Chapter 3

Characterization of PVC/PMMA Blends

Abstract

This chapter gives an account of the characteristics of PVC/PMMA blend in different weight proportion (70/30, 50/50 and 30/70) which is prepared by solution cast technique. These blends are investigated by spectroscopic techniques like FTIR, UV-Vis and RAMAN. Mechanical, Thermal and Morphological properties are investigated. The results obtained from different characterization techniques show the blending effect of different properties. These properties of PVC/PMMA blends are correlated with spectroscopic investigation.

3.1. Introduction

PVC is one of the most important and widely used thermoplastic polymers because of its well-known performance and properties like low cost, good processability, chemical resistance and low flammability. The modification of polyvinyl chloride (PVC) to obtain different PVC copolymers and blends is of great significance to the plastics industry. 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.

Polymers and their blends are often processed in the melt, which makes them thermally stable. Several studies show that blending can alter the decomposition of individual polymers [1-4].PVC has low thermal stability which is its major drawbacks. Several polymers are mixed with PVC as plasticizers or processing aids. PMMA is used as processing aids for PVC [5]. I. C. Mc Neil et. al. [6] studied PVC/PMMA mixtures and showed that methacrylate (MMA) monomer formed at a much lower temperature than that of PMMA depolymerization when heated alone. D. Braun et al [7, 8] studied the thermal degradation of PVC with PMMA have shown that at higher concentrations of PMMA exhibit some stabilization of PVC, while lower concentrations leads to destabilization. Naima Belhaeche- Bensemra et. al. [9] showed that PMMA exerted a stabilizing effect on the thermal degradation of PVC by reducing de-hydro chlorination.

Miscibility and phase behavior of polymer blends is essential for controlling the properties of polymer blends. PVC/ PMMA blends has been studied by different approaches by different workers, it was well described by Chao Zhoul et.al.[10], Schurer [11] reported that PVC/ PMMA are miscible only in blends having PVC contents greater than 60%. Rupa Chakrabarti et. al. [12]

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 [13] concluded that PVC / PMMA blends at all compositions are wholly amorphous two-phase system. Varada [14] investigated the miscibility of PVC with PMMA by ultrasonic and refractive index method. They pointed out that PVC and PMMA are miscible in all compositions. Kamira Aouachria and Naima Belhaneche-Bensemra [15] studied about miscibility of PVC/PMMA blend. Shen and Torkelson [16] observed that PVC/ PMMA blends are miscible at all compositions, if they are prepared between T_g 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.

In the past recent years, the importance of using PVC/PMMA blend polymer electrolytes was used by many researchers. S. Ramesh et.al. [17] 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 [18] have suggested about the interaction among Camphor Sulphonic Acid (CSA), PVC, PMMA and PVC/PMMA blend in different weight percentage. 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[18].

The PVC and PMMA blend is a well known system in which hydrogen bonding type of specific interaction involving α-hydrogen of PVC and the carbonyl group of PMMA is expected [19].

The matrix structure of the blend is different than pure polymers which in turn affects the physical properties of the blend including the mechanical properties. Infrared spectroscopy is a tool to find out the possible interaction between the polymer matrixes. Several researchers have used this technique to study such interactions between polymers [20, 21].

Several 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 [22, 23]. In recent years, studies on optical and electrical characteristics of polymers have fascinated much consideration in their application in optical and electronic devices [24, 25]. Electrical and optical properties of polyvinyl alcohol thin films doped with metal salts have been investigated by Abd et al. [26]. Refractive index is an important optical parameter for the design of prisms, windows and optical fiber [27]. The absorbance process plays an important role in the optical properties of polymers. From the absorption spectra, it is possible to understand variation of molecular formation of polymer structures.

In the present chapter we studied different properties of PVC/PMMA blends in different weight percentage by different characterization techniques. We report evidence from Fourier Transform Infrared (FTIR) Spectroscopy for hydrogen bonding type interaction between α-hydrogen of PVC and carbonyl group of PMMA which supports earlier studies done by several researchers. We have also studied some optical properties such as absorption coefficient, optical (direct/indirect) energy band gap, Refractive Index, optical dielectric constant and constant B. In addition, Mechanical Properties of Blends, Thermal Characteristics by Thermal Gravimetric Analysis (TGA), and surface morphology by Scanning Electron Microscopy (SEM) are reported.

The effects of different blending weight percentage on these properties have been discussed and behaviors of all properties are investigated.

3.2. Results and Discussion

3.2.1. FTIR Analysis

Infrared spectroscopy is a tool to find out the possible interaction between the two polymer matrixes. The interaction can be studied by 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. Complexation may shift the polymer peak frequencies. FTIR would be sensitive both in situations where complexation has occurred in crystalline or amorphous phase [28]. **Figure 3.1** (a, b) shows the FTIR spectrum of Pure PVC, Pure PMMA and other polymer Blends. FTIR-ATR spectrum reveals molecular interactions between PVC and PMMA. Different Vibrational modes of Pure PVC, Pure PMMA and their Blends are described in **Table 3.1**. 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}) 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}) remains unchanged and the cis C-H wagging (613 cm^{-1}), C-H symmetric stretching (1385 cm^{-1}) and $-CH_3$ stretching + $-CH_2$ Symmetric Stretching (2951 cm^{-1}) shows a decrease in trend.

Rupa Chakrabarti et. al. [12] studied physical and mechanical properties of PVC/PMMA blend and suggested, hydrogen bond interaction between C-Cl group of PVC and C=O group of PMMA. So here also peak shifting are observed for C-Cl stretching group (834 cm^{-1} to 844 cm^{-1}) towards higher wave number side and for C=O stretching group (1723 cm^{-1} to 1732 cm^{-1})

Table 3.1 **Assignment of different vibrational modes of PVC, PMMA and various Blends.**

Vibrational Modes ↓	Peak	Pure		Wave number (cm^{-1})			
Sample (wt %) →	No.	Sample		90/10	80/20	60/40	40/60
-CH stretching	1	PVC	2911	2915	2920	2915	2911
-CH$_2$ deformation	2		1331	1328	1331	1332	1332
C-H rocking	3		1236	1233	1236	1236	1237
Trans C-H wagging	4		957	957	960	962	964
C-Cl stretching	5		834	832	844	841	841
cis C-H wagging	6		613	605	608	616	618
-CH$_3$ stretching	7	PMMA	2996	3004	2993	2992	2994
-CH$_3$ stretching + –CH$_2$ Symmetric Stretching	8		2951	2961	2946	2950	2950
–CH$_2$ Anti Symmetric Stretching	9		2851	2852	2852	2842	2841
C=O stretching	10		1723	1737	1732	1727	1726
C-H anti symmetric stretching	11		1481	1495	1495	1483	1483
C-H deformation	12		1434	1426	1434	1434	1434
C-H symmetric stretching	13		1385	1371	1371	1384	1385
-CH$_2$ twist	14		1238	1233	1236	1237	1237
C-O-C stretching	15		1190	1195	1194	1191	1191
C-O stretching	16		1141	1150	1149	1146	1145
C-C stretching	17		985	985	960	986	986

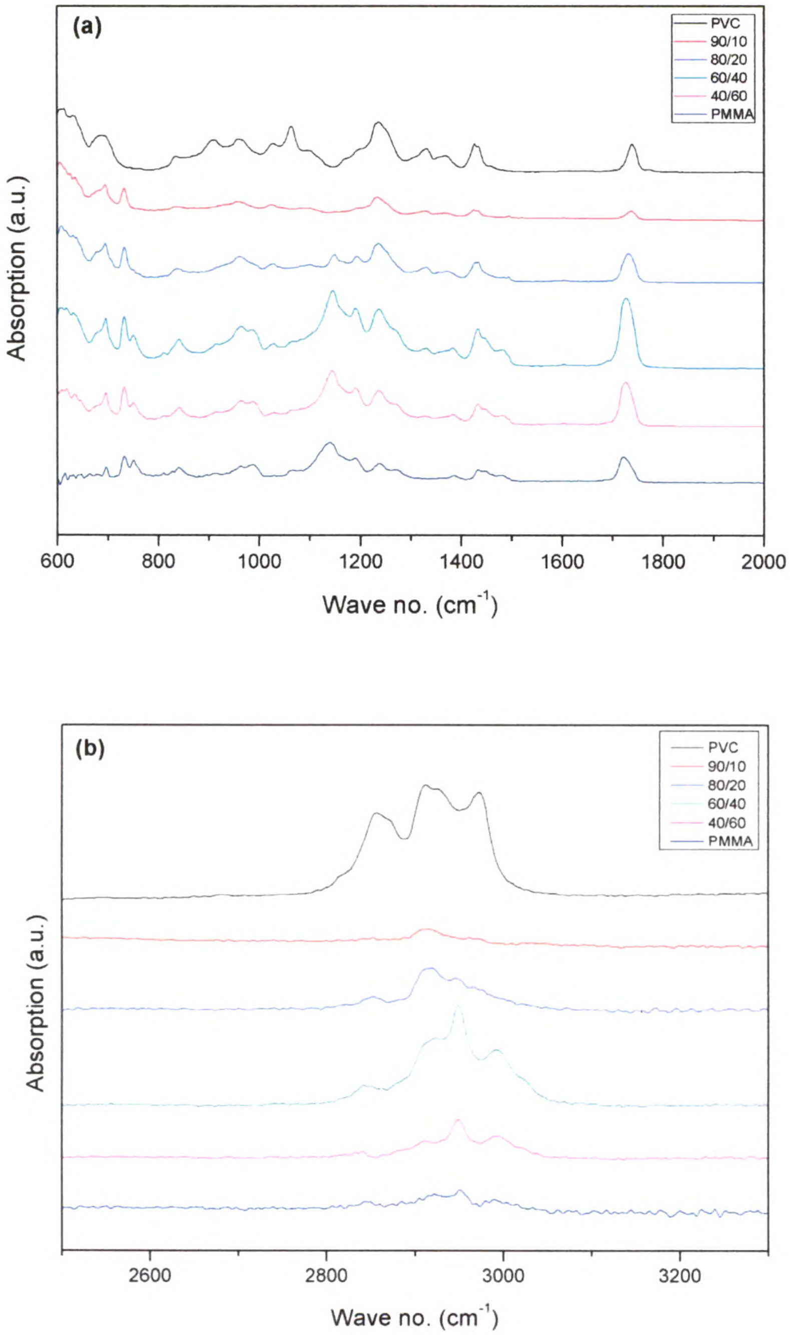

Figure 3.1 FTIR Spectra of pure PVC, pure PMMA and Their blends (a) in the range 600 – 2000 cm^{-1} (b) in the range 2500 – 3300 cm^{-1}

towards higher wave number side, which clearly indicate the hydrogen bonding intermolecular interaction between PVC and PMMA polymer chains. These peaks are shifted towards higher wave number side which reveals increase in the strength of the bonds. S. Ramesh [17] has reported the shift in the carbonyl absorption peak to higher wave number side from 1721 cm^{-1} to 1732 cm^{-1}. Our results also verify these results.

3.2.2. UV-Vis Analysis

The absorbance process plays an important role in the optical properties of polymers. From the absorption spectra, it is possible to understand variation of molecular formation of polymer structures. From the absorption spectra, (**Figure 3.2 (a)**), a sharp increase in absorption below 220 nm, which corresponds to $\pi \rightarrow \pi^*$ transitions of carbonyl groups in macromolecules is observed [29]. The absorption edges were observed around 250 to 300 nm (**Figure 3.2 (b)**). A shift in band edges toward the higher wavelengths with different absorption intensity for PVC doped PMMA was observed. These shifts indicate the formation of inter/ intra bond between PVC and PMMA. The direct optical energy gap, can be obtained from the plot of $(\alpha h\nu)^2$ versus hv (photon energy) (**Figure 3.2(c)**), while indirect energy gap obtained from the plot of $(\alpha h\nu)^{1/2}$ versus hv (**Figure 3.2(d)**), is believed to be appropriate for the higher energy absorption (**Eq. 2**). The intercept on the energy axis on extrapolating the linear portion of the curves to zero absorption value may be interpreted as the value of the band gap. The various optical properties obtained for different samples are listed in **Table 3.2**. These results are in consistence with FTIR results. Also, the shift in absorption edge reflects the variation in the optical energy band gap. Absorption edge shifted towards higher wavelength side as the PMMA content in PVC increases. It is clear that the indirect optical energy band gap increases with increasing PMMA content. The existence and variation of optical energy gap may be explained by invoking the occurrence of local cross linking within the amorphous phase of PMMA and PVC.

Table 3.2 Variation of absorption edge and direct/indirect band gap with different blend percentage

PVC/PMMA blend percentage	**Absorption edge (ΔE) (eV)**	**Direct band gap ($E_{g(Dir)}$)**	**Indirect band gap ($E_{g(Indir)}$)**
Pure PVC	3.91	4.09	3.65
80/20	4.05	4.21	3.92
60/40	4.11	4.24	4.05
40/60	4.19	4.30	4.15
Pure PMMA	4.42	4.46	4.31

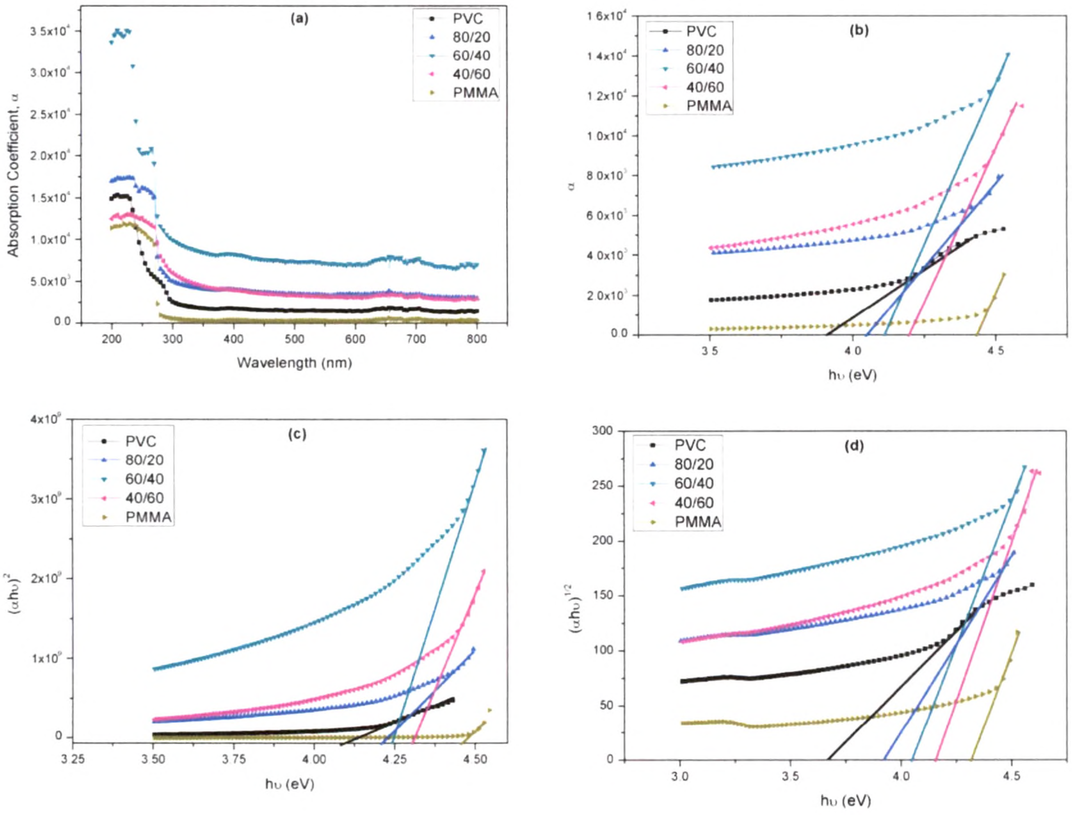

Figure 3.2 Plot of (a) Absorption coefficient (α) vs Wavelength (λ), (b) Absorption coefficient (α) vs Photon Energy (hν), (c) $(\alpha h\nu)^2$ vs hν, (d) $(\alpha h\nu)^{1/2}$ vs hν

3.2.3. RAMAN Analysis

The Raman spectra of the blends of PVC and PMMA are shown in **Figure 3.3**. Spectral shifts have been observed in the blends of PVC/PMMA polymers. The same trend can be found from both IR and Raman data, i.e. a shift in the C-Cl stretching region of PVC and a clear shift of the carbonyl stretching (C=O) of the PMMA component.

The C-Cl stretching peak shows the shift towards higher wave number. i.e. blue shift for the blends spectra (828 cm^{-1} to 867 cm^{-1}). The magnitude of the blue shift of the C=O stretching mode of PMMA (1917 cm^{-1} to 1935 cm^{-1}) is shown in **Figure 3.3(a, b)**. Both peaks shows maximum peak shift for 80/20 wt % content, which is indicating strong hydrogen bonding between two polymers.

The hydrogen bonding which occurs between C-Cl group in PVC and C=O group in PMMA is significant. Spectral changes in the C-Cl stretching region and C=O stretching region of the blends are a mixed contribution from both the C-Cl...O=C interaction and the local conformational structures of pure polymers, PVC and PMMA.

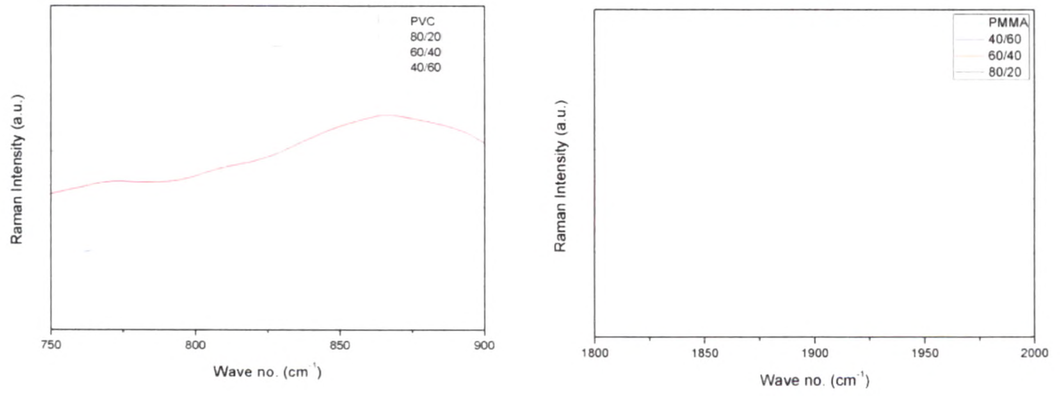

Figure 3.3 Raman Spectra of Pure PVC, Pure PMMA and their blends (a) in the C-Cl stretching region of PVC (b) in the C=O stretching region of PMMA

3.2.4. Mechanical Analysis

Mechanical properties of PVC-PMMA polymer blend were carried out to study the Young's modulus (YM), Ultimate Tensile Strength (UTS), Stress at Peak load and Elongation at Break (EB). The values of all mechanical parameters 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 corresponding to PMMA % is shown in **Figure 3.4**. The **Figure 3.4** shows that PVC/PMMA blends exhibit lower YM to the extent of 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. The values of Ultimate Tensile Strength (UTS) and Stress at Peak load for PVC/PMMA blends are shown in **Figure 3.4** corresponding to PMMA %. All these values also exhibit minimum value at 10% of PMMA and then give 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 to pure PVC.

The breaking elongation of various blends of PVC/PMMA is shown in **Figure 3.4**, confirmed 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. The introduction of PMMA into PVC increases the Mechanical properties such as Young's Modulus (YM); Ultimate Tensile Strength (UTS) 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.

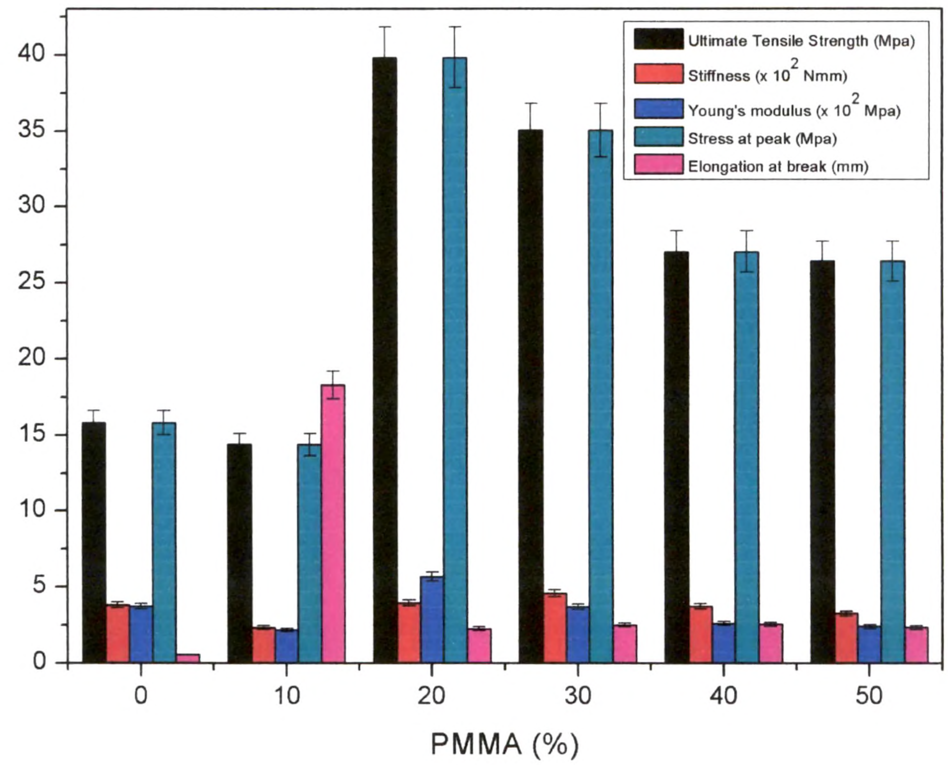

Figure 3.4 Variation in Ultimate tensile strength, Stiffness, Young's Modulus, stress at peak, Elongation at break, as a function of PMMA content

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 [30]. 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.

3.2.5. Thermal gravimetric Analysis

The thermo grams, **Figure 3.5 (a)** of PVC, PMMA, and its various blends with PMMA clearly point out general increase in thermal stability of the blends. The increase in the onset temperature of degradation for the blends in both the stages of degradations is a leading feature of the thermal characteristics of such blends, which further increase with increasing proportion of PMMA. The initial weight loss was observed for all samples due to moisture evaporation. The major weight losses occurred in the range of 240 – 360 °C for all the blend samples. The difference in the thermal decomposition was observed clearly from derivative TG (DrTG) curve as shown in **Figure 3.5 (b)**.

The thermo gravimetric data for pure PVC, pure PMMA and their blend films are given in **Table 3.3**. From thermographs, initial weight loss occurs, which is attributed due to the presence of moisture and impurities at the time of loading the samples [31]. After complete dehydration, above 100 °C, no further weight loss is observed for PVC, until irreversible decomposition commenced at approximately around 253 °C. and it shows a weight loss of 59.95%. The loss may be due to the decomposition of PVC occurred [32]. When the temperature rose to 383°C, the samples exhibit a gradual weight loss of about 78.14%. This shows that the occurrence of another irreversible decomposition. For PMMA, single decomposition peak around 378 °C is observed which start at 325 °C and end at 426 °C with almost weight loss 99.37%. PMMA showed one main decomposition weight loss in this region.

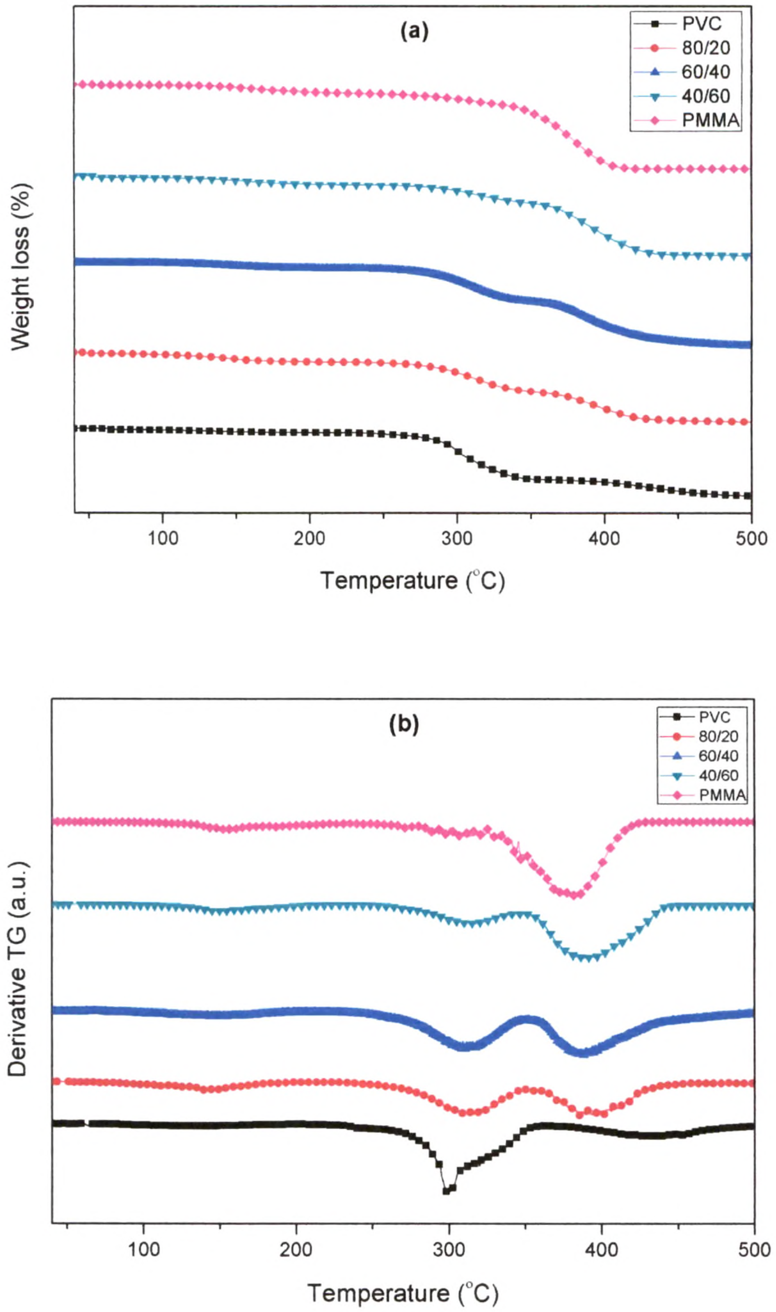

Figure 3.5 (a) TG of pure PVC, pure PMMA and their blends (b) Derivative TG of pure PVC, pure PMMA and their blends

For the 80/20 wt % PVC/PMMA blend film, the first decomposition took place at 266 °C which induced 46.66% weight loss and second decomposition occurred at 357 °C which showed weight loss of 78.35 %. This indicates that the film is stable up to 266 °C. Since the first decomposition of 80/20 wt % blend film occurred at higher temperature and bore a lower weight loss, this proves that the thermal stability increased with addition of PMMA. Polymers of higher PVC content and lower PMMA amount are proven to have a relatively good stability as they have the first decomposition at higher temperature bearing a lower weight loss. From the table we conclude that 80/20 wt % have maximum thermal stability. For 60/40 wt % and 40/60 wt %, the first decomposition occurred at 248 °C and 265 °C with 47.83 % and 31.12 % weight loss respectively and second decomposition took place at 356 °C and 353 °C with 95.13 % and 93.58 % weight loss.

T_p (peak temperature) of DrTG was a function of blend weight percentage. T_p was used as a measure of thermal stability. The shift in T_p toward higher temperature showed thermal stability of the blend was higher than the pure PVC. T_p was maximum for 80/20 wt%, so this blend was more stable. This higher thermal stability was observed for 80/20 blend sample by TGA and DrTG which was due to the intermolecular cross-linking reaction giving highly compatible impact blend system [33]. TGA curves indicated the possibility of a strong hydrogen bond intermolecular interaction between PVC and PMMA due to –CHCl groups of PVC and C=O group of PMMA [34].

Table 3.3 TG and DrTG data of Pure PVC, PMMA and their blended samples

PVC/PMMA	Temperature(°C)			Weight loss (%)
	Starting	Ending	T_p	
100/0	253	352	300	59.95
	383	479	432	78.14
80/20	266	353	316	46.66
	357	446	397	78.35
60/40	248	349	312	47.83
	356	462	388	95.13
40/60	265	343	313	31.12
	353	451	388	93.58
0/100	325	426	378	99.37

3.2.6. Scanning Electron Microscopy

SEM micrographs of pure PVC and Pure PMMA are shown in **Figure 3.6 (a, b)**. The SEM micrographs of brittle fractured surface of blends with various amount of PVC in PMMA are shown in **Figure 3.6 (c – d)**. These micrographs show almost discrete phases and clearly indicate changed surface morphologies of the various blends compared to that of pure PVC. As the amount of PMMA increases, the morphology of blends shows a uniform dispersion of PVC particles in the blends. But for other than 80/20 wt% SEM micrograph shows agglomeration in blend system, while 80/20 wt% have good homogeneity **(Figure 3.6(c))**. From this image one can show, the blend exhibit uniform morphological feature without any phase separation. In phase mixing homogeneity occurs at the lower level of PMMA (for 20% of PMMA), however, it is absent in higher concentration of PMMA in PVC polymer matrix. This may probably be recognized to the increase in mechanical and thermal properties as it shows the regularity in stiff chain structure of PVC.

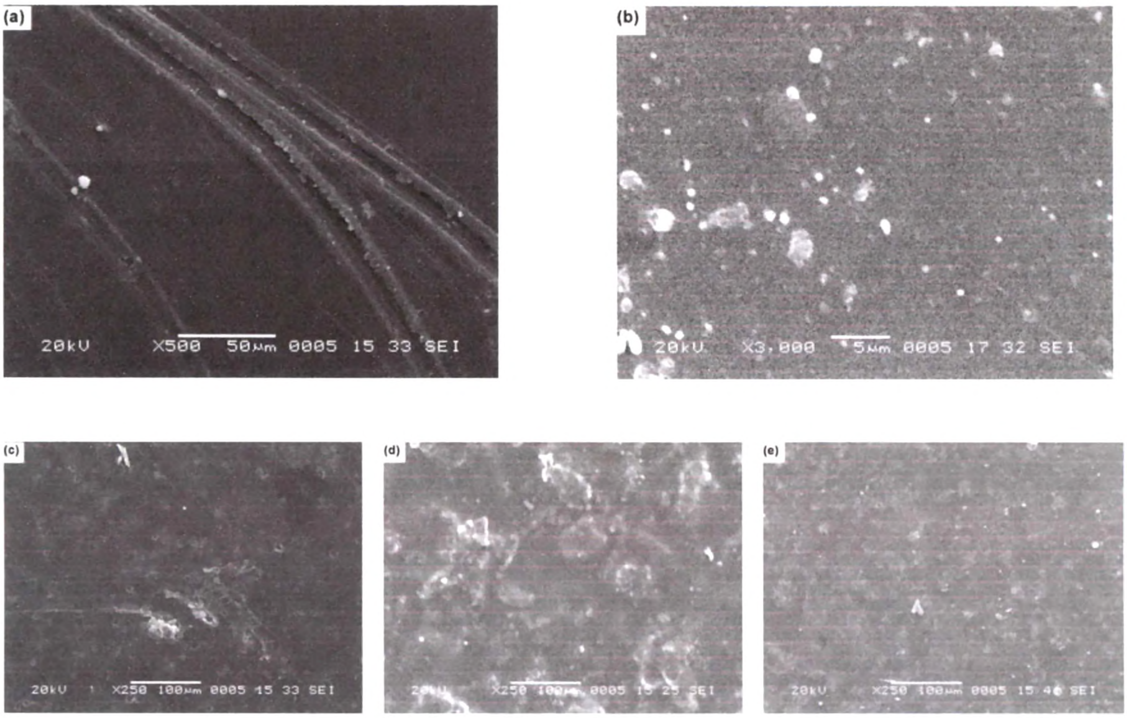

Figure 3.6 Scanning Electron Micrograph of (a) Pure PVC (b) Pure PMMA (c) 80/20 (d) 60/40 (e) 40/60

3.3. Conclusions

From the FTIR and Raman spectra, it is observed that strong hydrogen bond interaction between C-Cl group of PVC and C=O group of PMMA occurs. For 80/20 wt% has maximum peak shifting on higher wave number side is observed. Mechanical properties, mainly ultimate tensile strength and young's modulus, increase beyond 10% of PMMA and exhibit maximum value for 80/20 wt% of PVC/PMMA blend. From TGA, we observed that 80/20 wt% have maximum thermal stability than pure polymers. SEM analysis showed that other than 80/20 wt%, all others have agglomeration in blends system, while 80/20 wt% has good homogeneity. So from above conclusion, In 80/20 wt% of PVC/PMMA exhibit good and enhanced properties than pure constituents.

3.4. References

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