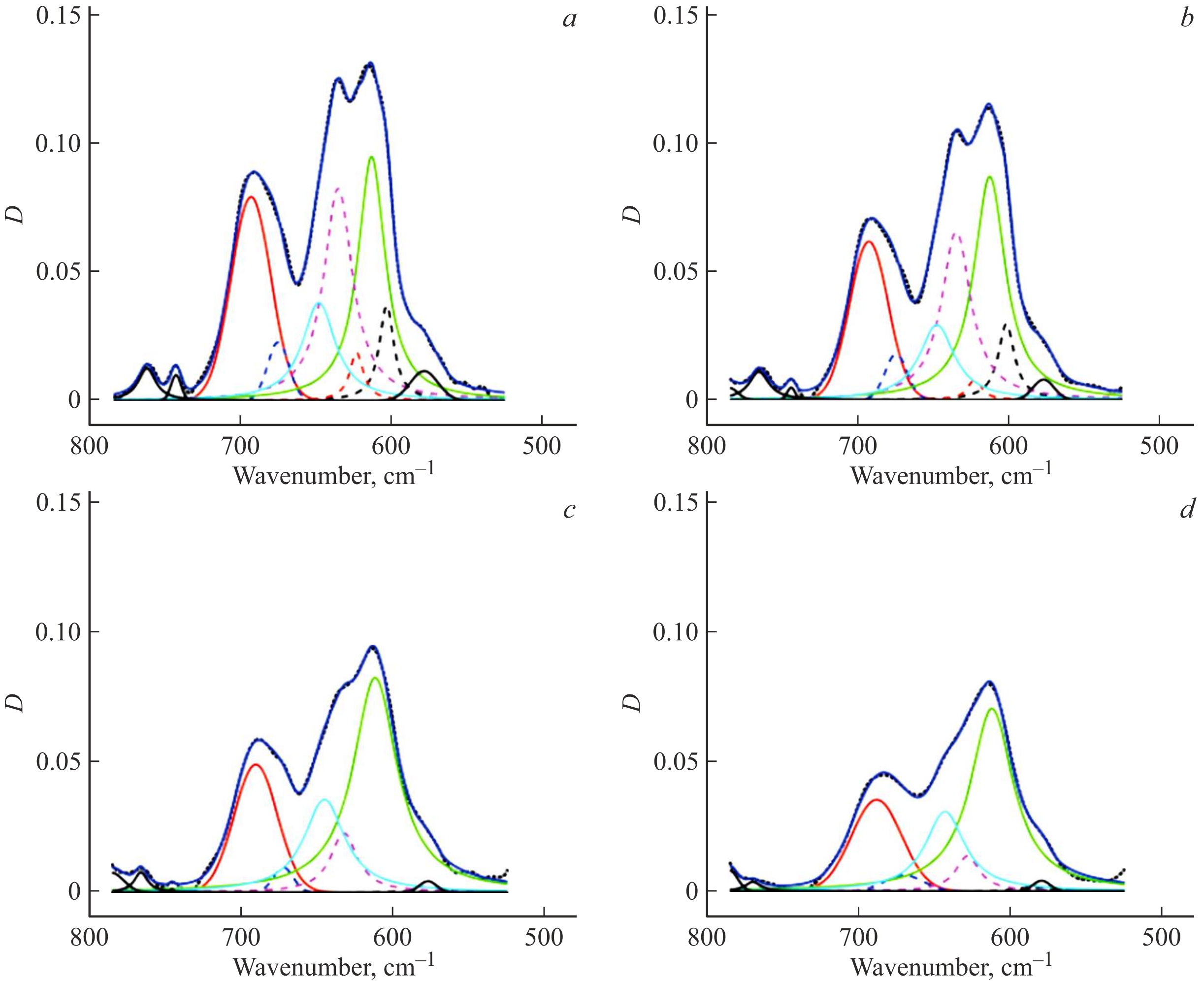

Figure 3. Fragments of FTIR spectra of 50 : 50 PVC/PVB mixture at temperatures: 303 (*a*), 373 (*b*), 453 (*c*), 523 K (*d*).

noted that this combination of contour shapes was stable for spectra in both low-temperature and high-temperature regions. The best match of the experimental and reconstructed contours was achieved when approximated by Lorentz contours with maxima at 604, 613, 624, 636 and 649 cm^{-1} and Gaussian contours with maxima at 694 and 676 cm^{-1}. This mathematical analysis was performed for all temperature spectra of PVC/PVB systems of various percentage compositions (Fig. 2).

To identify absorption bands sensitive to changes in the supramolecular structure of the PVC/PVB polymer system, temperature changes in FTIR spectra in the range 500−800 cm^{-1} were studied. Fig. 3 illustrates as an example the fragments of FTIR spectra of PVC/PVB mixture (50/50) at different temperatures. As can be seen, with a change in the temperature of the mixture sample, a change in the intensities of the contour components is observed.

In paper [16] it was demonstrated for an individual PVC that optical densities of absorption bands 636 and 604 cm^{-1} decrease with the heating of a sample, while optical densities of 613 and 649 cm^{-1} bands increase with the rise of the temperature. This confirms that bands 636, 604 cm^{-1} are attributed to the crystalline phase of individual PVC, and bands 613, 649 cm^{-1} — to the amorphous phase and complies with the data [9] in terms of ordering and disordering bands of semi-crystalline polymers. The ordering bands 636 and 604 cm^{-1} correspond to the stretch vibrations ν(C−Cl) and relate to the symmetry types A_1 and B_1 respectively, the disordering bands 613 and 649 cm^{-1} also correspond to the stretch vibrations ν(C−Cl) [6].

As for the studied PVC-PVB mixtures, the decomposition of complex contours into components and the analysis of temperature dependences of their optical densities showed that they are also characterized by similar changes in the optical intensities of the analyzed absorption bands with temperature. Fig. 4 illustrates ordering band optical density versus temperature at 636 cm^{-1} for all studied PVC/PVB systems. The curves have sharp bends that illustrate the samples temperature transitions. For individual PVC, the temperature corresponding to such curve bend is close to the glass transition temperature of PVC, which allowed us to attribute this temperature transition to glass transition. For all studied PVC/PVB mixtures,

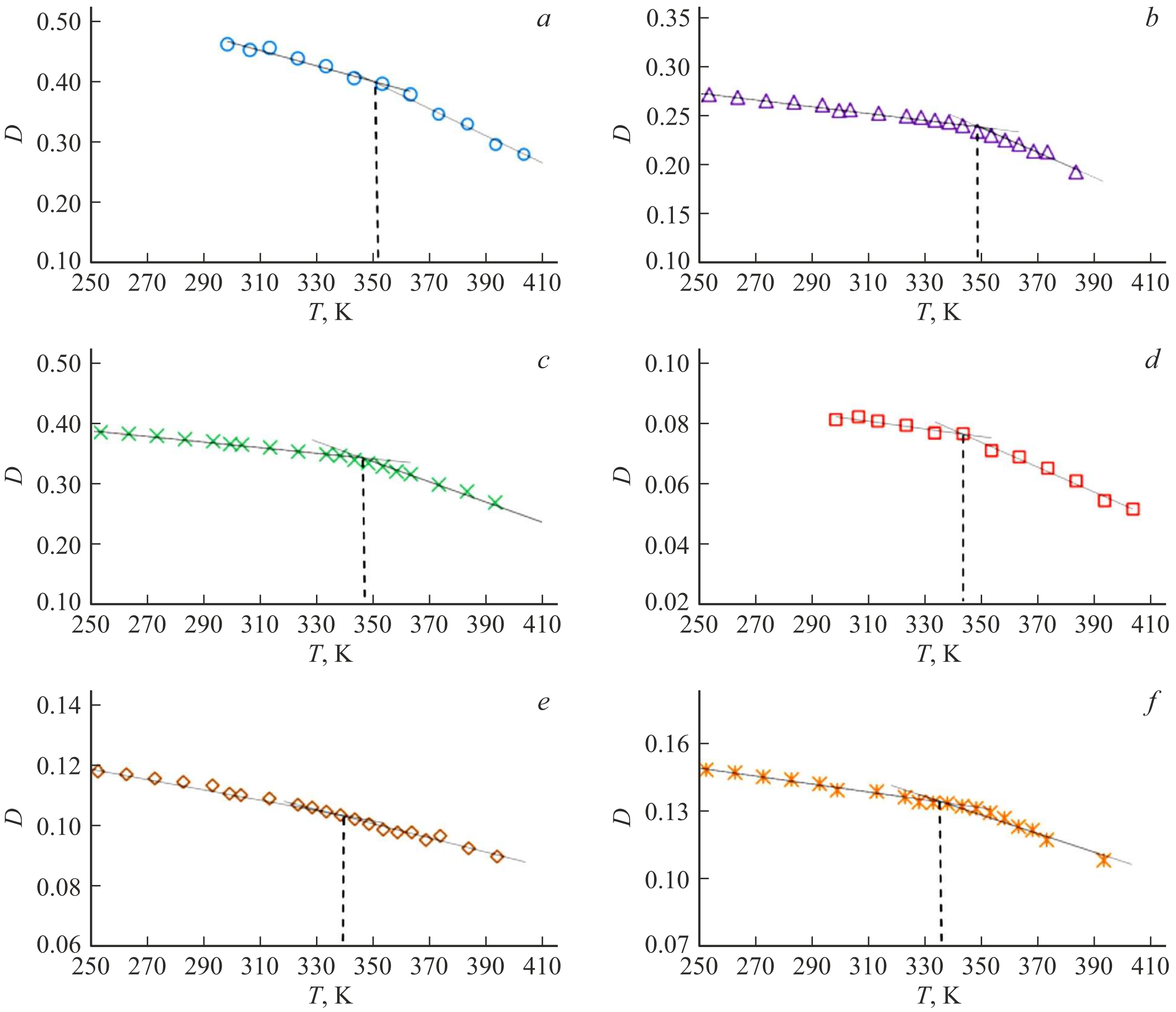

Figure 4. Temperature dependencies of optical density of 636 cm^{-1} absorption band for PVC/PVB mixtures in ratios: 100 : 0 (*a*), 80 : 20 (*b*), 60 : 40 (*c*), 50 : 50 (*d*), 40 : 60 (*e*), 20 : 80(*f*).

Table 1. Glass transition temperatures T_g for PVC/PVB mixtures

PVC fraction, wt.%	100	80	60	50	40	20	0
T_g, K	353	348	346	343	338	335	330

Table 2. Degree of crystallinity (%) for mixtures of PVC with PVB with different mass fraction of PVC at temperature 303 K

PVC fraction, wt.%	100	80	60	50	40	20
For band 613 cm^{-1}	42.0 ± 0.5	37.8 ± 0.4	25.8 ± 0.2	25.3 ± 0.1	23.5 ± 0.4	14.9 ± 0.1
For band 649 cm^{-1}	40.8 ± 0.5	37.1 ± 0.5	24.4 ± 1.0	25.8 ± 0.4	23.6 ± 0.5	15.8 ± 0.2
Average for two bands	41.4	37.4	25.1	25.5	23.6	15.3

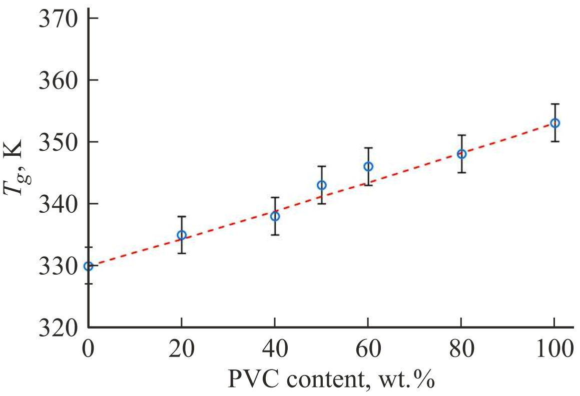

Figure 5. Glass transition temperature for PVC/PVB mixtures of various percentage. The dotted line corresponds to the dependence of the glass transition temperature on composition, as expressed from Fox equation for fully compatible polymers.

the observed bends in the curve of the ordering band optical density versus temperature were used to determine the glass transition temperature of mixtures of different percentages. The temperatures T_g are given in Table 1. The error of determination of the glass transition temperature was ± 3 K. As can be seen from the table, the glass transition temperature of polymer mixtures shifts towards lower temperatures as the content of PVB in the mixture increases. The presence of an amorphous high-molecular compound can increase the free volume of the system and, as a result, lower the glass transition temperature of the mixture.

Figure 5 shows the dependence of the glass transition temperature on the percentage composition of the PVC/PVB mixture, and also shows the glass transition temperature of PVC/PVB mixtures calculated using Fox equation, assuming that all components are fully compatible. PVC/PVB glass transition temperatures were assumed equal 353 and 330 K respectively. The values of glass transition temperatures calculated and obtained experimentally by IR spectroscopy are in good agreement. Thus, we may make a conclusion that the mixture components are compatible in terms of thermodynamics.

Based on the integral optical density of the disordering bands 613 and 649 cm^{-1}, relating to PVC amorphous phase, we assessed the degree of PVC/PVB mixtures crystallinity for various percentages. At the same time, assuming the amorphous part fraction in the melt to be equal to unity, the fraction of the amorphous part at a temperature of 303 K was determined as the ratio of the optical densities of the absorption band at a temperature of 303 K and at a temperature of the melt (453 K). Since optical densities of two disordering bands were used, the degree of crystallinity was determined as the average of two values. In Table 2 the calculated degrees of crystallinity for all studied mixtures are provided. It can be seen that with a decrease in the PVC content in the mixed systems, the degree of crystallinity decreases, i.e. addition of amorphous PVB reduces the proportion of ordering regions in the studied mixtures.

Conclusion

In this paper, FTIR absorption spectra of mixtures of semicrystalline and amorphous polymers of different percentages were studied for a wide temperature range. Analysis of PVC disordering bands intensity versus temperature allowed defining the glass transition temperatures of PVC/PVB mixtures in the ratios of 100/0, 80/20, 60/40, 50/50, 40/60, 20/80. At that compatibility of the mixtures components is shown. The degree of crystallinity of mixtures of different percentages was determined using IR absorption bands related to the amorphous phase of PVC. Thus, knowledge of the polymer mixtures critical parameters, such as glass transition temperature and degree of crystallinity that affect the permeability of separating membranes, makes it possible to forecast an optimal material composition for the mixed ultrafiltration membranes.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] A. Tausif, G. Chandan. J. Water Process Eng., **45**, 102466 (2022). DOI: 10.1016/j.jwpe.2021.102466

[2] H. Yu, H. Chang, X. Li, Z. Zhou, W. Song, H. Ji, H. Liang. J. Membr. Sci., **630**, 119320 (2021). DOI: 10.1016/j.memsci.2021.119320

[3] H. Xu, H. Liu, Y. Huang, C. Xiao. J. Membr. Sci., **620**, 118905 (2021). DOI: 10.1016/j.memsci.2020.1189.05

[4] L. Chi, J. Wang, T. Chu, Y. Qian, Z. Yu, D. Wu, Z. Zhang, Z. Jiang, J.O. Leckie. RSC Adv., **6**, 28038 (2016). DOI: 10.1039/c5ra24654g

[5] M. Mulder. *Vvedenie v membrannuyu tekhnologiu* (Mir, M., 1999) (in Russian).

[6] M. Hedenqvist, U.W. Gedde. Prog. Polym. Sci., **21** (2), 299 (1996). DOI: 10.1016/0079-6700(95)00022-4

[7] A.Kh. Malamatov, G.V. Kozlov, A.K. Mikitaev Higher school Severo-kavkazskiy region. Ser. Estestv. Nauki, **S1**, 41 (2006) (in Russian).

[8] J. Leisen, H.W. Beckham, M.A. Sharaf. Macromolecules, **37** (21), 8028 (2004). DOI: 10.1021/ma0489974

[9] I. Dekhant. *Infrakrasnaya spektroskopia polimerov* (Khimiya, M.,1976) (in Russian).

[10] A. Mushtaq, H.B. Mukhtar, A.M. Shariff. Procedia Eng., **148**, 11 (2016). DOI: 10.1016/j.proeng.2016.06.448

[11] B. Sanchez-Lengeling, L.M. Roch, J.D. Perea, S. Langner, C.J. Brabec, A. Aspuru-Guzik. Adv. Theory Simul., **2** (1), 1800069 (2019). DOI: 10.1002/adts.201800069

[12] C. Wang, W. Luan, Z. Zeng, H. Wang, L. Sun, J.H. Wang. J. Macromol. Sci. Part B, **61** (1), 92 (2022). DOI: 10.1080/00222348.2021.1971370

[13] J. Zhu, R. Balieu, H. Wang. Road Mater. Pav. Design., **22** (4), 757 (2021). DOI: 10.1080/14680629.2019.1645725

[14] D.W. van Krevelen. *Properties of polymers: their correlation with chemical structure; their numerical estimation and prediction from additive group contributions* (Elsevier, Amsterdam, 2009).

[15] A.Kh. Kuptsov, G.N. Zhizhin. *Furier spektri kombinatsionnogo rasseyania* (Fismatlit, M., 2001) (in Russian).

[16] D.I. Kamalova, O.A. Kochurova, M.E. Sibgatullin. Izv. RAN. Ser. fiz., **86** (12), 1731 (2022) (in Russian). DOI: 10.31857/S0367676522120146 [D.I. Kamalova, O.A. Kochurova, M.E. Sibgatullin. Bull. Russ. Acad. Sci. Phys., **86** (12), 1473 (2022). DOI: 10.3103/S1062873822120127].

Translated by T.Zorina