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FTIR Studies of Doped PMMA - PVC Blend System

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Summary: The IR spectroscopy study shows miscibility between PMMA-PVC blends due to hydrogen bonding between C=O of PMMA and hydrogen from CHCl of PVC. This blend system is doped by Camphor Sulphonic Acid (CSA) in the entire composition range. The doping of CSA in PVC, in PMMA and in PMMA-PVC blends shows changes in FTIR spectra. The interaction between PVC and CSA is through hydrogen bonding between C=O of CSA and CHCl of PVC. Doping PMMA with CSA, indicate an interaction between H^+ ion of CSA and oxygen atoms of C=O and $-OCH_3$ of PMMA. Whereas in PMMA–PVC blend interaction between H^+ ion of CSA and oxygen atom of C=O of PMMA.

Keywords: blends; CSA; doping; FTIR; PMMA; PVC

Introduction

Polymer blends mostly exhibit properties that are superior to any one of the component polymers. Miscibility of the constituent polymers decides the structure of the blend which in turn, decides the properties of the blend. Negative enthalpy of mixing of polymers is required for miscibility. This condition is satisfied when strong specific intermolecular interactions exist between the constituent polymers.[1–4] It has been observed that miscibility depends on several factors like the tacticity of polymers, method of preparation etc. and as such lot of contradictory results about the possibility to predict miscibility have been reported.[5–12] In case of moderate or weak interactions, the miscibility of polymer pairs is limited. Fowkes[13,14] has pointed out that dipole–dipole interactions are not important in the molecular interactions of solids and besides the dispersion forces, acid–base interactions have also to be considered.

These days blending technique has gained lot of commercial as well as academic importance. Enhancement in ionic conductivity and mechanical strength has been reported in polymer electrolytes by modifying them in the form of blends.[4,15] In addition to blending one of the ways to improve the mechanical properties of the polymer is to add dopant material. It has been observed that use of inorganic dopants improves stiffness whereas using a rubbery phase improves the toughness of the polymer.[16–18]

In the present study an attempt has been made to modify the blend by doping with an organic salt Camphor Sulphonic Acid (CSA) in the entire composition range with an aim to further enhance the mechanical properties of the blends. The use of a dopant influences the matrix structure of the blend which in turn affect the physical properties of the doped blend including the mechanical properties. Infrared spectroscopy is a tool to find out the possible interaction between the dopant and the polymer matrix. Several researchers have used this technique to study such interactions between polymers and the dopants.[19,20]

These research groups have reported the interaction by the study of shift of the peaks, developments of new peaks, changes in shapes like changes in peak intensity, development of shoulders in the existing peaks in the FTIR spectrum. A comparative study of FTIR spectra of doped and

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Table 1.
Samples and their codes used in this study with their observed Tg.

Name of Sample	Code	Tg (°C)	Name of Sample	Code	Tg (°C)
Pure PVC	A0	72.85	Pure PVC + CSA	D0	83.43
90% PVC + 10%PMMA	A1	66.38	90% PVC + 10%PMMA + CSA	D1	84.56
70% PVC + 30%PMMA	A3	86.80	70% PVC + 30%PMMA + CSA	D3	64.76
50% PVC + 50%PMMA	A5	92.23	50% PVC + 50%PMMA + CSA	D5	77.87
30% PVC + 70%PMMA	A7	95.31	30% PVC + 70%PMMA + CSA	D7	92.89
10% PVC + 90%PMMA	A9	95.31	10% PVC + 90%PMMA + CSA	D9	114.03
Pure PMMA	A10	107.90	Pure PMMA + CSA	D10	96.01

undoped blends has been made in this work in order to examine the possible interactions between constituent polymers and the dopant.

Experimental Part

PMMA (Aldrich, Mol. Weight 120000), PVC (Fluka, Mol. weight 48000) are the polymers and CSA (Lancaster) is the dopant, used in this study. The blends of PMMA-PVC have been prepared by dissolving the polymers in Ethyl Methyl Ketone procured from Merck in the proper weight proportions so as to obtain blends over entire composition of constituent polymers. (Table 1) along with the codes of samples and the observed glass transition temperature (Tg). These blends were prepared by film cast method. CSA doping is 20 wt % of the total mass of the polymer. Uniform films of thickness of about 20 to 30 μm were obtained. Traces of solvent were removed.

The FTIR spectra of all of them along with CSA have been recorded with a Thermo Electron Corporation Madison, WI spectrometer between 4000 cm^{-1} and 450 cm^{-1} in the transmittance mode (written as %T on Y-axis of graphs). Mechanical property of D10 could not be studied due to its brittleness. Whereas mechanical properties of all other 13 samples have been reported in this study. These measurements were made on Lloyds LR30 K instrument with a crosshead speed of 5 mm/min. The DSC study was carried out with Mettler instruments with a heating rate of 5 °C/min from 30 °C to 350 °C in nitrogen atmosphere.

Results and Discussion

DSC Results

The DSC analysis shows the existence of a single glass transition temperature (Tg) for all the blends indicating the miscibility of the constituent polymers. The Tg's are shown in Table 1.

FTIR of Pure PVC and PMMA

Various vibrational modes and their respective wave numbers observed in A0 and A10 are shown in Table 2 and Table 3 respectively and Figure 1 and Figure 2 show their respective FTIR spectra.

FTIR of Pure PMMA-PVC Blends

The blends A1, A3, A5, A7, A9 show characteristic vibrational modes as summarized in Table 4. FTIR analysis of the blends show a significant shift of carbonyl band of PMMA to lower wavenumber. This fact indicates that there is a miscibility of

Table 2.
Vibrational Modes observed in PVC.

Modes of vibration	Wavenumber (cm^{-1})
–CH stretching	2911
$-CH_2$ deformation	1330
CH rocking	1253
trans CH wagging	961
C–Cl stretching	835
cis CH wagging	613

Table 3.
Vibrational Modes observed in PMMA.

Modes of vibration	Wavenumber (cm^{-1})
–CH stretching	2951
C=O stretching	1743
CH_3 stretching	1449
$-OCH_3$ stretching	1199

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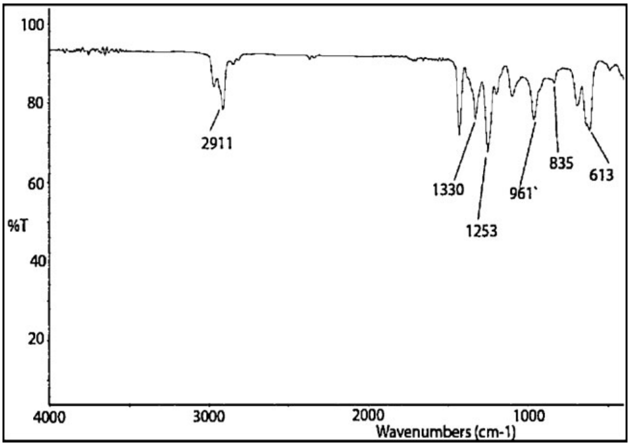

Figure 1.
FTIR of PVC

PMMA and PVC in their blends over the entire blend compositions. This miscibility is due to the specific interaction of hydrogen bonding between carbonyl group (C=O) of PMMA and hydrogen from (CHCl) of PVC.[25] On the other hand Erika Fekete[4] has reported a small shift in this carbonyl absorption band peak from 1735 cm^{-1} to 1732 cm^{-1}. Whereas S. Ramesh[21] has reported the shift in the carbonyl absorption peak to higher wave number side from 1721 cm^{-1} to 1732 cm^{-1}.

FTIR of PVC Doped with CSA

Figure 3 shows the FTIR spectra of PVC doped with CSA. Table 5 compares the vibrational modes of A0 and D0, which shows slight shifts in all vibrational modes except for the band due to $-CH_2$ deformation at 1330 cm^{-1}. CSA has 793 cm^{-1} and 1038 cm^{-1} sulphonic acid group and 1738 cm^{-1} ketone group peaks.[22] Figure 4 shows the FTIR of CSA. There is a shift of 1038 cm^{-1} peak to 1741 cm^{-1}; 1738 cm^{-1} to 1740 cm^{-1}. The

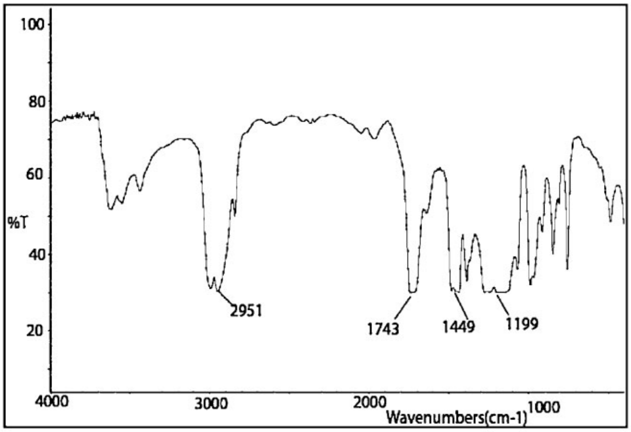

Figure 2.
FTIR of PMMA

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Table 4.
Vibrational Modes observed in undoped blends.

Vibration Modes ↓	Wavenumber (cm^{-1})				
Sample code →	A1	A3	A5	A7	A9
CH stretching	2911	2948 +sh	2949 +sh	2911	2950 +sh
CH_2 deformation	1330	1329	1329	1330	Too weak to be marked
CH rocking	1251	1245	1250	1253	1242
trans CH wagging	963	964	966	961	966
cis CH wagging	838	842	843	835	842
C-Cl stretching	613	615	615	613	615
C=O stretching	1731	1730	1736	1710	1739
CH_3 stretching	1431	1433	1435	1430	1435
$-OCH_3$ stretching	1151	1151	1150	1199	1150

+sh stands for development of shoulder.

793 cm^{-1} peak is very weak to be detected and to be marked in Do. The shift in sulphonic acid and ketone group peaks can be due to change of environment for CSA in the PVC matrix and the shift in ketone group peak can be due to hydrogen bonding between C=O of CSA and CHCl of PVC. This suggests the interaction between CSA and PVC.

FTIR of PMMA Doped with CSA

Figure 2 and Figure 5 show the FTIR spectra of PMMA and CSA doped PMMA respectively and Table 6 compares the vibrational modes of them. There is no shift in –CH stretching and CH_3 stretching of PMMA even after doping. But C=O stretching, $-OCH_3$ stretching vibrations in PMMA show a significant shift after doping. The carbonyl group peak at 1743 cm^{-1} and $-OCH_3$ stretching peak at 1199 cm^{-1} in A10 are quite broad. After doping PMMA with CSA they shift to 1732 cm^{-1} and 1192 cm^{-1} respectively and become very sharp. The 1192 cm^{-1} peak is associated with another sharp peak of little higher intensity at 1150 cm^{-1} which is not distinctly observed in A10. The sulphonic acid peaks at 793 cm^{-1} and 1038 cm^{-1} peaks shift to 751 cm^{-1} and 1042 cm^{-1} respectively. The ketone group peak at 1738 cm^{-1} shifts to 1732 cm^{-1}. Thus the observed

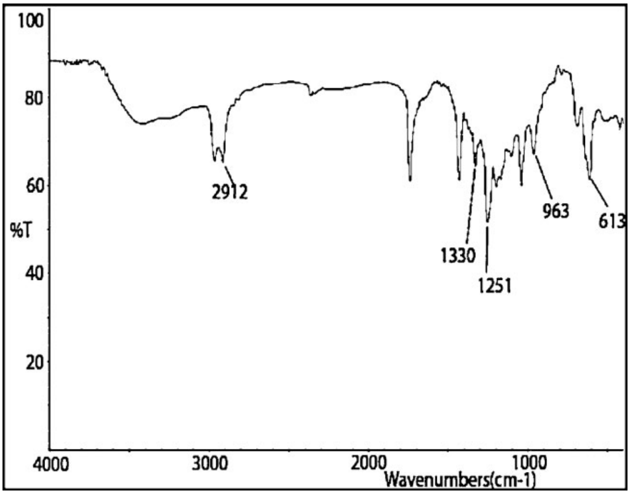

Figure 3.
FTIR spectra of PVC doped with CSA

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Table 5.
Vibrational Modes in A0 and D0

Modes of vibration	Wavenumber (cm^{-1})	
Sample code →	A0	D0
–CH stretching	2911	2912
$-CH_2$ deformation	1330	1330
CH rocking	1253	1251
Trans CH wagging	961	963
C-Cl stretching	835	Very weak peak
cis CH wagging	613	613
	CSA	D0
Sulphonic acid group peak	793	Very weak peak
Sulphonic acid group peak	1038	1041
Ketone group	1738	1740

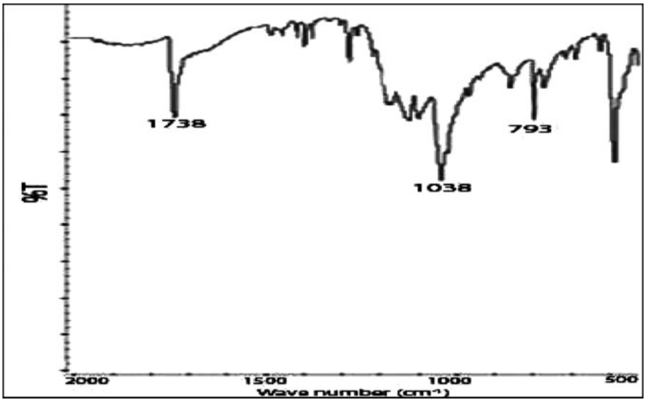

Figure 4.
FTIR of CSA

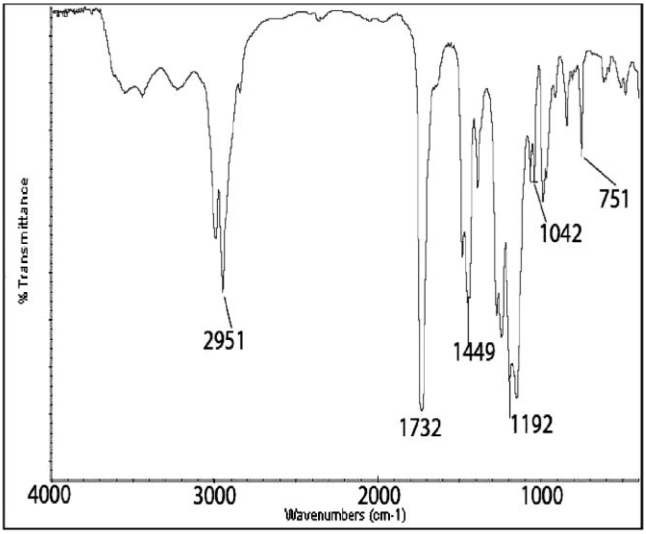

Figure 5.
FTIR of PMMA doped with CSA

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Table 6.
Vibrational Modes observed in A10 and D10

Modes of vibration ↓	Wavenumber (cm^{-1})	
Sample code →	A10	D10
–CH stretching	2951	2951
C=O stretching	1743	1732
CH_3 stretching	1449	1449
–OCH3 stretching	1199	1192
	CSA	D10
Sulphonic acid group peak	793	751
Sulphonic acid group peak	1038	1042
Ketone group	1738	1732

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 doping PMMA with CSA, indicate an interaction between H^+ ion of CSA and oxygen atoms of C=O and –OCH_3 of PMMA.[21]

FTIR of Blends Doped with CSA

A1, A3, A5, A7, A9 are PMMA-PVC blends. These blends have been modified by 20 wt. % doping with CSA resulting in the modified blends D1, D3, D5, D7, D9 respectively as explained in Table 1. Though the FTIR spectra of all these five undoped blends and five doped blends have been recorded, the spectra of A1, D1 (PVC rich blends) and A9, D9 (PMMA rich blends) are only given in Figure 6–9 respectively. Table 7 summarizes the comparative shifts in the vibrational modes of all of these blends.

The FTIR spectra show that the sulphonic acid peaks at 793 cm^{-1} shifts to 751 cm^{-1} and peak at 1038 cm^{-1} shifts to 1041 cm^{-1} in all blend compositions.

The CH rocking peaks of pure PMMA-PVC blends are shifted to lower wavenumbers after doping.

The trans CH wagging peaks also show a significant change in their shapes with the development of new shoulders and small peaks as summarized in Table 7. The positions of these peaks also show a small shift. The C-Cl stretching peaks show shifts after doping (except in A5, D5). From Table 7 it is further observed that C=O peak in pure blends and doped blends indicate a shift in all compositions, whereas

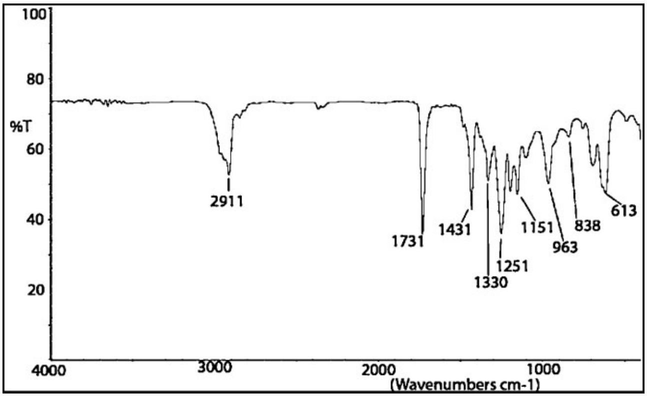

Figure 6.
FTIR of A1

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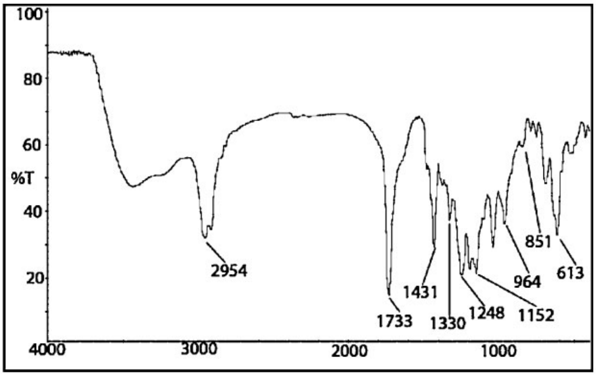

Figure 7.
FTIR of D1

–OCH_3 stretching peak does not show any shift in all compositions (except in A7, D7). These observations indicate that H^+ ion in CSA further interacts with Cl of CHCl (PVC). CHCl has already taken part in hydrogen bond formation with C=O of PMMA. The interaction of H^+ ion with oxygen of –OCH_3 of PMMA in the blends is not observed as there is no shift in –OCH_3 stretching peaks in any of the blend compositions (except in A7, D7).

Mechanical Properties

The FTIR results indicate an interaction is taking place between PMMA and PVC, CSA and PVC, CSA and PMMA, CSA and PVC-PMMA blends. If there is an interaction between polymer-polymer and polymer-dopant and blend-dopant then changes in the mechanical properties of polymers are expected. Therefore to support the observations made from FTIR results, about possible interactions, mechanical properties of all samples were recorded. Figure 10 and 11 show the change of Youngs modulus (YM) and Tensile strength (TS) respectively, with respect to PMMA content in the blend. These graphs also compare the values of YM and TS for undoped and doped samples.

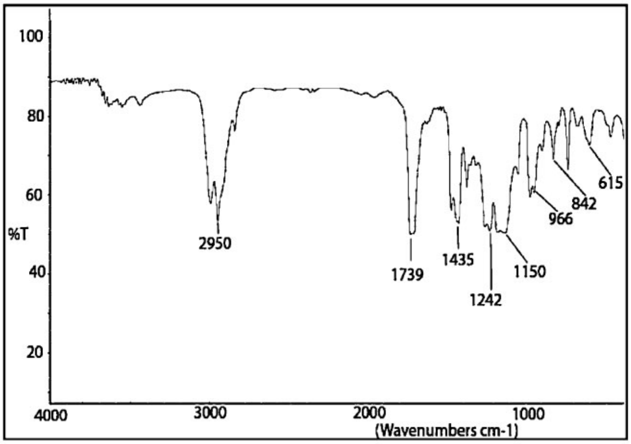

Figure 8.
FTIR of A9

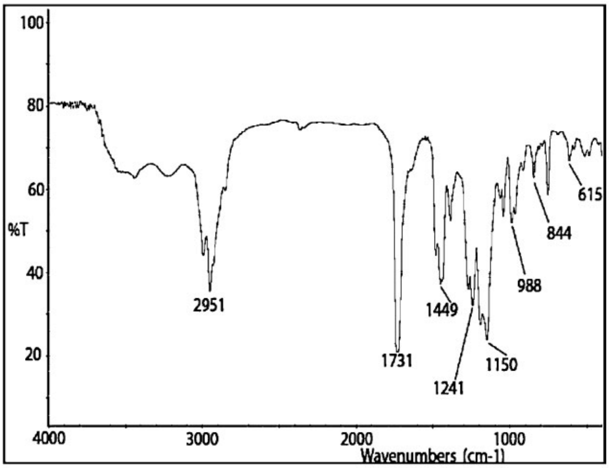

Figure 9.
FTIR of D9

It is observed from these graphs that there is a slight increase in YM and TS for doped PVC as compared to undoped PVC. This result can be attributed to the fact that there is an interaction between PVC and dopant CSA as discussed in Section 3.3.

It is further seen from Figure 10 and 11 that for samples D1 and D3 (PVC rich blends), there is an increase in YM and TS as compared to corresponding values in A1 and A3 blends. On the other hand in D5 and in the PMMA rich blends D7, D9 there is a decrease in YM and TS as compared to corresponding values in A5, A7 and A9 blends. Thus in some blends increase in YM and TS is observed whereas in some blends decrease in YM and TS is observed.

Whenever an impurity is added to a polymer it can act as a plasticizer or antiplasticizer.[23] Ghersa and Jackson[23,24] have reported that a certain salt when added in small quantity to a polymer may act as an antiplaticizer and the same salt when added in a large quantity may act as a plasticizer for the polymer. The same authors have reported that plasticizer causes decrease in YM and TS whereas antiplasticizer causes increase in YM and TS. Blends of PMMA and PVC mixed with 20%(w/w) dopant CSA show complex

Table 7.
Vibrational Modes observed in blends and doped blends

Vibration Modes ↓	Wavenumber (cm^{-1})									
Sample code →	A1	D1	A3	D3	A5	D5	A7	D7	A9	D9
CH stretching	2911	2954 + sp	2948 +sh	2950 +sp	2949 +sh	2950 +sp	2911	2951 +sp	2950 +sh	2951 +sh
CH_2 deformation	1330	1330	1329	1330	1329	1330	1330	pw	pw	pd
CH rocking	1251	1248	1245	1241	1250	1242	1253	1241	1242	1241
trans CH wagging	963	964	964	966 +sh	966	966 +sp	961	988 +sp	966	988 +sp
C-Cl stretching	838	851	842	844	843	843	835	843	842	844
cis CH wagging	613	613	614	614	615	614	613	614	615	615
C=O stretching	1731	1733	1730	1732	1736	1732	1710	1732	1739	1731
CH_3 stretching	1431	1431	1433	1433	1435	1435	1430	1437	1435	1449
-OCH_3 stretching	1151	1152	1151	1151	1150	1150	1199	1193	1150	1150

Where, + sh - stands for development of a shoulder, +sp - stands for development of a small peak, pd - peak disappears, pw - peak too weak to be marked.

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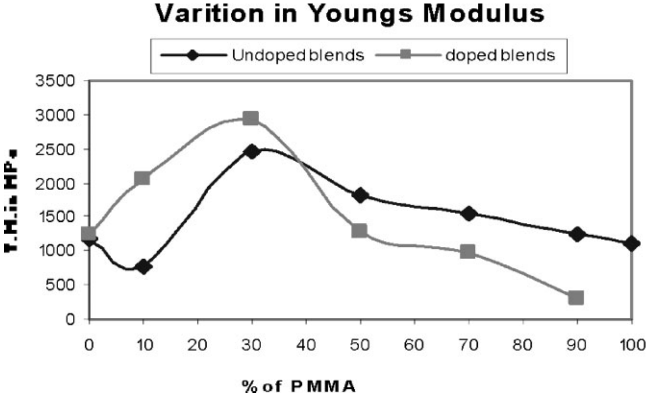

Figure 10.
change in Youngs Modulus with composition

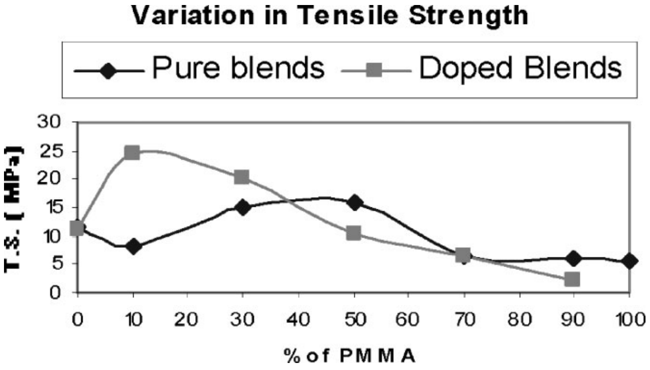

Figure 11.
change in Tensile strength with composition

formation over the entire range of the composition of the binary polymer blend. The dopant acts as an antiplasticizer in blends with up to about 50%(w/w) PVC, while it plasticizes in PMMA-rich blends.

The strong interaction leading to complex formation results in stiffening of chains and is one of the effects of antiplasticizing action of the additive. Antiplasticizing action should cause an increase of the frequency of the vibration and vice versa. This fact is observed in the C=O shifts in all doped and undoped samples (except in A7, D7) as seen in Table 7. Thus the complex formation in PVC rich blends has an antiplasticizing action leading to increase in YM and TS in D1, D3 blends.

The plasticizing action of plasticizer is due to the weakening of second order (Van der Waals) attraction forces between the polymer chains. This takes place because of interposition of the plasticizer molecules and the screening of the polar groups of the polymer. The weakening of the attractive forces results in decrease in YM and TS as observed in sample D5 and PMMA rich blends namely D7, D9. The plasticizing action seems to be very large in D10 and as such a free standing film of it could not be obtained to have the measurements of its mechanical properties.

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Conclusion

Table 1 shows the existence of a single Tg value for all the blends. This shows that even after doping the blends with CSA, the miscibility in the polymers is not disturbed.

PMMA and PVC are miscible over entire blend compositions (Table 1). This miscibility is due to hydrogen bonding between CHCl of PVC and C=O of PMMA.

The interaction between CSA and PVC is also observed due to hydrogen bond between ketone group of CSA and CHCl of PVC.

The interaction of CSA and PMMA is also seen in FTIR study. This system has an interaction between H^+ ion of CSA and oxygen atoms of C=O and $-OCH_3$ of PMMA as both these groups show significant shifts after PMMA is doped with CSA.

On the other hand when CSA is doped in PMMA-PVC blend matrix, H^+ ion has an interaction with Cl of CHCl (from PVC). CHCl of PVC has already formed a hydrogen bond with C=O of PMMA. Thus the interaction of H^+ ion with CHCl of PVC shifts the C=O peak position after doping. However no interaction of H^+ ion with $-OCH_3$ of PMMA is seen in the blends. This observation is supported by the fact that in the blends there is no shift in the $-OCH_3$ stretching peaks (except A7, D7).

From the mechanical properties it is seen that the interaction of CSA with PVC rich blends has an antiplasticizing action whereas the interaction of CSA with PMMA rich blends has a plasticizing action.

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