ELSEVIER

polymer

Polymer 40 (1999) 2465–2468

Polymer Communication

The study of miscibility and phase behaviour of phenoxy blends using Raman spectroscopy

Yanling Ward*, Yongli Mi

Department of Chemical Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

Received 6 March 1998; revised 10 June 1998; accepted 11 June 1998

Abstract

The miscibility and phase behaviour of poly(hydroxy ether of bisphenol-A) (phenoxy)/poly(methyl methacrylate) (PMMA) blends were investigated using Raman microscopy. It was shown that while phenoxy/PMMA blends prepared by casting from chloroform at room temperature are immiscible, the blends prepared at high temperature are miscible. The Raman technique revealed the shift of the PMMA carbonyl stretching band in the miscible blends and its absence in the immiscible blends. This may be explained by the presence of specific interactions between the groups in phenoxy and PMMA due to the increased chain mobility during the mixing at high temperature. The changes of the special features in the Raman spectra were found to be useful in identifying different phase structures and their compositions in the blends. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Raman spectroscopy; Phenoxy/PMMA blends; Miscibility

---

1. Introduction

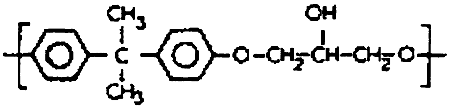
Polymer blending is one of the common methods used for improving existing polymers and developing new polymer materials. Blending may be carried out by either solution casting or by melt mixing. A lot of work has shown that phenoxy resin exhibits miscibility with a number of polymers like polyoxides [1], polyester [2], [3], polyether [4], poly(vinyl pyrrolidone) (PVPr) [5] and poly(methyl methacrylate) (PMMA) [6], [7]. Chiou and Paul [6], and Soh [7] showed that phenoxy/PMMA blends prepared by melt mixing at 260°C are miscible over the entire composition range and exhibit lower critical solution temperature (LCST) behaviour at around 300°C. Erro et al. [8] found that the injection temperature can affect the blend miscibility; blend miscibility can only be achieved by mixing at well above 180°C. Goh et al. [9] showed that phenoxy is also miscible with poly(2,2-dichloroethyl methacrylate) (PDCEMA), but has an immiscible window with the copolymer DCEMA–MMA. All the studies mentioned above suggested [1], [2], [5], [7] that the formation of hydrogen bonds between the hydroxyl groups in the phenoxy and carbonyl, carbonate and ether groups in the other components in the system is energetically favourable to the mixing process and is the driving force for the observed miscibility in the blends.

In the past, FTIR has been a common technique for studying polymer blends, particularly concerning their miscibility and specific interactions. With recent improvements in instrumentation, Raman spectroscopy is becoming more routinely used for polymer analysis. The Raman technique can be applied to polymers as received or in film, powder, solution and bulk form so that little or no sample preparation is needed.

In this paper the effect of preparation methods, and solvent and thermal history on the miscibility of phenoxy with PMMA is investigated using Raman microscopy. Some preliminary results of this study are presented.

2. Experimental

PMMA with M_w of 100 000 was purchased from Polysciences, and poly(hydroxy ether of bisphenol-A) (phenoxy)



$$\left[-C_6H_4-C(CH_3)_2-C_6H_4-O-CH_2-CH(OH)-CH_2-O- \right]$$

with M_w of 65 000 was synthesized and provided by S. Zheng. Phenoxy/PMMA blends of various compositions were made via solution casting from chloroform. The blends of 0, 10, 30, 50, 70, 90, and 100 wt% of PMMA were prepared by dissolving in chloroform and mixing for a few days

---

* Corresponding author.

PII: S0032-3861(98)00446-7

and then casting on clean glass slides at room temperature. The solvent was evaporated slowly, and then the films were dried in a vacuum oven at room temperature for 72 h, or at a high temperature of 120°C for 2 h to remove the residual solvent.

The Raman spectra were obtained from a Renishaw (model 3000) Raman spectrometer coupled with an OLYMPUS BH2 optical microscope. An exciting wavelength of 632.8 nm was provided by a 25 mW He–Ne laser source. The laser power at the sample was kept below ~1 mW to avoid degradation problems or peak shifts due to overheating effects. The laser was focused to a 2 μm diameter spot on the sample using a 50 × objective lens. The spectral and spatial resolutions were 2 cm^{-1} and 1 μm, respectively. The Raman spectra were collected and recorded using a Peltier cooled charge-coupled device (CCD) detector with an exposure time of about 30 s. The Raman spectra obtained were analyzed using a Lorentzian function to determine the band intensities and positions.

3. Results and discussion

The miscibility of the polymer blends can be determined by the existence of a single glass transition temperature, T_g, as a function of blend composition on the DSC thermograms as well as optical clarity of the blends [10]. For the phenoxy/PMMA system being studied, the glass transition temperatures of phenoxy and PMMA are 100 and 105°C, respectively. Taking into account the resolution of the instrument and the glass transition width, the determination of a single T_g could not be used for the evaluation of the blend miscibility in such a system. All the blends prepared at room temperature are observed to be translucent or opaque, suggesting phase separation and a heterogeneous nature of the blends.

Fig. 1 shows Raman spectra for PMMA and phenoxy in the range 1000–3200 cm^{-1}. Distinctive differences between PMMA and phenoxy can be observed from their Raman spectra in the 1550–1800 cm^{-1} region. PMMA shows a Raman band at 1730 cm^{-1}, which is attributed to the stretching mode of the carbonyl groups, while phenoxy shows a 1610 cm^{-1} band, which is ascribed to the stretching mode of the phenyl rings. Only the Raman band at 1730 cm^{-1} appears in pure PMMA while only the Raman band at 1610 cm^{-1} appears in pure phenoxy. Mixed phase of phenoxy/PMMA blends shows both Raman bands at 1610 and 1730 cm^{-1}. The intensity ratio of Raman bands at 1610 and 1730 cm^{-1} is a function of composition in the blends. One of the advantages of the Raman technique in studying polymer blends, particularly phase separation, is its microsampling capability. Thin films of all the blends were observed under an optical microscope in transmission. Fig. 2(a) and Fig. 3(a) show the optical micrographs of the phenoxy blends containing 10 and 50 wt% PMMA, both of them showing phase separation with a multi-phase structure. Raman spectra of each phase of the different phase structures allow each phase to be identified and the differences in polymer composition can also be determined from the intensity ratio of Raman bands at 1610 and

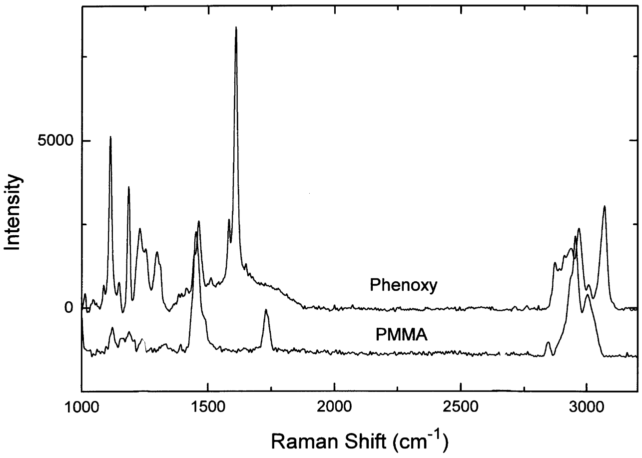


Fig. 1. Raman spectra of PMMA and phenoxy obtained in the range 1000–3200 cm^{-1}.

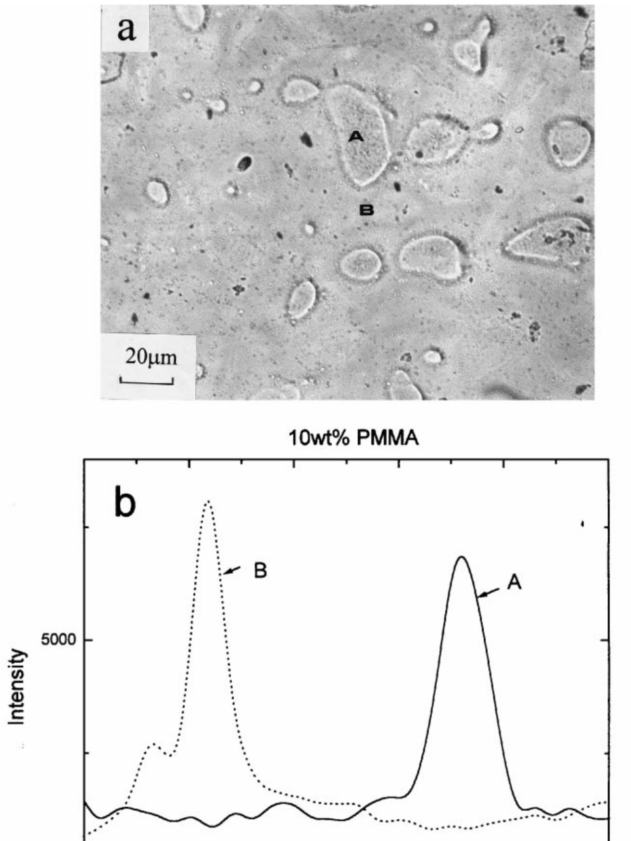


Fig. 2. (a) Optical micrograph of phenoxy blend containing 10 wt% PMMA; (b) Raman spectra obtained in the different phases corresponding to the optical micrograph.

1730 cm^{-1}. Fig. 2(b) shows the Raman spectra obtained from different phases in the phenoxy blend containing 10 wt% PMMA, corresponding to the optical micrograph shown in Fig. 2(a). No mixed phenoxy/PMMA domains are found. Fig. 3(b) shows the Raman spectra from the phenoxy blend containing 50 wt% PMMA, corresponding to those phases shown in Fig. 3(a). No pure PMMA and pure phenoxy phases are observed. Three different mixed phenoxy/PMMA domains exist and their compositions can be indicated from the difference in the intensity ratio of Raman bands at 1610 and 1730 cm^{-1}. It appears that the level of mixing between phenoxy and PMMA improves as the amount of PMMA in the blends increases although complete miscibility is not achieved.

It is known that the Raman band at 1730 cm^{-1} is due to the carbonyl stretching groups in the PMMA and it is sensitive to intermolecular interactions. The shift of this band region is an indication of the presence of hydrogen bonding between the hydroxyl groups in phenoxy and the carbonyl groups in PMMA. By contrast, no obvious shifts were detected from the Raman spectra in the carbonyl stretching region around 1730 cm^{-1} for all the blends, supporting the visual observation of immiscible blends. It is no surprise, since the *k* value of the Gordon–Taylor equation for such a system was found by Soh [7] to be only 0.3, suggesting a very weak specific interaction between phenoxy and PMMA. It has also been indicated by FTIR [7] that the interaction between phenoxy and PMMA is much weaker than the self-associated hydroxyl groups of phenoxy. It is therefore reasonable to suggest that slight changes in the blend preparation methods or other underlying factors could affect significantly the miscibility. The blend miscibility could also be influenced by the choice of solvents [11]. Chloroform as casting solvent could compete for intermolecular interaction with the polymers. The existence of a hydrogen bond structure supplies the possibility of miscibility; however, other factors such as solvent, molecular weight, and thermal history may also affect the phase structure of the blends obtained.

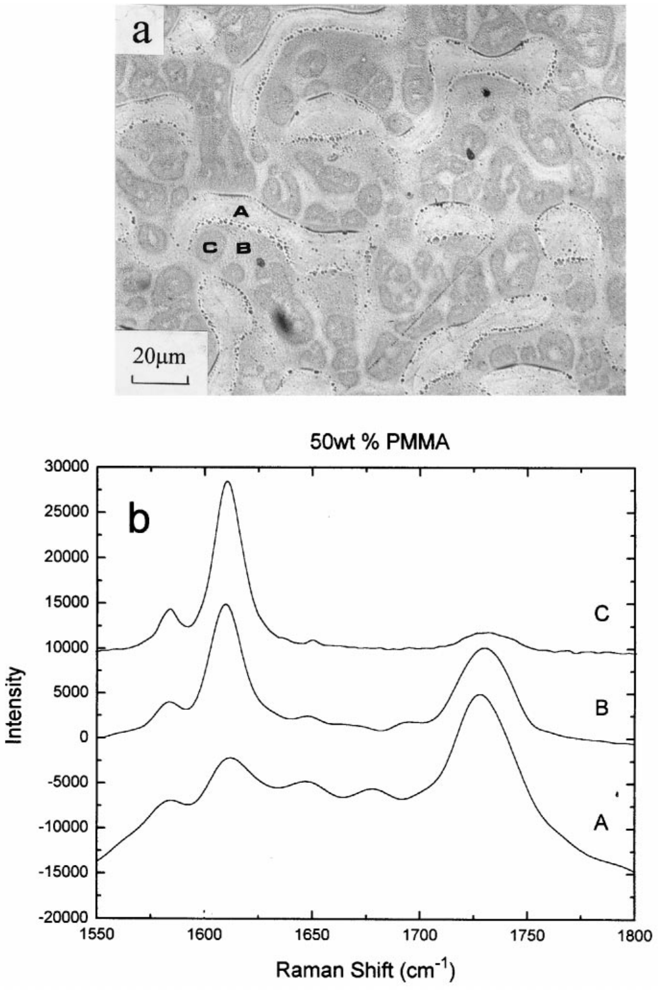


Fig. 3. (a) Optical micrograph of phenoxy blend containing 50 wt% PMMA; (b) Raman spectra obtained in the different phases corresponding to the optical micrograph.

All the phenoxy/PMMA blends were also prepared at a high temperature of 120°C, which is above the T_g values of both polymers. They were observed to be transparent, suggesting a macroscopically homogeneous structure in the blends. It implies that a greater degree of mixing can be achieved from the preparation of blends at high temperature. Fig. 4 shows Raman spectra in the carbonyl stretching region for pure PMMA and phenoxy/PMMA blends. It can be seen that there is an apparent shift of the Raman band at 1730 cm^{-1} towards lower frequency as the amount of phenoxy

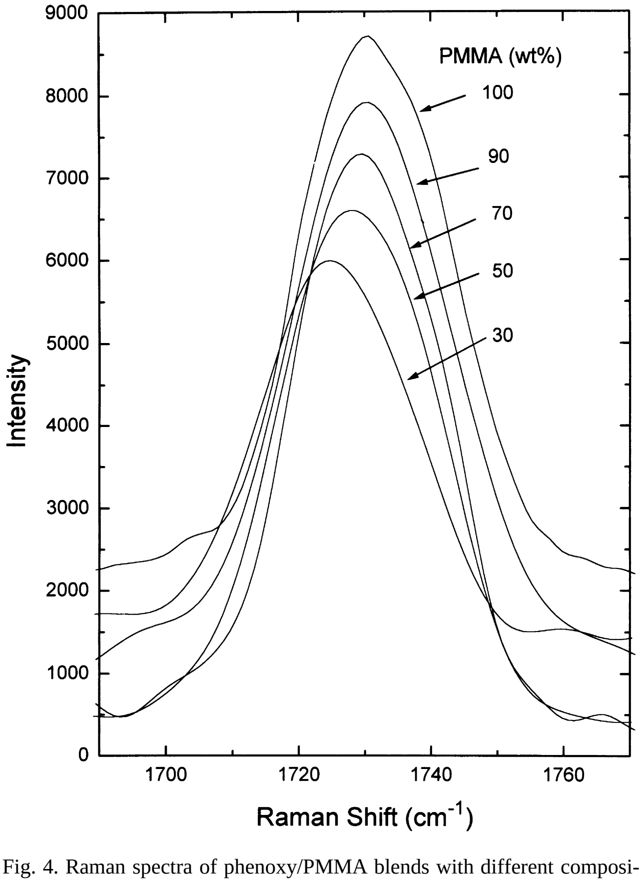


Fig. 4. Raman spectra of phenoxy/PMMA blends with different compositions in the carbonyl stretching region.

increases. It is likely that the increased chain mobility at higher temperature makes it possible to form hydrogen bonds between the hydroxyl group of phenoxy and the carbonyl group in PMMA. At high temperature (above T_g of the polymer), there is sufficient energy to disrupt the self-associated hydroxyl groups in phenoxy. Most importantly, chain mobility of the polymers is significantly improved so that the functional groups are more accessible for participating in the intermolecular interactions. Dong and Ozaki [12] showed that the fraction of hydrogen bonding is increased dramatically after PVPh/PMMA blends were heat treated at a temperature above T_g.

4. Conclusions

It is demonstrated that Raman spectroscopy is a very promising and powerful technique for detailed characterisation of polymer blends. It can not only detect the phase and composition of the blends, it can also provide information on the existence of specific interactions in the blends. The present study shows that the blends prepared at room temperature are immiscible, whereas the blends prepared at high temperature are miscible. The difference lies in the existence of a specific interaction between phenoxy and PMMA, which is responsible for the miscibility.

Acknowledgements

This work was supported financially by HongKong Chroucher Foundation (grant no. CF 95/96 EG04). The authors would also like to acknowledge the technical help with the Raman work from Jason Squire of the Materials Characterisation and Preparation Centre at HKUST.

References

[1] Fernandez-Berridi MJ, Valero M, Martinez de Ilarduya A, Espi E., Iruin JJ. Polymer 1993;34 (1):38.
[2] Coleman MM, Moskala EJ. Polymer 1983;24:251.
[3] Harris JE, Goh SH, Paul DR, Barlow JW. J Appl Polym Sci 1982;27:3038.
[4] Robeson LM, Hale WF, Merriam CN. Macromolecules 1981;14:1644.
[5] Eguiazabal JI, Iruin JJ, Cortazar M, Guzman GM. Makromol Chem 1984;185:1761.
[6] Chiou JS, Paul DR. J Appl Polym Sci 1991;42:279.
[7] Soh YS. J Appl Polym Sci 1992;45:1831.
[8] Erro R, Gaztelumendi M, Nazabal J. J Appl Polym Sci 1992;45 (2):339.
[9] Goh SH, Lee SY, Low SM. Macromolecules 1994;27:6736.
[10] Olabisi O, Robeson LM, Shaw MT. Polymer–polymer miscibility. New York: Academic Press, 1979.
[11] Lu S, Pearce EM, Kwei TK. Polym Eng Sci 1995;35:1113.
[12] Dong J, Ozaki Y. Macromolecules 1997;30:286.