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DC Electrical Study of Modified PMMA, PVC and their Blend

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Summary: Thin films of high molecular weight PMMA, PVC and their blend were prepared with solution cast method. Further they were modified by adding Camphor Sulphonic Acid (CSA) to them. DSC studies indicate single glass transition temperature (Tg) for unmodified as well as modified blends indicating the miscibility of polymers. FTIR studies show the interaction between CSA-PVC, CSA-PMMA, CSA-(PVC+PMMA) blend. The D.C. electrical study was carried out at various temperatures from room temperature (307 K) to 373 K. After modification the variation of DC conductivity (σ) is found to decrease in PVC and the PVC-PMMA blend whereas it is found to increase in PMMA with rise in temperature.

Keywords: blend; D.C. conductivity; FTIR; PMMA; PVC

Introduction

The theoretical study of electrical conduction in polymers is very interesting as lot of contradictory results on their conduction mechanism have been reported. Such as Seanor [1,2] has reported that in nylon 6-6, above 120 °C, there is an ionic conduction while below and at least upto 80 °C it is electronic. In PVC, electronic conduction is reported by Flemming and Renicar[3] whereas Kosaki[4] favors hoping ionic mechanism.

This study has a commercial importance as well. This is because the polymers have inherent properties like light–weight, rust proof, easily processible etc. Hence constant attempts are being made to improve the conductivity in polymers. Organic light emitting diodes,[5] low power rechargeable batteries, plastic batteries, gas sensors, super capacitors, photovoltaic cells,[6] liquid crystal displays,[7,8] and Schottky devices[9–11] are some of the potential applications of doped polyaniline. Conductivities of range 10^{-6} to 10^{-5} S/cm are useful in antistatic applications. Doped polythiophene is being used for this purpose. As such conducting polymers like polyaniline, polythiophene, polypyrrole have gained attraction of the researchers.

Bulk polyaniline in its pure form is an insulator. However, adding Camphor Sulphonic Acid (CSA), methane sulphonic acid etc. to it has enhanced its electrical conductivity by many orders.[12]

PMMA and PVC are vinyl type polymers and have carbon-carbon main chains but different side groups. Both these polymers are basically classified as insulators due to very small number of charge carriers and their low mobility. The conductivity of polymers and their blends when modified with various lithium salts show a significant increase in their ionic conductivity and thus have applications in rechargeable lithium polymer batteries using polymer electrolytes.[13]

In a similar way an attempt has been made to study the effect of adding of CSA on the DC electrical conductivity of high molecular weight PMMA, PVC and their blend.

Experimental Part

PMMA (Aldrich, Mol. Weight 120000), PVC (Fluka, Mol. weight 48000) are the

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Table 1.
Samples, their codes used in this study and Tg values.

Name of sample	Code	*Tg* °C	Name of sample	Code	*Tg* °C
Pure PVC	A0	72.85	PVC + CSA	D0	83.43
50% PVC +50% PMMA	A5	92.23	50% PVC+50% PMMA+CSA	D5	77.87
Pure PMMA	A10	107.90	PMMA + CSA	D10	96.01

polymers and CSA (Lancaster) are used in this study. Quantity of CSA is 20 wt % of the total mass of the polymer. Uniform films of PMMA, PVC, and their blend (with and without addition of CSA) have been prepared by dissolving the polymers in Ethyl Methyl Ketone procured from Merck. These films of thickness 20 to 30 μm were prepared by film cast method. Traces of solvent were removed.

FTIR spectra of all the six samples have been recorded with Thermo Electron Corporation, Medison, WI spectrometer between 450 cm^{-1} and 4000 cm^{-1} range in the transmittance mode.

DSC study was carried out with Mettler Toledo DSC 822e instrument at a heating rate of 5 °C/min from 30 °C to 350 °C in nitrogen atmosphere.

The I–V measurements were made by two probe method at eight different temperatures from room temperature (307 K) to 373 K in a specially fabricated setup under vacuum of 10^{-3} torr order. The vacuum was generated with rotary pump. A regulated power supply provides a variable d.c. voltage which itself has a digital display of voltage applied across the sample. In order to ensure a proper electrical contact the polymer films were coated with aluminium metal in vacuum deposition unit. The voltage was varied from 4V to 52 V in steps of 4 V. The current in the sample was measured by Keithley-6514 system electrometer. Log I vs log V and log σ vs 1000/T curves are also plotted at a field of 2×10^6 V/m.

Results

Table 1 summarizes sample codes used in the study along with their Tg. Tg is obtained from the DSC curves. The existence of a single Tg for A5 and D5 indicates that the blends are miscible before and after modification also.

These observations of Tg and mechanical properties have already been reported elsewhere[14] and have been explained as follows: Whenever an impurity is added to a polymer it can act as a plasticizer or an antiplasticizer.[15] A plasticizer decreases the Tg value and also decreases Youngs Modulus (YM) and Tensile Strength (TS) of the polymer. In the present study a decrease of Tg is observed in D5 and D10 as compared to A5 and A10 respectively whereas an increase in Tg is seen in D0 as compared to A0. Moreover a decrease of TS and YM is observed in D5 and D10 as compared to A5 and A10 and a slight increase of TS and YM is observed in D0 as compared to A0. Thus the addition of CSA, has a antiplasticizing effect in D0 whereas a plasticizing effect in observed in D5 and D10.

The FTIR spectra of A10 and A5 are shown in Figures 1 and 2 respectively. The C=O stretching of PMMA at 1743 cm^{-1} shows a significant shift to 1739 cm^{-1}. This fact indicates that in the blend A5 there is a miscibility of PMMA and PVC due to hydrogen bonding between carbonyl group

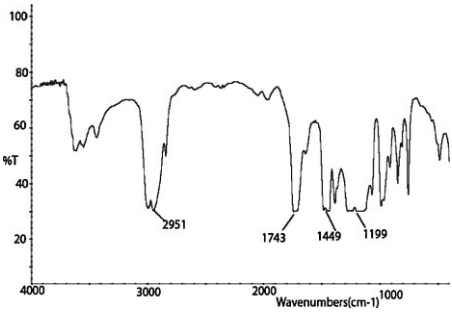

Figure 1.
FTIR of Pure PMMA.

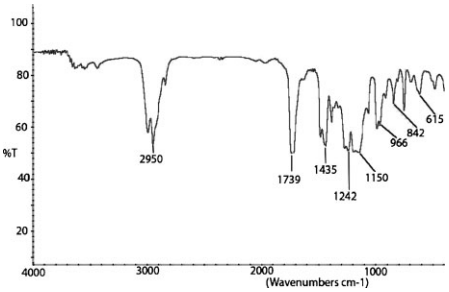

Figure 2.
FTIR of PMMA-PVC blend.

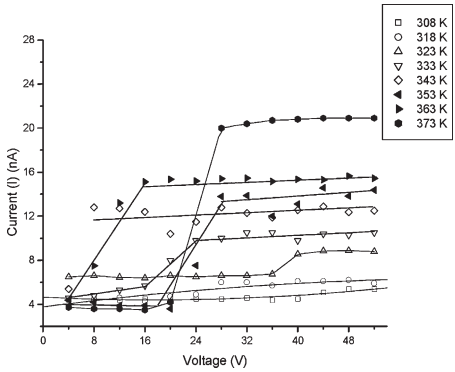

Figure 3.
I –V characteristics of A0.

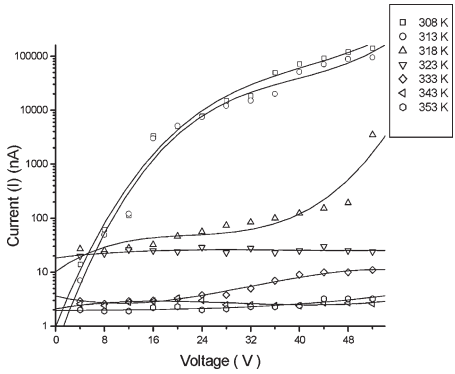

Figure 4.
I –V characteristics of D0.

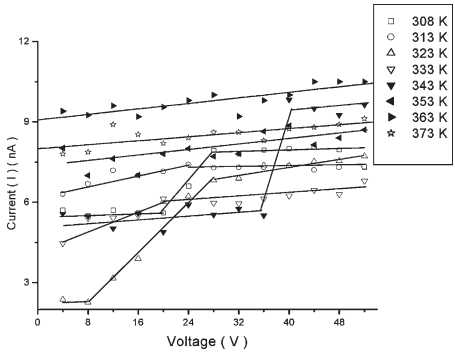

Figure 5.
I –V characteristics of A5.

of PMMA and CHCl of PVC. FTIR study[14] also confirms the following interactions:

- CSA has 793 cm^{-1} and 1038 cm^{-1} sulphonic acid group and 1738 cm^{-1} ketone group peak.[12] It is observed in D0 that there is a shift of 1038 cm^{-1} peak to 1041 cm^{-1} and 1738 cm^{-1} peak to 1740 cm^{-1}.This indicates that in D0, CSA interacts with PVC through a bonding between C=O of CSA and CHCl of PVC.
- In D10 it is observed that the sulphonic acid peaks at 793 cm^{-1} and 1038 cm^{-1} shift to 751 $cm^{-1}$and 1042 cm^{-1} respectively. The ketone group peak shows a shift from 1738 cm^{-1} to 1732 cm^{-1}. Thus the observed shifts in sulphonic acid groups, shifts in C=O of PMMA from 1743 cm^{-1} to 1732 cm^{-1} and $-OCH_3$ of PMMA from 1199 cm^{-1} to 1192 cm^{-1} after adding CSA in PMMA, indicate an interaction between H^+ ion of CSA and oxygen atoms of C=O and $-OCH_3$ of PMMA.
- In D5 it is observed that, H^+ ion of CSA interacts with the hydrogen bond which is already formed between C=O of PMMA and CHCl of PVC. Whereas, the interaction of H^+ ion with oxygen of $-OCH_3$ of PMMA is not observed as $-OCH_3$ stretching peak does not show any shift.

The I-V characteristics of A0, A5, A10 and D0, D5, D10 are shown in Figures 3–8 respectively. It is observed in A0 that the current increases gradually till a certain voltage and beyond that voltage there is a sudden rise in current with further rise in voltage. These curves are similar to vacuum tube diode characteristics. In general it is observed that beyond a certain voltage the

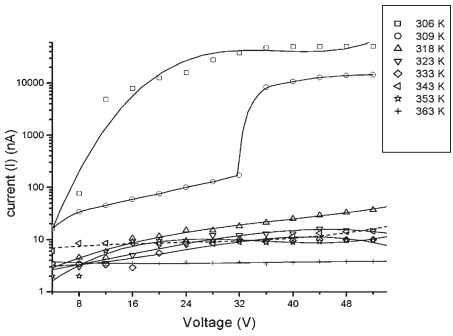

Figure 6.
I –V characteristics of D5.

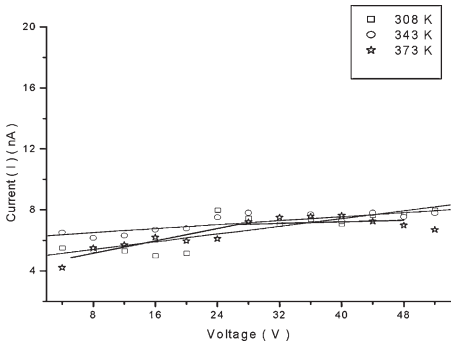

Figure 7.
I-V characteristics of A10.

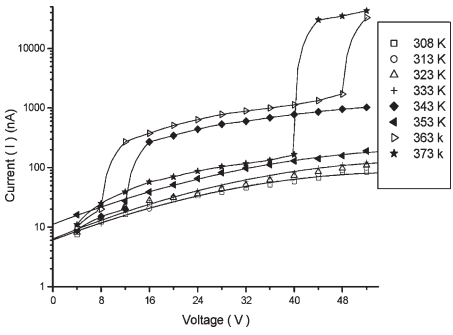

Figure 8.
I-V characteristics of D10.

current increases with increase in temperature. After modification of A0, with CSA, D0 is obtained and D0 shows a sudden rise in current by about four orders of magnitude at room temperature. However it shows a decrease in the magnitude of current with rise in temperature. The characteristics of A5 are shown in Figure 5 which indicate that the current is voltage dependent at some temperatures but shows a very small change with change in voltage at some other temperatures. The magnitude of current in D5 is greater than that in A5 at room temperature but gradually decreases with rise in temperature as shown in Figures 6 and 11. In pure PMMA (A10) it is observed that the current is neither much voltage dependent nor temperature dependent and as such only three representative curves are drawn at temperatures 307 K, 343 K and 373 K (Figure 7). On the contrast in D10 it is observed that the current rises gradually with rise in temperature and at higher temperatures (beyond 353 K) the current is observed to be increased by three orders of magnitude.

In order to find out the possible processes of electrical conduction in these modified samples various mechanisms like Poole-Frankel, Schottky, Fowler-Nordheim, Richardson, Ohmic conduction, Space Charge limited Conduction (SCLC) were tried and it was observed that first four mechanisms are not at all followed. The nature of curves of these mechanisms is quite complex and hence cannot be explained on the basis of conventional theories. However, on obtaining log I vs log V curves for D0, D5 and D10 it was observed that in D0 and D5 though the curves resemble with those of standard SCLC type, the values of their slopes do no confirm the possibility of SCLC type of mechanism. However, in D10 the current and voltage are related by the equation $V = K\ I^n$, where $n = 0.96$ (very close to 1) which indicates that an ohmic conduction is taking place in CSA modified PMMA. These curves have been drawn at room temperature and shown in Figure 9.

To make a comparative study of the variation of conductivity (σ) with variation in temperature, the variation of log σ versus 1000/T for unmodified and modified materials are drawn in Figures 10 and 11 respectively. It can be observed that in A0 the conductivity increases with rise in

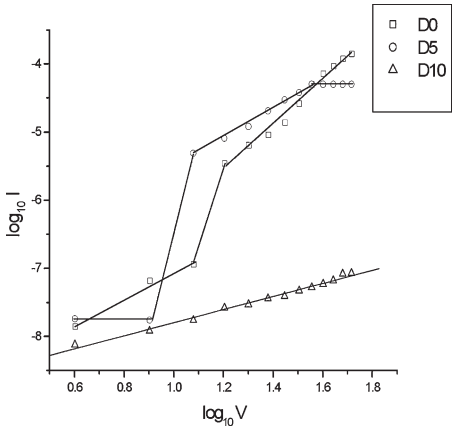

Figure 9.
log I versus log V curves.

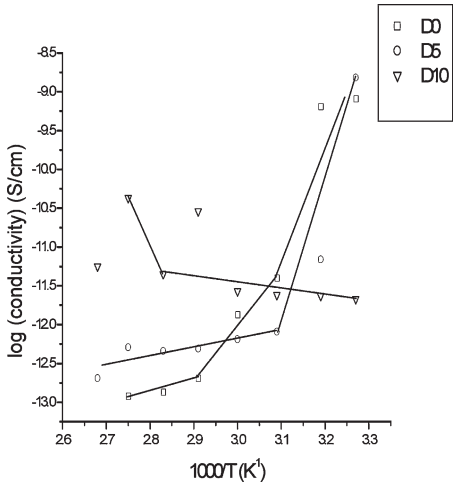

Figure 11.
log σ versus 1000/T of D0, D5 and D10.

temperature. On the other hand in A10 it is observed that the conductivity remains constant for the complete temperature range of study. The properties of A0 and A10 are observed to be similar to those reported by A. A. El Sayed et. al.[16] But the conductivity observed in A10 is about 42 times greater than the one observed by A. A. El Sayed. The blend A5 shows two distinct electric behavior above and below 343K. When modified, a complete change in the electrical properties is observed. It shows that the overall features of the Arrehenius plots for D0 and D5 are similar showing a decrease in conductivity with rise in temperature. In D10 however, conductivity is found to increase with rise in temperature.

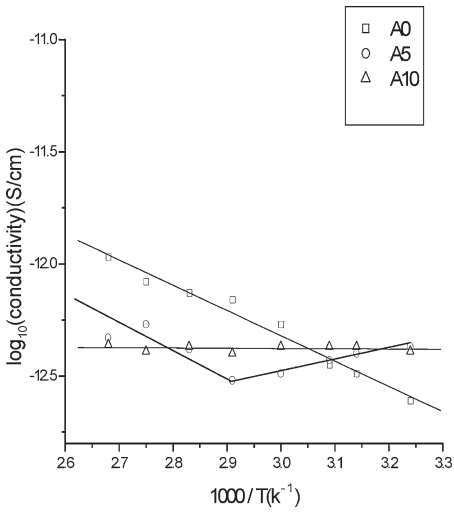

Figure 10.
log σ versus 1000/T of A0, A5 and A10.

Discussion

Incorporation of CSA modifies the structural properties of the polymers. This modification plays an important role in the generation of extended states in the modified molecules or by the generation of charged defects. The factors that decide the conductivity in such materials are – segmental mobility of side groups of polymers which influences the mobility of charge carriers, the concentration or charge density and the ability of the charges to percolate along the polymer matrix under the influence of electric field.

The process of d.c. conduction in polyamides is discussed by Baker et.al.[17], Eley et.al.[18] and Kryszewski,[19] where it is proposed that the conduction takes place due to wandering of a proton of an amide group over short distances. An intermolecular hydrogen bonding is also proposed in

nylon-6 between the adjacent C=O and NH groups of adjacent chains. The transport of charges can take place through such interactions. The transfer of protons also depends upon the rate of rotation of an amide group which is a function of temperature.

The process of electrical conduction in the present study is explained on the basis of model proposed above. A transfer of charge should be taking place in a similar way among the adjacent chains of A0. A weak dipole interaction is reported[20] to exist between H^+ and Cl^- of adjacent chains in PVC. This interaction must be providing a path for the flow of charge under the influence of electric field. The rise in temperature increases the segmental motilities in A0, thereby giving rise to enhancement of current, consequently showing semiconductor like property in A0 as shown in Figure 10. In D0, in addition to the intermolecular interaction between H^+ and Cl^- in the adjacent chains of PVC matrix, a hydrogen bonding exists between C=O of CSA and CHCl of PVC. The flow of charge through these interaction paths results in the enhanced conductivity of D0. The decrease in the conductivity of D0 with rise in temperature is attributed to the fact that with rise in temperature the hydrogen bond between CHCl of PVC and C=O of CSA gets gradually weaken and finally gets broken and as such the path for the flow of charge ceases to exist.

The current in A10 shows almost no change with change in voltage and temperature (Figures 7 and 10). This result can be explained on the fact that at a field of the order of 10^6 V/m both the side groups of PMMA must be rotating and contributing to the transport of charge carriers for the entire temperature range of 307 K to 373 K. This explains the observations made in Figure 10. In D10 the interaction is reported[14] to exist between H^+ ion of CSA and oxygen of C=O and $-OCH_3$ of PMMA. This interaction seems to facilitate the generation of charges as well as the flow of these charges via these interaction paths.

Table 2.
Comparative conductivity (σ) values at 307 K and 363K.

Sample code	$\sigma \times 10^{-13}$ S / cm		Sample code	$\sigma \times 10^{-10}$ S / cm	
	at 307 K	at 363 K		at 307 K	at 363 K
A0	2.41	8.23	D0	8.05	0.001
A5	4.26	5.37	D5	15.03	0.001
A10	4.00	4.00	D10	0.02	0.41

That is why the current increases by about five times at room temperature (Table 2).

In D10 with increase in temperature the mobility of these interacted side groups must be increasing thereby further facilitating the flow of charges. Hence D10 exhibits a semiconductor like nature.

In A5 a hydrogen bond exists between CHCl of PVC and C=O of PMMA. Almost constant conductivity is shown by A5 till 343 K and beyond this temperature, more and more free rotation of the side chains is giving rise to enhanced conductivity thereby exhibiting a semiconductor like nature.

In D5 an interaction of H^+ ion of CSA with C=O of PMMA exists in addition to the hydrogen bond existing between C=O of PMMA and CHCl of PVC. However no interaction between $-OCH_3$ and H^+ ion of CSA seems to exist. As such the only path available for the percolation of charge is via this interaction. At higher temperatures these interactions seem to get broken, as such the path for the flow of charges ceases to exist. Thus D5 shows metal like property.

Conclusion

FTIR studies indicate that CSA forms complex with PMMA, PVC and their blend. Since the matrix structure of each polymer is different the role of added CSA in PVC, PMMA and their blend is also different. At room temperature conductivity is enhanced by about four orders of magnitude in PVC and its blend whereas a small increase in conductivity is observed in

PMMA. After modification with CSA, PVC and its blend shows metal like properties whereas PMMA shows semiconductor like property.

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[1] D. A. Seanor, *J. Polym. Sci. PartC* **1967**, *17*, 195.
[2] D. A. Seanor, *J. Polym. Sci.* Part A2 **1968**, *6*, 463.
[3] R. Flemming, J. Renicar, *J. Aust. J. Phys.* **1971**, *24*, 325. *J.Macromol.Sci.Chem.* **1970**, *A4*(5), 1223.
[4] M. Kosaki, K. Sugiyama, M. Ieda, *J. Appl. Phys.* **1971**, *9*. 3388.
[5] H. L. Wang, A. G. Mac Dirmid, W. Z. Wang, D. D. Gebler, A. Jepstein, *Synth. Met.* **1996**, *78*, 33.
[6] L. Ding, M. Jonforsen, L. S. Roman, M. R. Anderson, O. Inganas, *Synth.Met.* **2000**, *110*, 133.
[7] S. A. Jenekhe,, K. J. Wynne, Eds., *Photonic and optoelectronic Polymers, ACS, symposium series* American Chemical Society, Washington,DC 1997, Vol. *672*, 395.
[8] A. G. Mac Dirmid, Photonic and Optoelectronic Polymers, Naval Research Reviews, Office of Naval Research, Two / **1997**, Vol. XLIX 6–11.
[9] S. S. Pandey, M. K. Ram, V. K. Shrivastava, B. D. Malhotra, *J. Appl. Polym. Sci.* **1997**, *65*, 2745.
[10] S. S. Pandey, C. K. Mishra, S. Chandra, B. D. Malhotra, *J. Appl. Polym. Sci.* **1992**, *44*, 911.
[11] H. K. Choudhari, D. S. Kelkar, *J. Appl. Polym. Sci.* **1996**, *61*, 561.
[12] S. Sarvanan, C. Joseph Mathai, M. R. Anantharaman, S. Venkatachalam, P. V. Prabhakaran, *Journal of Physics and Chemistry of Solids*, **2006**, *67*, 1496–1501.
[13] S. Rajendran, T. Uma, T. mahalingam, *European Polymer Journal*, **2000**, *36*, 2617–2620.
[14] Vijay. V. Soman, Deepali. S. Kelkar, *Macromol. Symp.* **2009**, *277*, 152–161.
[15] W. J. Jackson, Jr., J. R. Caldwell, *J.Applied Polym Sci.* **1967**, *11*, 211.
[16] A. A. El. Sayed, A. M. Mousa, S. A. El. Konsol, A. F. Basha, W. M. Khalil, *Polymer Bulletin* **1981**, *5*, 209–215.
[17] W. O. Baker, W. A. Yager, *J. Am. Chem. Soc.* **1942**, *64*, 2171.
[18] D. D. Eley, D. I. Spivey, *Trans. Fara. Soc.* **1961**, *57*, 2280.
[19] M. Kryszewski, *J. Polym. Sci. Polym. Symp.* **1975**, *50*, 359.
[20] Gloria Maria Vinhas, Rosa Maria Souto-Maior, Camia Maria Lapa, Yeda Medeiros Bastos de Almeida, *Materials Research*, **2003**, *6*(4), 497.

