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Spectroscopic Correlation of Mechanical Properties of PVC/PMMA Polymer Blend*

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Abstract: PVC/ PMMA polymer blends are characterized at molecular level by FTIR-ATR spectroscopy providing important insight into the molecular interactions responsible for the enhancement of its mechanical properties. The changes in mechanical properties are reflected by the changes in the FTIR-ATR spectrum. The mechanical properties of such poly blends revealed a substantial increase in Young's modulus and ultimate tensile strength after initial drop at 10% of PMMA. A comparative study of mechanical properties of PVC/ PMMA polymer blends with different weight percentage are carried out and their results are co-related with FTIR – ATR spectral studies and important conclusions are drawn about the possible molecular interactions between constituent polymers.

Key words: Polymer blends, Mechanical properties, Molecular interaction, Young's Modulus, Ultimate Tensile Strength.

1. Introduction

The modification of polyvinyl chloride (PVC) to obtain different PVC copolymers and blends is of great significance to the plastics industry. Polymer blends exhibit properties that are superior to any one of the component. Miscibility of the constituent polymers decides the structure of the blend which in turn, decides the properties of the blend. If there is weak interaction between constituent polymer, miscibility of polymers is weak. Blending offers a unique tool for overcoming the deficiencies of the polymer without much loss in the mechanical properties. Knowledge of the miscibility and phase behavior of polymer blends is essential for controlling

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*Presented at CONIAPS XI, University of Allahabad, India, Feb. 20-22,2010 the properties of polymer blends. Enhancement in ionic conductivity and mechanical strength has been reported in polymer electrolytes by modifying them in the form of blends [1,2]. PVC is one of the most widely used polymers because of its well-known performance and low cost. The aim for modifying PVC by blending is to manufacture new PVC polymers that combine desired physical properties at low cost. Blending technique has gained a lot of commercial as well as academic importance. In addition to blending, we can also improve stiffness by adding inorganic dopant materials whereas using rubbery phase improves toughness of the polymers. PVC/ PMMA blends has been studied by different approaches by different workers, it was well described by Chao Zhoul et.al [3]. Schurer [4] reported that PVC/ PMMA are miscible only in blends having PVC contents greater than 60%. Rupa Chakrabarti et. al[5] studied physical and mechanical properties of PVC/PMMA blend and suggested that a substantial increase in toughness accompanied with unusual increase in modulus and ultimate tensile strength occurred after initial stages of PMMA incorporation compared to pure PVC. Wlochowicz and Janicki[6] concluded that PVC / PMMA blends at all compositions are wholly amorphous two-phase system. Varada[7] investigated the miscibility of PVC with PMMA by ultrasonic and refractive index method. They pointed that PVC and PMMA are miscible in all compositions. Kamira Aouachria and Naima Belhaneche-Bensemra[8] studied about miscibility of PVC/PMMA blend. Shen and Torkelson [9] observed that PVC/ PMMA blends are miscible at all compositions, if they are prepared between Tg and their lower critical solution temperature. This discrepancy in the miscibility may be due to the different methods used for sample preparation and polymers used are having different molecular weights. S.Ramesh et.al[10] studied PVC/PMMA blend based polymer electrolytes and reported about interaction of PVC/PMMA blend with lithium triflate salt, ethylene carbonate (EC), dibutyl phthalate (DBP) plasticizers and also with silica. Vijay V. Soman and Deepali S. Kelkar [11] have suggested about the interaction among Camphor Sulphonic Acid (CSA), PVC, PMMA and PVC/PMMA blend in different weight percentage. The present study involves the blending of PVC with amorphous and a rigid polymer, poly (methyl methacrylate) (PMMA) having a very high glass transition temperature (Tg). PMMA might be expected to counter balance the fall in mechanical properties of PVC is attributed to the disruption in molecular packing of stiff and rigid chains of PVC.

In the present study we have added PMMA to modify PVC by blending method to enhance the mechanical properties of the PVC. PMMA influences the matrix structure of PVC which in turn affects physical properties like mechanical properties of PVC. We have studied here the change in mechanical properties due to the intermolecular interaction between PVC and PMMA polymers. We have correlated the change in the mechanical properties by noting the shifts of the peaks, developments of new peaks and change in the peak intensity in the FTIR spectrum. The aim of the current work is to study the mechanical properties in detail and to correlate their results with spectroscopic investigations using FTIR-ATR spectra.

2. Experimental

PVC and PMMA were obtained from local Chemicals supplier and are used as received and the blends were prepared by the solution casting method. The weighed fractions of PVC and PMMA were dissolve in acetone plus toluene solution in 1:3 fraction at room temperature and stirred for approximately 24 hrs at different proportions starting from 90/10, 80/20, 70/30,etc. And the solution was cast on a clean and flat petty dish. Then petty dish is kept open at room temperature to evaporate the solvent. Then the films were lifted from the petty dish. The FTIR spectra of all polymer blend samples have been recorded on a JASCO- FTIR- 4100 Spectrometer, between 4000 cm^{-1} and 600 cm^{-1} in the ATR mode. Mechanical properties of all polymer blend samples have been reported in this study. These measurements were made on Lloyds LR30 K instrument with a crosshead speed 10 mm/min and a gauge length of 10 mm. All testing were carried out at room temperature. Pores or nicks free samples were used for measurements.

3. Result and Discussion

Mechanical properties of PVC-PMMA polymer blend were carried out to study the Young’s modulus (YM), Ultimate Tensile Strength (UTS), Breaking Load Per Volume (BLPV), Yield Load Per Volume (YLPV), Stress at Peak load, Elongation at Break (EB). The values of all mechanical properties obtained for PVC/PMMA blends are higher than the values of the Pure PVC except the blend of 10% of PMMA.

Young’s Modulus (YM) values for PVC/PMMA blends are calculated from the slope of stress-strain curve. YM values corresponding to PMMA % is shown in fig.1. The fig.1 shows that PVC/PMMA blends exhibit lower YM to the extent 10% of PMMA, beyond which there is sudden increase in YM and it reaches maximum value for 20% of PMMA and after that it again exhibits a decreasing trend.

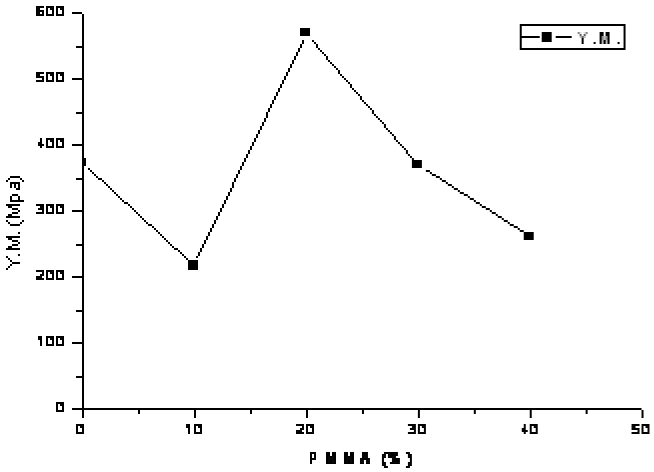


Fig. 1 Change in Young's Modulus (Y.M.) with blend composition

The values of Ultimate Tensile Strength (UTS), Breaking Load per Volume (BLPV), Yield Load per Volume (YLPV) and Stress at Peak load for PVC/PMMA blends are shown in fig.2 to fig.5 corresponding to PMMA %. All these values also exhibit minimum value at 10% of PMMA and then sharp increase in such properties beyond 10% of PMMA and gives maximum value at 20% of PMMA. After 20% of PMMA, blend exhibit decreasing trend but their corresponding values of such properties for different blends are quite high in comparison of pure PVC.

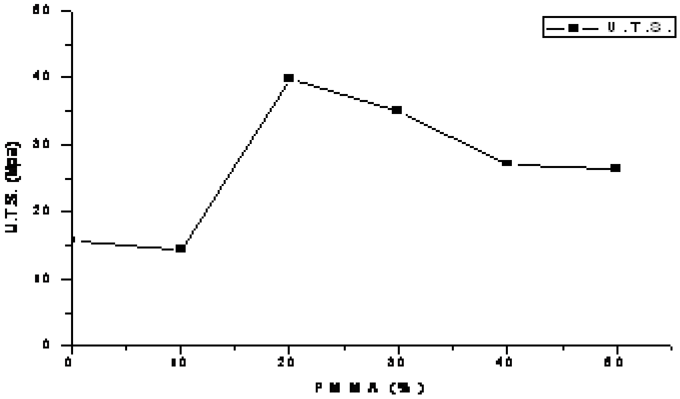


Fig. 2 Change in Ultimate Tensile Strength (UTS) with blend composition

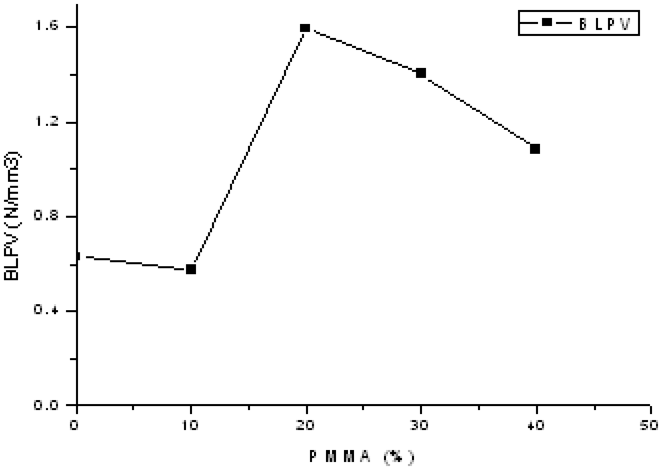


Fig. 3 Change in Breaking Load Per Volume (BLPV) with blend composition

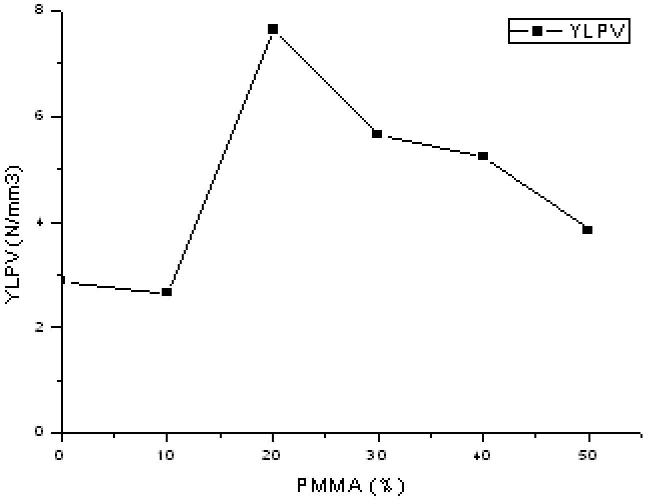


Fig. 4 Change in Yield Load Per Volume (YLPV) with blend composition

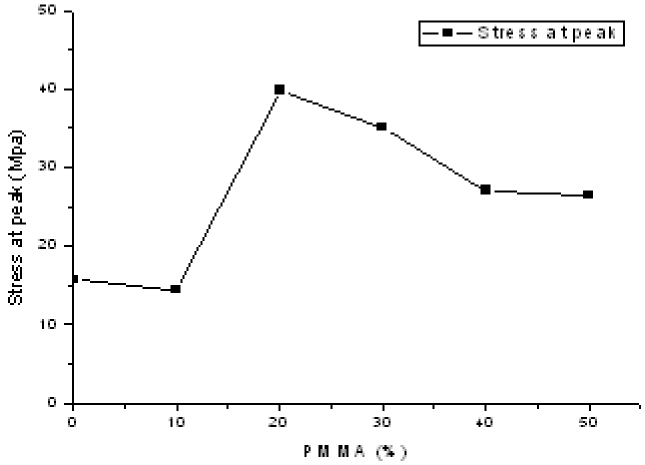


Fig. 5 Change in stress at peak with blend composition

The breaking elongation of various blends of PVC/PMMA is shown in fig.6, confirmed to our expectation. In this case there is a sudden jump in its values initially up to a level of 10% PMMA. Beyond which there is a steady decrease in its values which also confirmed by a decrease in Young's Modulus (YM), Ultimate tensile strength (UTS) etc.

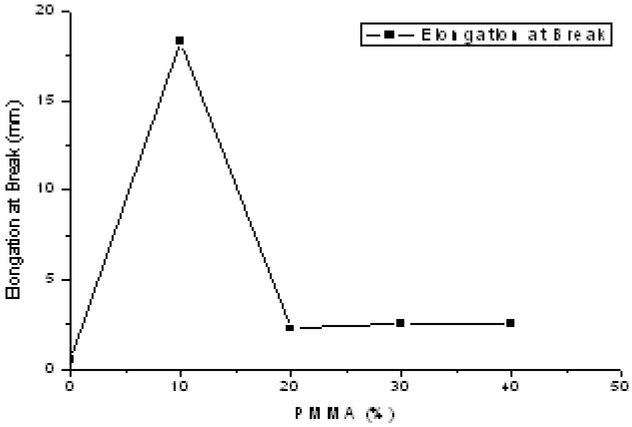


Fig. 6 Change in Elongation at Break (E.B.) with blend composition

The introduction of PMMA into PVC increases the Mechanical properties such as Young's Modulus (YM), Ultimate Tensile Strength (UTS), Breaking Load per Volume (BLPV), Yield Load per Volume (YLPV) and Stress at Peak load. The different Young's Modulus (YM) values in PVC blends are due to the difference in cross linking density provided by PMMA with different weight fraction values. In general polymers having either a high degree of crystallinity, cross linking or rigid chain exhibit a high strength and low extendibility, thereby giving a high Young's Modulus (YM) values, high stress at peak value and low elongation value.[12] PVC is a hard and strong materials and it shows the dipole-dipole type attraction as a result of electrostatic interaction between the chlorine atom of one chain and hydrogen atom of another. When PMMA is blended with PVC these interaction are weakened by the presence of PMMA up to 10% of PVC. Beyond 10% of PMMA, we observed reversal behavior of PMMA affecting on PVC. So the mechanical properties increase beyond 10% of PMMA and exhibit higher values at 20% of PMMA. Because at 20% of PMMA, the interaction between PVC and PMMA molecules is higher and the dipole-dipole attraction is also reaches at maximum value.

Samples and their codes are given in Table 1. Various vibrational modes and their respective wave numbers (cm^{-1}) observed in P_0 P_1, P_2, P_3, P_4, P_5 and P_6 are shown in Table 2. The FTIR-ATR spectra of pure PVC (P_0), pure PMMA (P_6) and PVC:PMMA (80:20) blend (P_2) are shown in fig. 7, 8 and 9 respectively.

Table1. Samples and their codes used in this study

Name of Sample	Code
Pure PVC	P_0
90% PVC + 10% PMMA	P_1
80% PVC + 20% PMMA	P_2
70% PVC + 30% PMMA	P_3
60% PVC + 40% PMMA	P_4
50% PVC + 50% PMMA	P_5
Pure PMMA	P_6

FTIR-ATR spectrum reveals molecular interactions between PVC and PMMA. The following characteristic frequencies, C- Cl stretching (834 Cm^{-1}), Trans C-H wagging (957 Cm^{-1}), C-O stretching (1141 Cm^{-1}), C-O-C stretching (1190 Cm^{-1}), C-H anti symmetric stretching (1481 Cm^{-1}), C=O stretching (1723 Cm^{-1}), $-CH_2$ Anti Symmetric Stretching (2851 Cm^{-1}) and -CH stretching (2911 Cm^{-1}) shows a shift in the frequency towards the higher frequency side. While the following characteristic frequencies, $-CH_2$ deformation (1331 Cm^{-1}), C-H rocking (1236 Cm^{-1}) and C-H deformation (1434 Cm^{-1}) remains unchanged and the frequencies cis C-H wagging (613 Cm^{-1}), C-C stretching (985 Cm^{-1}), $-CH_2$ twist (1238 Cm^{-1}), C-H symmetric stretching (1385 Cm^{-1}), -CH_3 stretching + –CH_2 Symmetric Stretching (2951 Cm^{-1}) and -CH_3 stretching (2996 Cm^{-1}) shows a decrease in trend.

Table2. Vibrational Modes observed in the pure PVC, PMMA and its blends

Vibrational modes ↓	Peak No.		Pure Sample	Wave Number (Cm^{-1})				
Sample Code ⟶				P_1	P_2	P_3	P_4	P_5
-CH stretching	1	**PVC(P_0)**	2911	2915	2920	2915	2911	2926
-CH_2 deformation	2		1331	1328	1331	1332	1332	1325
C-H rocking	3		1236	1233	1236	1236	1237	1238
Trans C-H wagging	4		957	957	960	962	964	965
C-Cl stretching	5		834	832	844	841	841	841
cis C-H wagging	6		613	605	608	616	618	615
-CH_3 stretching	7	**PMMA(P_6)**	2996	3004	2993	2992	2994	2992
-CH_3 stretching + -CH_2 symmetric stretching	8		2951	2961	2946	2950	2950	2949
-CH_2 antisymmetric Stretching	9		2851	2852	2852	2842	2841	2843
C=O stretching	10		1723	1737	1732	1727	1726	1724
C-H antisymmetric stretching	11		1481	1495	1495	1483	1483	1482
C-H deformation	12		1434	1426	1434	1434	1434	1434
C-H symmetric stretching	13		1385	1371	1371	1384	1385	1385
-CH_2 twist	14		1238	1233	1236	1237	1237	1238
C-O-C stretching	15		1190	1195	1194	1191	1191	1190
C-O stretching	16		1141	1150	1149	1146	1145	1144
C-C stretching	17		985		960	986	986	988

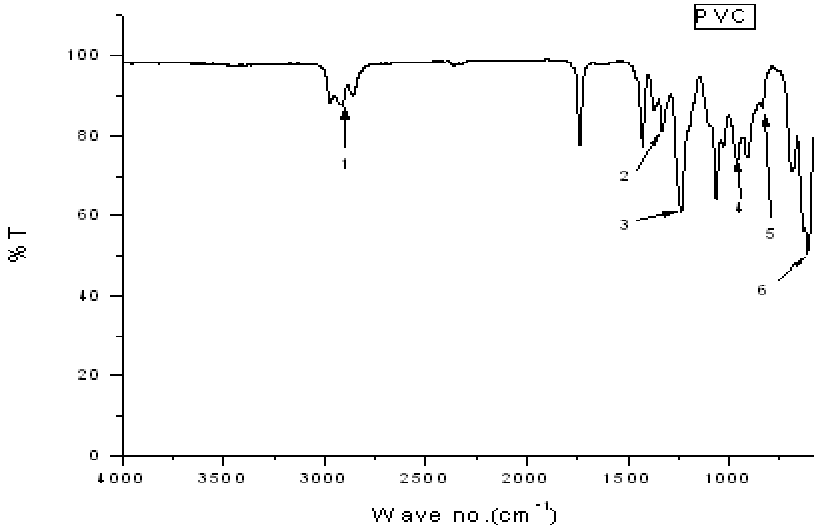


Fig. 7 FTIR spectra of pure PVC (P_0)

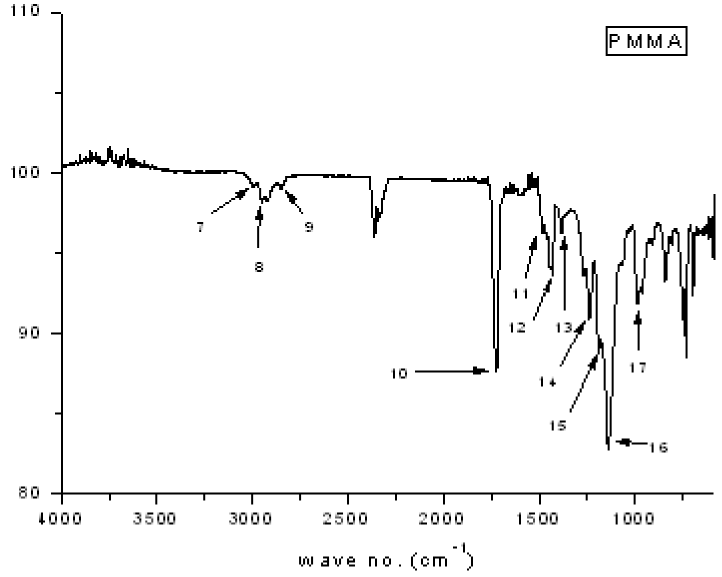
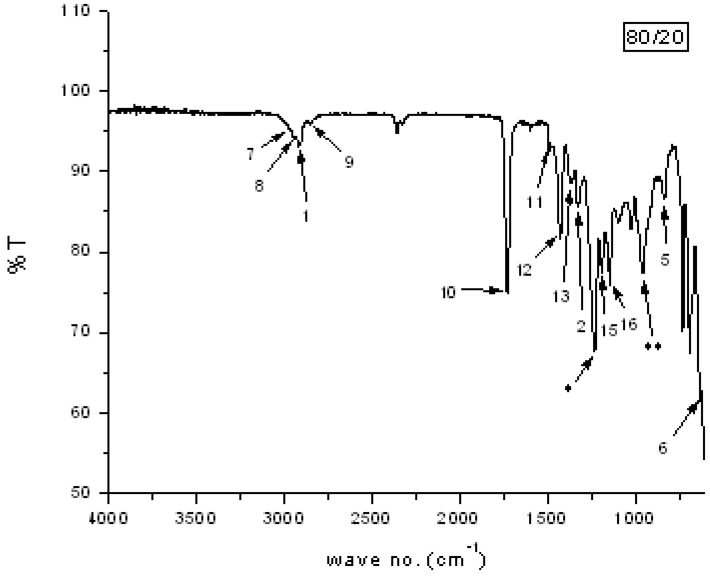


Fig. 8 FTIR spectra of pure PMMA (P_6)



* indicates peak no.3 and 14 are overlap, **indicates peak no.4 and 17 are overlap

Fig. 9 FTIR spectra of PVC:PMMA (80:20) blend (P_2)

By the careful study of the mechanical properties and the shift shown by the FTIR- ATR spectra, it is clearly seen that there is a trend in the peaks to shift to the higher wave number side. This increase in wave numbers is due to the increase in the vibrational frequency. This increase in frequency is due to the increase in strength of the bond and hence increases the mechanical properties of the polymer blend. Therefore we can conclude that by noting shift of the peaks in the FTIR-ATR spectrum we can draw conclusion about the mechanical properties of the polymer blend. Thus we are correlated mechanical properties with spectroscopic investigation by FTIR-ATR spectral studies.

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