The Swelling Behaviour of Polystyrene (PS)/ Polyvinylacetate (PVA) Blends in Different Solvents and the Effects of α-Cellulose used as Filler on the Electrical Conductivity.

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ABSTRACT: The effect of the variation of the type of solvent responsible for the differences in the swelling kinetics of Polystyrene (PS) and Polyvinyl acetate (PVA) blends was studied. The results showed that the nature of solvent control or affects the degree of swelling. Also, I-V characteristics at temperature range of 323-363K shows promising semi conducting ability which appreciated with amount of filler in the polymer-polymer matrix.

Keywords: Swelling behavior, Polystyrene (PS) - Polyvinyl acetate (PVA) blends, electrical conductivity, filler composition.

INTRODUCTION

When using polymeric materials, environmental factors play significant role in determining their operational characteristics. Chemical interaction of a polymer with solvents is one such factor that can limit the service life of polymeric materials, other important delimitating factor is electric field.

In this study the swelling behaviours of pure PS-PVA blends are compared with α-cellulose-filled PS- PVAc blends under the influence of different solvents i.e water, 0.05M HCl, 0.05M NaOH and acetone. Also, the variation in its electrical conductivity due to the filler-composition was assessed by their I-V plot characteristics.

The water sorption kinetics in light-cured PolyHEMA and Poly (HEMA–co-TEGDMA) by assessing the self–diffusion coefficient through a new Iterative method was reported earlier (Sideridon et al., 2007). The electrical conduction in iodine doped Polystyrene (PS) and Poly (MethylMethacrylate) (PMMA) has already been reported (Chakraborty et al., 2004). Khare (1994) studied the current-voltage characteristics of malachite green doped cellulose acetate films. Deshmukh et al (2005) reported electrical conduction in semi conducting PVC-PMMA thin film. Microhardness and X-ray diffraction studies on Polymer blends of Polyethylene Methacrylate (PEMA) and Polyethylene oxide (PEO) have been reported by Awasthi and Bajpai (2001). Also, Deshmukh et al (2007) reported the electrical conductivity of Polyaniline doped PVC-PMMA polymer blends.

Theoretical section
Swelling behavior

According to Liao et al (1997), the swelling ratio (S.R) of a polymer can be calculated assuming additivity of volume by

\[ S.R = \frac{W_d}{\rho_{\text{polymer}}} + \frac{W_s - W_d}{\rho_{\text{solvent}}} \]

Where \( W_d \) and \( W_s \) are the weight of dry and swollen polymers respectively and \( \rho \) is density.

The weight of the swollen blends was measured at certain time intervals. The Quotient, Q of the blends was calculated using the equation.

\[ Q(\%) = \frac{W_s - W_d}{W_d} \times 100 \]

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Where $W_s$ and $W_d$ are the weights of the swollen blends for each time period and the dried one, respectively.

**Electrical conductivity**

There are four possible mechanisms/models of electrical conduction as reported by Deshmukh et al., (2007), however the fifth which is the Arrhenius plots reveals greater details. In this work the Arrhenius plots ($\ln(\sigma)$ vs. $1000/T$) at all values of applied voltage was adopted.

**MATERIALS AND METHODS**

**Materials**

Polystyrene (PS) was supplied by Philip Marris Limited, England, Polyvinylacetate ($\text{PVAc}$), $\alpha$-cellulose filler, hydrochloric acid and acetone were purchased from BDH, Poole, England. Digital Metler Balance AT400, Ammeter, Voltmeter, Platinium electrodes were some instruments used.

**Film casting and measurement**

Different compositions of PS/$\text{PVAc}$ blend solutions were prepared in Toluene. 20cm$^3$ of the 2% solution of $\text{PVAc}$ were poured carefully into a clean dry Petri dish placed on a flat surface in a fume cupboard and left for 24hours for the solvent to evaporate. 10cm$^3$ of distilled water were then poured on the dry film in the dish. The dish with the content was left for 20minutes to allow the water penetrate the sides of the dish to release the films from the base of the dish. The procedure was repeated in turn for PS, and all the blend solutions. A micrometer screw gauge was used to measure the thickness of the films. Films of thickness of 70μm were used in this study.

**Swelling properties measurement**

The specimens were placed in a desiccator and transferred to a preconditioning oven at 50°C. After 24hours they were removed, stored in the desiccator for 1hour and weighed to an accuracy of ± 0.0001g using a Mettler balance. This cycle was repeated until a constant mass ($m_i$) was obtained. The films were in turn immersed in water, HCl, NaOH and acetone at 50°C. At fixed time intervals they were removed, blotted dry to remove excess liquid, weighed and returned to the solvent. The uptake of the liquid was recorded for time intervals up to 30hours.

**Electrical conductivity measurements**

A thermostatically controlled oven was used for heating purpose. The sample films with silver electrodes were sandwiched between two platinum electrodes (diameter, 2.5cm) and currents measured using an ammeter while the voltage was assessed using a voltmeter.

**RESULTS AND DISCUSSION**

Previous studies (Mamza and Folaranmi, 1996, Mamza and Nwufo, 2008) showed that the PS/$\text{PVAc}$ ratio corresponding to 20%/80% composition has some considerable degree of compatibility. This was concluded from the plots of reduced viscosity versus concentration, which revealed higher value of observed intrinsic viscosity over the calculated one using Krigbaum- Wall equations. The mechanical properties observed from the Stress–Strain measurements also supported this. It is based on this, that a further study of the swelling and electrical properties are needed in order to investigate any correlation between the two, it will also give insight into the micro structural arrangements of the composite. Figures (1 & 2) show the swelling behaviors of the PS/$\text{PVAc}$ blend films in water, acid, base and acetone. Both plots show the following general trend; acetone<NaOH <water <HCl, with $\alpha$-cellulose filled polymer blends exhibiting greater swelling characteristics in all the solvents when compared with the virgin PS/$\text{PVAc}$ blend. The explanation is that the $\alpha$-cellulose filler itself, possesses sites for solvent interactions through solubilizing mechanism. In general, $Q$ is related to the osmotic pressure, cross-linking density and copolymer affinity to absorb water (Higgs, and Joanny, 1991; Flory, 1953). In this particular study the main effect on $Q$ is the affinity to solvents (water, base, acid and acetone) and filler concentration. The higher $Q$ values obtainable from the $Q$(%) versus $t$(h) dependence is in conformity with the results of the earlier studies carried out on the blends (Mamza and Folaranmi, 1996; Mamza and Nwufo, 2008). However, the sharp discrepancies observed is attributable to the mode of aggregation with filler in solvent cast-films as
compared with articles obtained from a compression press.
The electrical conductivity of the blends were evaluated from the observed behaviour of I-V characteristics and the possibility of ohmic conduction as well as space charge, limited conduction is ruled out (Figures 3 and 4). The polymers generally falls at low conductivity spectrum and most effects may be due to adventitious ions and hence, the reasons for the observed current-voltage characteristics, with the filler-incorporated blends showing reluctantly an improvement in this regard (Fig. 4). From the Arrhenius plots (Fig 5. and 6), it was observed that the α-cellulose filler enhanced the thermal activation energies and decreased the semiconducting behavior of between -0.18 to -0.49eV i.e -0.20 eV from the slope of the plot. It is therefore evident that by a careful consideration of the micro structural arrangement in the polymer matrix a conduction mechanism that would offer considerable impetus for impedance analyses is required especially in the α-cellulose filled PS/PVAC blend.

CONCLUSION
The results of the swelling behaviour and electrical conductivities of Polystyrene (PS) and Polyvinyl acetate (PVA\textsubscript{C}) blend showed that the choice of solvent, filler content and mode of processing appreciably determines a possibility for specific applications according to standard methods. The reinforced PS/PVAC\textsubscript{C} blends can be utilized as semi conductors.

![Fig. 1: Swelling Kinetics (Q) of 20%/80%, PS/PVAc Blend without filler](image1)

![Fig. 2: Swelling Kinetics (Q) of 20%/80%, PS/PVAc Blend with α-cellulose filler](image2)
Fig. 3: Current-voltage characteristics for 20%/80%, PS/PVAC blend without filler

Fig. 4: Current-voltage characteristics for 20%/80%, PS/PVAC blend incorporated with α-cellulose filler
Fig 5: Arrhenius plot for 20%/80% PS/PVAc blend without filler

Fig. 6: Arrhenius plot for 20%/80% PS/PVAc blend incorporated with $\alpha$ - cellulose filler
REFERENCES


