

Characterization Of Polymer Blends With FTIR And UV-VIS Spectroscopy

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Abstract

The commercial application of polymer blend technology has grown significantly such that, today, compositions are available with properties that once were substantially unattainable with homopolymers. We prepared blends of Polysulfone and Poly (methyl methacrylate) with various compositions Fourier Transform Infrared (FTIR) spectroscopy was utilized to study the interaction between two polymers and to analyze the type of bonding present. No shift in the characteristic peaks of PMMA and PSF is seen in the FTIR spectra of PSF/PMMA blends. This indicates that the two polymers are immiscible. The UV-VIS spectroscopy measurements were carried in the wavelength range of 800–200 nm.

Keywords: *Fourier Transform Spectroscopy; Immiscible ; UV-VIS Spectroscopy; Blends*

1. Introduction

The Polymer blends are generally defined as mixtures of at least two polymers or copolymers that may be either homogeneous or heterogeneous at the molecular level. Number of polymeric components that comprise a blend is often designated by an adjective such as binary, ternary or quaternary. Manufacturer of polymer blends has opened an exciting new direction for modification of the structure and physical properties of these materials, while extensive academic research and commercial interest have together led to the development of many applications for these materials. The process of blending of different polymers provide the ability to adapt new types of polymers varying in order to obtain products with physical and chemical properties of various essential and optimally for use in applications required . Molecular structure and the way in which the overlap of the molecules in the solid state are the most important factors that affects the characteristics of the macroscopic and microscopic blending of these polymers.

The miscible polymer blends show homogeneity down to the molecular level and are associated with a negative free energy of mixing, whereas immiscible polymer blends are heterogeneous at the molecular scale and are associated with a positive free energy of mixing. Three different types of blend can be distinguished: completely miscible blends; partially miscible blends; and fully immiscible blends. As the gain in mixing entropy is negligible due to the high molecular weight of polymer, and the mixing is endothermic in the majority of cases, miscible polymer blends are usually an exception. In fact, few miscible blends have been identified recently. Most polymer blends form immiscible blends, revealing a prominent interface. It is generally observed that most compatible blends are immiscible. The major reason for blending polymers is economics; typically, a material can be produced at a lower cost but have the desired synergistic properties that meet the required specifications.

There are three main reasons for formulating polymer blends: (1) To develop materials with a full set of desired properties.(2)To obtain a high performance through synergetic interaction. (3) To adjust the composition of the blend, as per the requirements of customer specifications that satisfies their end use.

In recent years, extensive efforts have been made to characterize various useful properties of the Polymer Blends (PBs) and the PBs matrices-based Polymer Nano Composites (PNCs) with the aims to explore their tunable character of optical, dielectric, as well as thermo-mechanical parameters that could help in the design guidelines for the creation of advanced electronic and optoelectronic devices.

Recent literature surveys reveal an increasing number of polymers, copolymers and blends that are being considered as potential materials that can be used to modify membrane morphology; The blending technique not only provides

improved chemical and thermal stability but is also efficient enough to improve the permselective properties with economical viability. Polymer blending with amines is considered as time and cost effective method to develop materials with desirable properties. A number of glassy and rubbery blend membranes are reported in literature e.g., PC/PSF), PU/PVAc, PS/PPO and PBI/Matrimid [1-8]

The commercial application of polymer blend technology has grown significantly such that, today, compositions are available with properties that once were substantially unattainable with homopolymers. To date, polymer blends have been applied in optical fibers, microlenses, liquid crystal display components, solar cells nonionizing radiation detection and polymer light-emitting diodes. In particular, the use of developed polymer blends in optoelectronics applications appears unlimited [9–12],

Polysulfone (PSF) is a polymer thermoplastic material having high thermal stability and good mechanical strength. It is tough, rigid, high strength, and transparent, retaining its properties between -100°C and $+150^{\circ}\text{C}$. The density of PSF is 1.24 g/cm^3 . Its glass transition temperature is about 185°C . PSF is used in electrical and electronic applications, medical components requiring repeated sterilisation, microwave cookware and under bonnet and aerospace components. Its resistance to high temperatures gives it a role of a flame retardant. PSF gets their name because of *sulfone* groups in their backbone chains. PSF polymers have high glass transition temperature due to high stiffness of sulfone. Polysulphone (PSF) also contains bisphenol-A moiety in its backbone.

The PMMA is a low-cost amorphous material, and its solution cast film has several excellent properties like high optical clarity, low refractive index, lightweight, high mechanical strength, good environmental inertness, and attractive dimensional and thermal stabilities. The amorphicity of the PMMA matrix is due to the presence of bulky ester functional group as a pendant in its chain backbone. It is a promising polymer matrix and frequently used for the development of a wide range of superior properties materials usable for sensors, solar cells, optical switches, optical fiber, transparent neutron stoppers, and radar wave magnifiers.

The chemical composition and interactions between the functional groups in a polymer blend can be obtained directly by using Fourier transform infrared (FTIR) spectroscopy. The technique has been made more versatile as a characterization tool and provide a deeper analysis of the local structure and the dynamics of blends under different environmental conditions. The measurement of FTIR spectra from polymeric samples is relatively rapid and straightforward; indeed, the technique provides high-precision, accurate and reproducible measurements that are accepted for most industrial and research purposes.

Infrared radiation is that part of the electromagnetic spectrum which lies between the visible and microwave regions. Although it is invisible, infrared variation makes a highly visible contribution to analytical chemistry. Infrared radiation is absorbed by organic molecules and converted into energy of molecular vibration, either stretching or bending. Although polymers are complex macromolecules their vibrational spectra are relatively simple where bands in the spectrum may be largely assigned on the basis of characteristic stretching and deformation vibrations of the specific group that comprise the polymer [13].

The physical property that is measured in infrared spectroscopy is the ability of some molecules to absorb the infrared radiation. Only those vibrations that result in the change of molecular dipole and having absorption frequencies in the infrared region of the spectrum absorb infrared radiation. By using characteristic absorption frequencies it is easy to identify the presence of functional groups in unknown compounds. These characteristic absorptions can sometimes used to show the purity of the sample.

Until now, numerous experiments have been conducted to investigate the relationship between the energy of electromagnetic radiation and matter, the aim being to characterize the properties of polymers and their blends. The techniques applied have included nuclear magnetic resonance (NMR) spectroscopy, ultraviolet/visible (UV/VIS) spectroscopy, mass spectroscopy, Raman spectroscopy, and infrared (IR) spectroscopy. Accordingly, spectroscopy is considered as one of the most popular techniques in modern laboratories. In particular, UV/VIS spectroscopy, as pioneered by Beckman in 1940, is one of the oldest and still widely used instrumental

techniques. Recently, however, there has been somewhat of a revival in UV spectroscopy, with many new techniques, instruments and data processing methods having been developed.

We have prepared blends of PMMA and PSF of different compositions. In this paper, we have reported the characterization of Polysulfone, poly (methyl methacrylate) and polysulfone/poly (methyl methacrylate) (PSF/PMMA) polymer blends by FTIR and UV-VIS measurements have also been done .

2. Experimental

Sample preparation

Polysulphone (PSF) supplied by Gharda Chemicals Ltd. Bharuch, Gujarat (India) and poly (methyl methacrylate) or (PMMA) supplied by Hi Media Laboratories Pvt. Ltd., Mumbai (India) were used for the study.

For Preparing the samples thin films of PMMA, PSF and PSF/PMMA blends were prepared by solution cast method. Blends of PSF/PMMA in the ratio, 10:90, 30:70, 50:50, 70:30, 90:10 were prepared. In order to prepare the blends of polysulphone and PMMA in variable proportions, the granules of PMMA and PSF were dissolved in common solvent i.e. dichloromethane, and stirred thoroughly for a few hours to ensure mixing. Stirred solution was then put into flat-bottomed Petri dishes floating on mercury. The solvent was allowed to evaporate slowly over a period of 10–12 h. The films (thickness ~ 100 μ m) so obtained were peeled off and dried in vacuum for 24 h in order to ensure the removal of the solvent. The cast films of PSF/PMMA blends were opaque in the entire composition range.

Fourier Transform Infrared Spectroscopy (FTIR)

Conventional infrared spectrometers are double beam instruments. This means there are two radiation beams, one passing through the sample and the other passing through a reference-, which can be air. A detector compares the energy that is transmitted by the sample with the radiation that is passing through the reference. From the difference the spectrum is then plotted. In Fourier transform infrared spectroscopy (FTIR) only one beam is used and all the required frequencies passed through the instrument at once. It is called FTIR spectroscopy because a mathematical treatment-Fourier transformation- is used to interpret the data and produce a spectrum. FTIR is a fast, sensitive technique and is used both to gather

information about the structure of a compound and as an analytical tool to assess the purity of a compound [14–15]. FTIR spectra (400–4000 cm^{-1}) were acquired on a FTIR-IR Prestige 21 (Shimadzu) spectrometer at a 4 cm^{-1} resolution, and 50 scan in absorbance mode.

UV/VIS Spectroscopy

The UV/VIS measurements were carried out on a UV – 1601 PC spectrophotometer (Shimadzu) in absorption mode in the wavelength range of 800–200 nm.

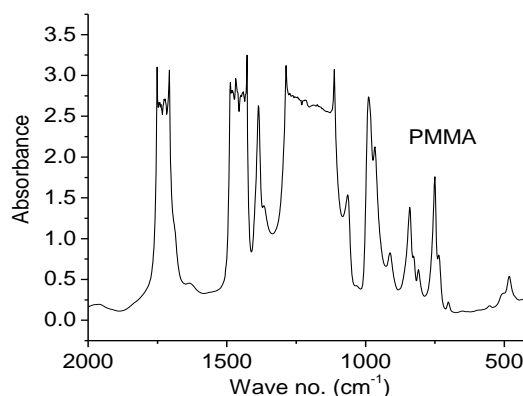
3. Results and discussion

FTIR measurements

Xie *et. al.* studied the miscible and immiscible blends of PS/PVME by FTIR spectroscopy. They separately reported that the miscible PS/PVME blends showed strong evidence of molecular interaction. Whereas no interaction was detected for phase-separated PS/PVME blends [16].

Figure 1 (a) shows the FTIR spectra of PMMA film. The peak centered at 1707 cm^{-1} is attributed to the C=O stretching vibrations in the pendant group (–COOCH₃) of PMMA. An absorption band in the range of 1500–700 cm^{-1} comes from the C–O stretching vibration (1285–990 cm^{-1}), C–H bending vibration (1480–1350 cm^{-1}) and CH₂ rocking vibration (810 cm^{-1} and 750 cm^{-1}) [17].

Figure 1 (b) shows the IR spectra of PSF film. The absorption bands, corresponding to the methyl group of the bisphenol group A appeared at 1362.5 and 1385.6 cm^{-1} . The absorption due to the asymmetric stress vibration of the S=O band appeared at 1275 cm^{-1} , and that of the symmetric stress appeared at 1139 cm^{-1} . At 2875 cm^{-1} , the absorption band characteristics of C-CH₃ bond appeared. The band centered at 694 cm^{-1} represented the phenyl group vibration.



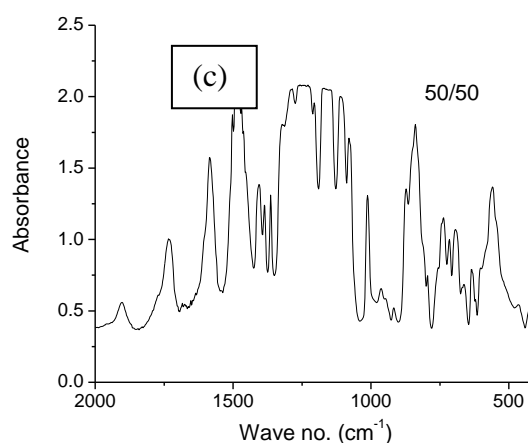
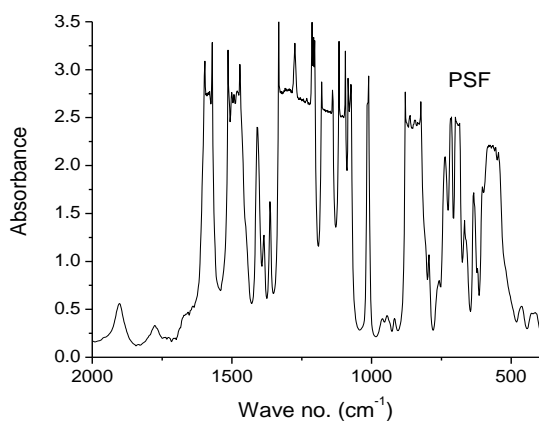


Figure 1: FTIR Spectra (a) PMMA, (b) PSF

Figure 2 shows the FTIR spectra of PSF/PMMA blend with varying composition. It is apparent in all the spectra that the carbonyl peak gets deformed in the blend. However, for 30/70 (PSF/PMMA) blend, deformation is not there but intensity has increased, change in intensity with PSF composition in the blend is observed. Deformation of carbonyl peak is an indication of presence of weak interaction in the interfacial regions.

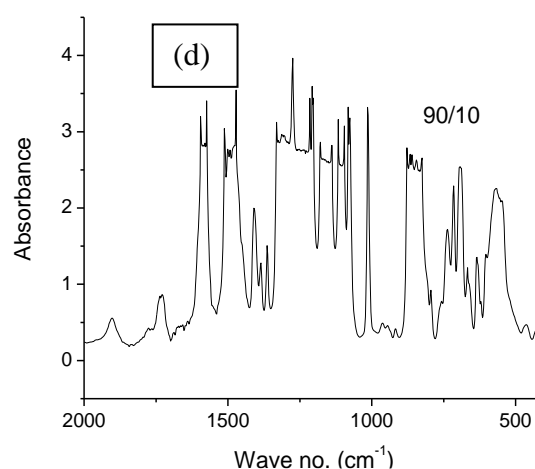
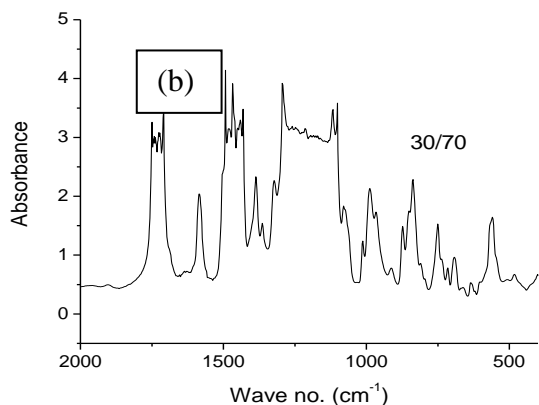
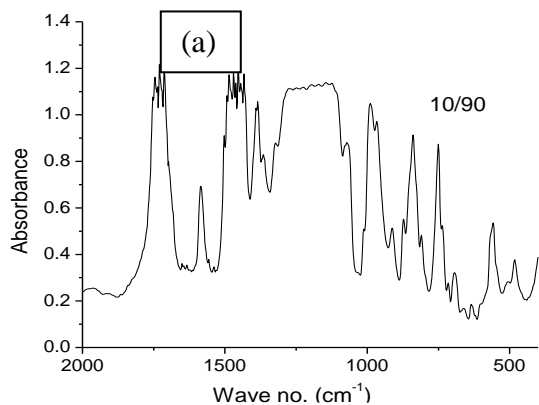


Figure 2: FTIR Spectra of PSF/PMMA Blends (a) 10/90, (b) 30/70, (c) 50/50, (d) 90/10



The absorption peak due to asymmetric stress vibration of S=O band appears as shoulder for 10/90, 30/70, 50/50, PSF/PMMA blends whereas it appears as intense peak for 90/10 blend. The absorption band at 694 cm^{-1} appears in 10/90 (PSF/PMMA) blend and its intensity is found to increase with increase of PSF composition in the PSF/PMMA blend.

No shift in the characteristic peaks of PMMA and PSF is seen in the FTIR spectra of PSF/PMMA blends. This indicates that the two polymers are immiscible. Khurma *et. al.* [18] found no shift in the characteristic peaks of immiscible blends of poly (lactic acid) and poly (vinyl butyral). Hung *et. al.* found no evidence in standard fourier transform infrared spectra for a specific interaction between PC and PMMA and characterized PMMA/PC blend as immiscible blend [19].

UV-VIS Measurements

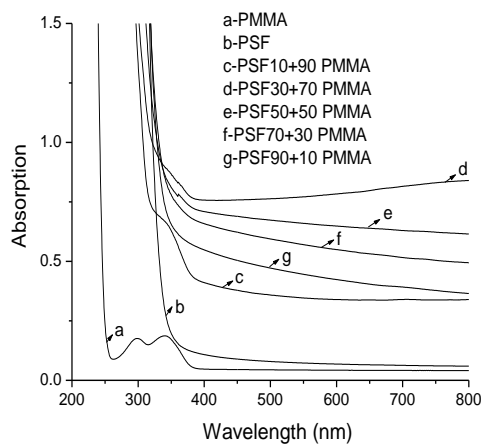


Figure 3. Absorption curves for PSF/PMMA

Figure 3 gives the UV/VIS spectra of virgin samples and PSF/PMMA blends. It can be seen from the figure that a strong increase in absorbance appears in the ultraviolet and visible region for PSF/PMMA blends. Shift of absorption edge towards longer wavelength with increasing percentage of PSF in the blends can be readily observed. The increase in absorption may be attributed to the presence of interfacial and co-continuous phases as the blends are immiscible.

Two absorption peaks have been observed for PMMA in UV/Visible region around 298 nm and 341 nm. With increase in percentage of PSF in the blend samples the peak at 298 nm disappeared and the peak at 341 nm broadened and shifted to longer wavelength up to 30% PSF. For 50% PSF and higher concentration both the peaks disappear and slight decrease in absorbance is observed.

4. Conclusion

It is apparent in all the spectra that the carbonyl peak gets deformed in the blend. However, for 30/70 (PSF/PMMA) blend, deformation is not there but intensity has increased, change in intensity with PSF composition in the blend is observed.. No shift in the characteristic peaks of PMMA and PSF is seen in the FTIR spectra of PSF/PMMA blends. FTIR results indicate weak interaction in the blends in interfacial regions. It is concluded from the study that PSF/PMMA blends are immiscible for selected compositions. Change in optical absorption has also been observed due to blending .This increase in absorption may be attributed to the presence of interfacial and co-continuous phases as the blends are immiscible.

This characterization will help in the use of these blends for different applications.

References

1. Lloyd, D.R., 1985. Membrane Materials Science: An Overview. In: Lloyd, D.R. (Ed.), Materials Science of Synthetic Membranes. ACS Symposium Series 269. American Chemical Society, Washington, DC, pp: 1-21.
2. Xu, Z.L. and F.A. Qusay, 2004 J. Appl. Polym. Sci., 91: 3398.
3. Yoo, M., S. Kim and J. Bang, 2013, J. Polym. Sci. Pol. Phys., 51(7): 494-507.
4. Acharya, N.K., V. Kulshrestha, K. Awasthia, A.K. Jaina, M. Singha and Y.K. Vijay, 2008, Int. J. Hydrogen Energ., 33(1):327.
5. Tanwar A, Gupta K K, Singh P J & Vijay Y K, Bull Mater Sci, 29, 2 (2006) 181.
6. Bahri R & Sood B R, Thin Solid Films, 100 (1983) L5
7. Mehendri P C, Agrawal J P & Jain K, Indian J Pure & Appl Phys, 34 (1996) 101.
8. Rawat A, Mahavar H K, Chauhan S, Tanwar A and Singh P J, Indian J Pure & Appl Phys, 34 (1996) 101.
9. Jouannet, D. and Pham, T.-N. (1997) Polymer, 38, 5137.
10. Demeuse, M.T. and Jaffe, M. (1990) Polym. Adv. Technol., 1, 181.
11. Ogo, H., Yamanari, T., Taima, T., Sakai, J., Tsukamoto, J., and Yoshida, Y. (2011) Physics Procedia, 14, 231.
12. Moore, J.R., Albert-Seifried, S., Rao, A., Massip, S., Watts, B., Morgan, D.J., Friend, R.H., McNeill, C.R., and Sirringhaus, H. (2011) Adv. Energy Mater., 1, 230.
13. Changlong L, Zhiyong Z, Youmeri S, Mingdong H, Zhiguang W, Yanbin W, Chonghong Z, Xiaoxi C, Jia L and Baoquan L, Nuclear Instrument and Method in Physics Research B, 169 (2000) 78.
14. Kumar R, Prasad R, Vijay Y K Acharya N K, Verma K C and Udayan De, Nuclear Instruments and Methods in Physics Research B, 212 (2003) 221.
15. Kulshrestha V, Awasthi K, Acharya N K, Singh M, Bhagwat P V, Vijay Y K, Polymer Bulletin, 56 (2006) 427.
16. Xie R, Yang B and Jaing B, J. Polym. Sci., Part B : Polym. Phys., 33 (1995) 25.
17. Choi H W, Woo H J, Hong W, Kim J K, Lee S K and Eum C H, Applied Surface Science, 169-170 (2001) 433.

18. Khurma J R, Rohindra D R and Devi R, The South Pacific Journal of Natural Science, **23** (2005) 22.
19. Hung C C, Carson W G and Bohan S P, J. Polym. Sci. Part B : Polym. Phys., **32** (1994) 141.