



## POLYVINYL CHLORIDE –POLYMETHYL METHACRYLATE MICRO-COMPOSITE POLYMERS: MISCIBILITY

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### Abstract

AC electrical conductivity and dielectric constants are measured at different temperatures (323K, 333K, 343K and 353K) and at the different frequencies (1KHz to 1MHz) using 4284 LCR meter (Agilent Technologies, Singapore). It is found that ac conductivity of thin film decreases with increase in temperature for all values of frequencies and it increases with increase in frequencies at constant temperature. The dielectric constants, also, increases with the increasing of the temperature of blends. In this blends the miscibility exists, as evidenced by FTIR spectroscopy.

**Keywords:** 4:1 (PVC+PMMA), AC conductivity, dielectric constants, miscibility.

### I. INTRODUCTION

Polymer blending is one of the most important contemporary ways for the development of new polymeric materials. Before 36 years Schurer *et al* [1] studied the addition of methyl methacrylate and its polymer (PMMA) to improve the thermal and mechanical properties of PVC, who concluded that PVC was partially miscible with atactic and syndiotactic PMMA but almost completely immiscible with isotactic PMMA. Polymethyl methacrylate (PMMA), also known as acrylic, offers glass-like properties for the production of soft and flexible elastomers, rigid thermoplastics, and thermosets. Co-extruders of acrylic on PVC are widely used for manufacturing window profiles, eaves, gutters, downpipes, and facade elements. Nunes and Peinmann [2], Belsare and Deogaonkar [3] reported on the theory of electrical conduction and experimental findings have appeared in a number of such blends. The conductivity studies on PVC/PMMA polymer blend electrolytes have shown that the polymer component would render stability [4]. Shukla and Gupta [5] studied the AC electrical conduction of polymethyl methacrylate (PMMA) and polyethyl methacrylate (PEMA) using dielectric data in the frequency range of  $10^2$ - $10^5$  Hz and temperature regions of 311-337 K and 89-114 K.

This present paper attempts to show the miscibility existing between Polyblends. In this work, PVC and PMMA were taken in the ratio 4:1 by weight and prepared the polyblends thin films using spin coating method. AC electrical conductivity and dielectric constants have been measured at different temperatures for the different frequencies. The structural studies' such as FTIR, XRD and SEM of this polymer composite is reported.

### II. EXPERIMENTAL

Polymethyl methacrylate (PMMA) in granule form obtained from Otto Kernl, Mumbai and PVC is prepared by the polymerization of vinyl chloride. Tetrahydrofuran (THF-E-Merck India Ltd., Mumbai) is being as a solvent for polyblending process. In the present work, thin films were prepared by isothermal evaporation technique [6,7].

The ac frequencies were applied (in the range 1 KHz –1 MHz) across the sample by using the 4284 A precision LCR meter (20 Hz –1 MHz) (Agilent Technologies, Singapore). The corresponding dielectric constants were measured and AC conductivity of the samples was calculated by using the following relation [6-8]:

$$\sigma_{ac} = \frac{f \cdot \epsilon' \cdot \tan(\delta)}{1.8 \times 10^{10}}$$

Where,

f = Frequency applied in Hz

$\epsilon'$  = Dielectric Constant at frequency f

$\tan \delta$  = Dielectric loss tangent.

### III. RESULTS AND DISCUSSION

#### III.1 Fourier transform infrared spectroscopy (FTIR) studies

Fourier transform infrared (FTIR) spectroscopy is one of the widely used optical methods to study the interaction of electromagnetic radiation in the infrared region with chemical compounds. The FTIR spectrum of pure PVC polymer in the frequency range 400 – 4000  $\text{cm}^{-1}$  is shown in **Figure 1 (a)** which spectrum is quite similar to the reported by Subban and Arof [9]. Vibrational bands of PVC are obtained at 2974  $\text{cm}^{-1}$  ( $\nu_{\text{C-H}}$  of CHCl), 2912.9  $\text{cm}^{-1}$  ( $\nu_{\text{as}}$ , C–H of  $\text{CH}_2$ ), 1435.9  $\text{cm}^{-1}$  ( $\nu_{\text{w}}$ ,  $\text{CH}_2$ ), 1334.1  $\text{cm}^{-1}$  ( $\delta$ , C–H of CHCl), 1257.6  $\text{cm}^{-1}$  ( $\delta$ , C–H of CHCl), 1068  $\text{cm}^{-1}$  ( $\nu$ (C–C)), 966  $\text{cm}^{-1}$  ( $\nu_{\text{r}}$ ,  $\text{CH}_2$ ), 698  $\text{cm}^{-1}$  ( $\nu$ , C–Cl), 638  $\text{cm}^{-1}$  ( $\nu$ (C–Cl)) and 616  $\text{cm}^{-1}$  ( $\nu$ , C–Cl).

**Figure 1 (b)** which is FTIR spectrum of pure PMMA, it is observed from the spectrum reported by Saikia and Kumar [10] is similar to our spectrum. Peak at 749  $\text{cm}^{-1}$  corresponds to out of plane C–H bending. Broader and stronger bands in the region 1300-1000  $\text{cm}^{-1}$  correspond to C–O stretching vibrations, which usually consists of two asymmetric coupled vibrations. i.e. C–C (=O)–O and O–C–C. At approximate 1025  $\text{cm}^{-1}$  ether lone pair peak is also present. The bands at 1387.2 and 1456.2  $\text{cm}^{-1}$  correspond to symmetrical bending vibration ( $\nu_{\text{s}}$   $\text{CH}_3$ ) and asymmetrical bending vibration ( $\nu_{\text{as}}$   $\text{CH}_3$ ) of methyl group, respectively. Strong peak appearing in the region 1730.14  $\text{cm}^{-1}$  corresponds to C–O stretching vibrations. Two distinct bands appeared at 2978.4 and 2877.8  $\text{cm}^{-1}$ , the first band arises from the asymmetrical (as) stretching mode in which two C–H bonds of the methyl group are extending, while the third one is contracting ( $\nu_{\text{as}}$   $\text{CH}_3$ ) and the second band arises from symmetrical (s) stretching ( $\nu_{\text{s}}$   $\text{CH}_3$ ) in which all three of the C–H bonds extend and contract in phase.

**Figure 1 (c)** which is FTIR analysis of the 4:1 (PVC+PMMA) blends shows small shifting of the carbonyl band of PMMA to lower wave numbers. The shift of the peak is about 4–6  $\text{cm}^{-1}$  within the domain of miscibility of the two polymers. The miscibility of PVC/PMMA blends is due to a specific interaction of hydrogen bonding type between carbonyl (C=O) of PMMA and hydrogen from (CHCl) groups of PVC [1], [11], [12] and [13].

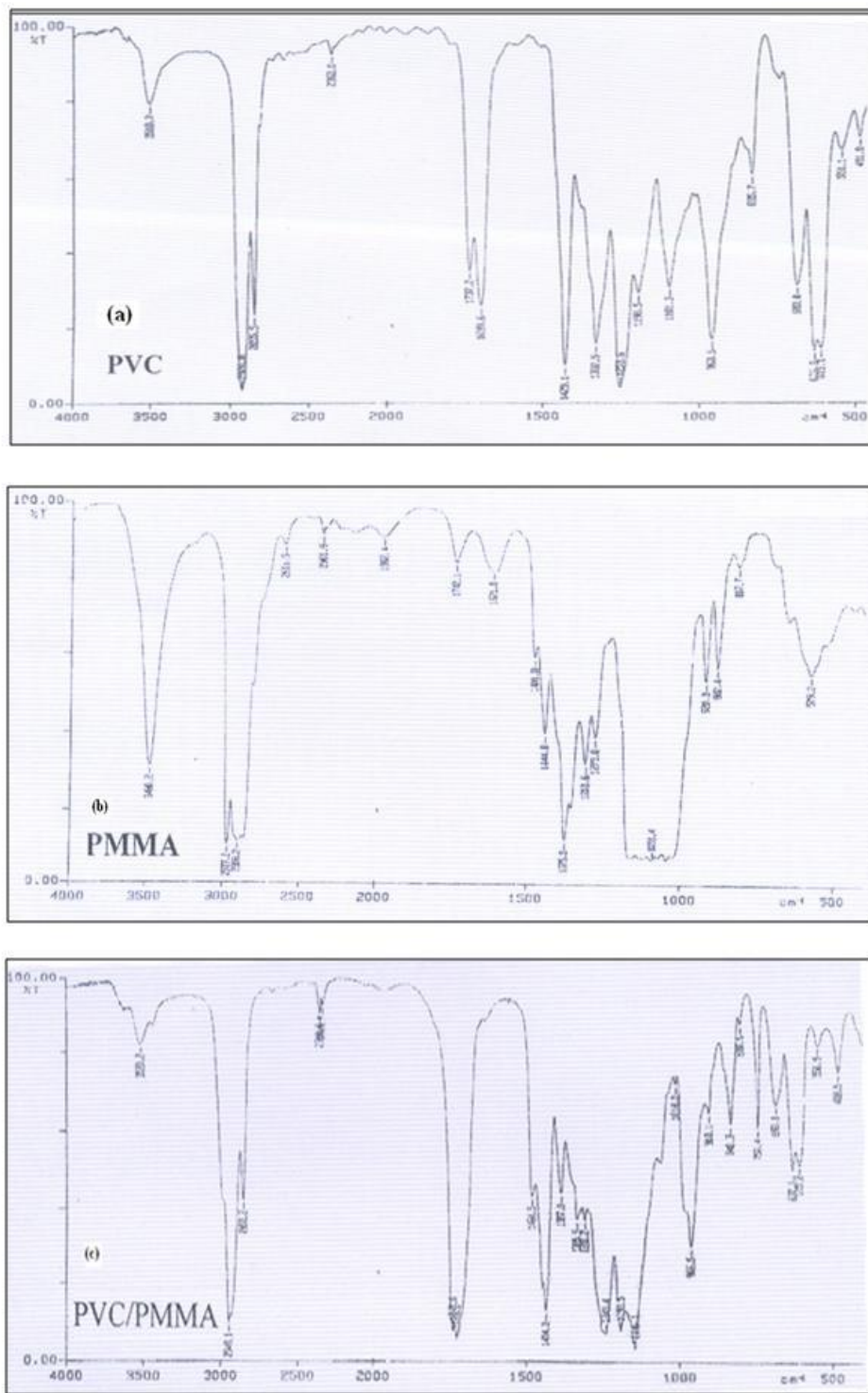
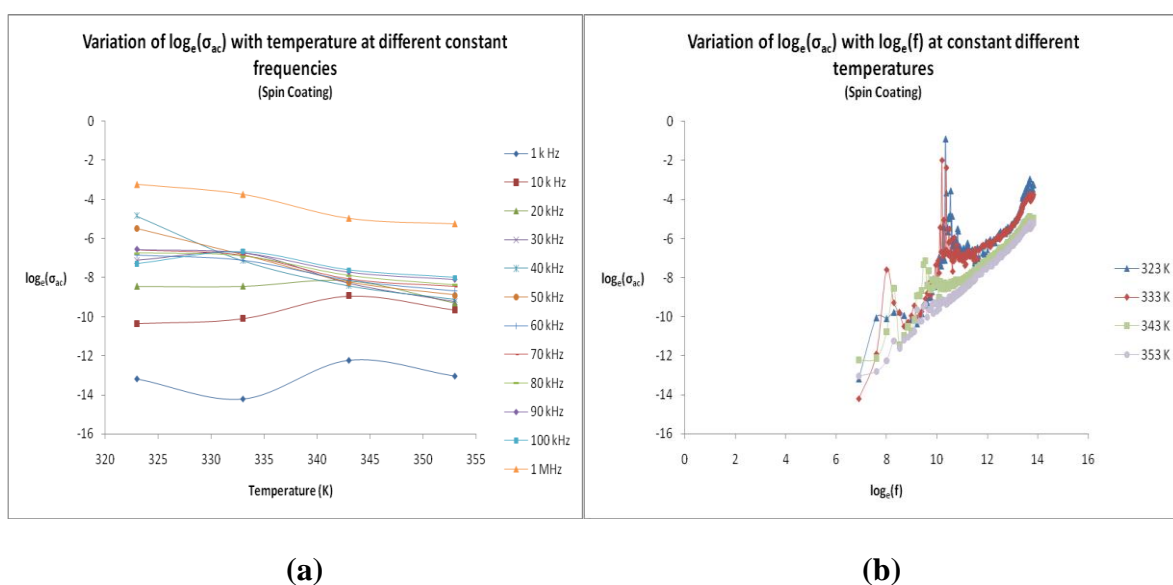


Fig. 1(a-c) FTIR of Pure PVC, Pure PMMA and PVC+PMMA Polyblends

### III.2 AC electrical conductivity and dielectric constant studies

**Figure 2 (a)** shows the relation between ac conductivity and temperature at different constant frequencies. It is observed that, ac conductivity of thin film decreases with increase in temperature for all values of frequencies. From these results, it is believed that in these film containing both PVC and PMMA, the PVC-rich phase acts as a mechanical support and the plasticizer-rich phase interconnected with each other acts as a tunnel for ionic transport. Since the PVC-rich phase is a solid-like medium, the ion is difficult to penetrate this phase. Due to such a blocking of the PVC-rich phase, the transport of ion must occur vice indirect motion along a convoluted path restricted to the plasticizer-rich phase. Hence this would be responsible for the decrease conductivity in content blend [14].



**Fig. 2 (a) Variation between ac conductivity and temperature at different constant frequencies. (b) Variation between ac conductivity and frequency at different constant temperatures.**

**Figure 2 (b)** shows the relation between ac conductivity and frequency at different constant temperatures 323K, 333K, 343K and 353K. Plot shows rise in conductivity with increasing frequencies from 1 KHz to 1MHz. The rise of conductivity upon increasing the frequency and temperature is a common respond for polymeric and semiconductor samples [15]. It is due to the tremendous increase of the mobility of charge carriers in the composite film i.e. at higher frequencies blends of molecules starts vibrating with large amplitude within the polymeric chains hence the effect of increase in conductivity of blends[16].

### IV. CONCLUSIONS

AC electrical conductivity and dielectric constants have been measured at different temperatures and at the different frequencies, it is found that ac conductivity of thin film decreases with increase in temperature for all values of frequencies and it increases with increase in frequencies at constant temperature and also the dielectric constant increases with the increasing of the temperature of blends. Hence in this blends the miscibility exists.

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## References

- [1] J.W. Shurer, A. de Boer, and G. Challa, "Influence of tacticity of poly (methylmethacrylate) on the compatibility of poly (vinyl chloride)", *Polymer*, **16**, 201 (1975).
- [2] Nunes SP, Peinmann KV, "Ultrafiltration membrane from PVDF/PMMA blends", *J Membr Sc* **73**, pp 25–35(1992).
- [3] Belsare N. G. and Deogaonkar V. S., "Electrical Conductivity of Iodine Doped Polyblend Films of Polystyrene (PS) and Polymethyl Methacrylate (PMMA)", *Indian J. Pure & Appl. Phys.* **36**, 280 (1998).
- [4] Rajendran S. and Uma T. "Conductivity studies on PVC-PMMA polymer blend" *Electrolytes Mater. Letts* **44**, 242-247 (2000).
- [5] Shukla J. P. and Gupta M.; *Indian Journal of Pure and Applied Physics*, **25**, 242- 244 (1987).
- [6] R. V. Waghmare, N. G. Belsare, F. C. Raghuvanshi and S. N. Shilaskar, "Study of DC Electrical Conductivity of paranitroaniline doped (1:1) Polyvinyl chloride and polymethyl methacrylate Polyblends", *Bull. Mater. Sci.*, **30**, 167-172 (2007).
- [7] Belsare N. G. and Deogaonkar V. S. "TSDC Study of Iodine Doped Polyblends of Polystyrene (PS) and Polymethyl Methacrylate (PMMA)", *Journal of Polymer Materials*, **15**, 157-170 (1998).
- [8] Rao Vijayalakshmi, Ashoakan P.V. and Shridhar M. H.; *Material Science and Eng.*, **A281**, 213-220 (2000).
- [9] Subban RHY, Arof A.K., "Plasticizer interactions with polymer and salt in PVC–LiCF<sub>3</sub>SO<sub>3</sub>–DMF electrolytes". *Eur. Polym. J.*, **40**, 1841-1847 (2004).
- [10] Saikia D, Kumar A., "Ionic transport in P(VDF-HFP)–PMMA–LiCF<sub>3</sub>SO<sub>3</sub>–(PC + DEC)–SiO<sub>2</sub> composite gel polymer electrolyte". *Eur Polym J.* **41**, 563-568 (2005).
- [11] N. Belhaneche-Bensemra and A. Bedda, "Analyse de la relation structure-propriétés des mélanges PVC-PMMA". *Ann. Chim. Sci. Mater.*, **26**, 79 (2001).
- [12] N. Belhaneche-Bensemra, B. Belaabed and A. Bedda, "Study of the miscibility and the thermal degradation of PVC/PMMA blends", *Macromol. Symp.*, **180**, 203 (2002).
- [13] N. Belhaneche-Bensemra, B. Belaabed and A. Bedda, "Study of the properties of rigid and plasticized PVC/PMMA blends". *Macromol. Symp.*, **202**, 151 (2003).
- [14] Hee-Jin Rhoo, Hee-Tak Kim, Jung-Ki Park and Taek-Sung Hwang, *Electrochimica Acta*, **42**, 1571-1579 (1997).
- [15] Dutta, P., S. Biswas, M. Ghosh, S. K. De and S. Chatterjee. "The dc and ac Conductivity of Polyaniline and Polyalcohol Blends", *Synth. Met.*, **12**, 455-461 (2000).
- [16] I.C. McNeill, "Thermal degradation mechanisms of some addition polymers and copolymers", *Journal of Analytical and Applied Pyrolysis* **43**, 21-41(1997).