Chapter 7

Conclusion and Future Work

Abstract

This chapter gives the details of correlations of the spectroscopic investigation results with those available from other studies and also summarizes the results obtained by various above mentioned experiments along with the future plan of work.

7.1. Conclusion

7.1.1. PVC/PMMA Blends

By the careful study of the FTIR and Raman spectra, hydrogen bond interaction between CH-Cl group of PVC and C=O group of PMMA occurs. It is clearly seen that there is a trend in these peaks to shift to the higher wave number side. For 80/20 wt% has maximum peak shifting on 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 the strength of the bond and hence increases the mechanical and thermal properties of the polymer blend. Therefore we can conclude that by noting shift of the peaks in the FTIR and Raman spectrum we can draw conclusion about the mechanical and thermal properties of the polymer blend. Thus we are correlated mechanical and thermal properties with spectroscopic investigation by FTIR-ATR spectral studies.

UV-VIS spectra have been studied by the Tauc model. The optical band gap (E_g) (Direct and Indirect) is found to be compositional dependent. Sharp increase of light absorption occurs in all the samples below 220 nm which corresponds to $\pi \rightarrow \pi^*$ transitions of carbonyl group. 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 crosslinking within the amorphous phase of PMMA and PVC.

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.

Peak temperature (T_p) was maximum for 80/20 wt%, so this blend was more stable. This higher thermal stability was observed for 80/20 wt% blend sample by TGA and DrTG which was due to the intermolecular cross-linking reaction giving highly compatible impact blend system.

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 by the increased mechanical and thermal properties as it shows the regularity in stiff chain structure of PVC.

7.1.2. PAM/PVA Blends

The results reported here in this study showed that compatible PAM/PVA blends were prepared successfully using solution cast technique. FTIR and Raman analysis cleared the conclusion about the specific hydrogen bonding interaction between $-CONH_2$ groups in PAM and $-OH$ group in PVA, these results in the higher thermal stability and improved mechanical properties. But the maximum shift on higher wave number side of IR and Raman peaks observed for 50/50 wt%, which implies that bond strength is increased. Therefore thermal stability and mechanical properties are also increased maximum for 50/50 wt%. It is noticeable that the blend with 50/50 wt% showed the most increased thermal stability and improved mechanical properties among the other blends.

From UV-Vis studies, intermolecular interaction was confirmed by noticeable changes in absorption spectra. The position of absorption edge was slightly shifted towards higher side.

Direct and indirect band gap also vary between 5.35 eV to 5.47 eV and 4.57 eV to 4.87 eV respectively.

Blend of PVA with PAM effectively improved the mechanical properties. When PVA is blend with PAM, interaction at molecular level occurs, which reveals the enhancement of mechanical properties. Enhancement in mechanical properties is due to a strong hydrogen bonding between –$CONH_2$ groups in PAM and –OH group in PVA. This interaction becomes maximum for 50/50 wt% therefore we obtain maximum value of mechanical properties for this blend.

From TGA, we conclude that the thermal stability regions of the blend samples were higher than the PAM and stability enhanced by increasing PVA content in PAM polymer matrix and it become more stable for 50/50 wt%.

From SEM micrograph, interaction between PAM and PVA is much greater than others (smaller domains of dispersed PVA) and surface of 50/50 blend ratio is rougher than the other blends. Morphological changes in the blend samples were also explained and results also correlated with the other studies.

7.1.3. PAM/PEO Blends

Blends of PAM and PEO were obtained as semi-transparent, flexible and free standing films with good thermal, optical and mechanical properties. FTIR and Raman analysis showed hydrogen bonding between –$CONH_2$ groups in PAM and –CH_2OH group in PEO. This intermolecular interaction is maximum for 70/30 wt% which exhibited the strong bond interaction.

Optical spectra provide proof for interaction between PAM and PEO. The shift of the absorption edge in the blends reflects the variation in the energy gap which arises due to the intermolecular interaction between PAM and PEO. This structural variation increases with increase in the concentration of PEO, which is reflected in the form of decrease in the energy gap of the blends. Direct gap decreases from 5.07 eV to 4.83 eV and indirect band also decreases from 4.59 eV to 4.09 eV.

Enhancement in mechanical properties is due to the strong hydrogen bonding between $-CONH_2$ groups in PAM and $-OH$ group in PEO. This interaction becomes maximum for 70/30 wt% which reveals in the form of higher mechanical properties like tensile strength and young's modulus.

From TGA and DrTGA, 70/30 wt% had maximum temperature value for different weight losses. So we can conclude that the 70/30 wt% have greater thermal stability as compared to pure component.

From SEM micrograph of 70/30 wt%, surfaces are quite homogenously dense and reduced domains with good dispersed PEO particle in PAM polymer matrix, which show the maximum strong intermolecular interaction between PAM and PEO for 70/30wt%.

So from this study we concluded that blend of PAM/PEO with 70/30 wt% is most suitable and compatible blend ratio with most enhancing properties.

7.1.4. PMMA/TiO_2 Composites

From FTIR spectral studies, we concluded that due to the interaction between PMMA and TiO_2, the mechanical and Thermal properties were enhanced greatly. The FTIR analysis clearly shows that $-COOCH_3$ group of PMMA bonding with the TiO_2 and it is maximum for 0.1 wt% of TiO_2. This indicates strong interaction occurred between PMMA and TiO_2, which results maximum values of mechanical and thermal properties.

UV-VIS spectra have been studied by the Tauc model. The optical band gap (E_{gopt}) (Direct and Indirect) is found to have compositional dependence. Sharp increase of light absorption occurs in PMMA below 220 nm which corresponds to $\pi \rightarrow \pi^*$ transitions of $-COOCH_3$ structures. In the absorption spectra, weak absorption peak near to 276 nm corresponds to $n \rightarrow \pi^*$ transition of aldehydic carbonyl group.

From DSC study miscibility behavior of PMMA/TiO_2 composites is proven. Glass transition temperature is also maximum for 0.1 wt% of TiO_2 which is directly correlate with the FTIR spectra.

From TGA analysis, there is no much difference observed between pure PMMA and 0.1% of TiO_2 doped polymer. But other than 0.1% of TiO_2 degraded TGA data were obtained.

We can conclude that by noting shift of the peaks in the FTIR and Raman spectrum we can draw conclusion about the mechanical and thermal properties of the polymer blend. Thus from the study of the spectra of the polymer blends we can draw some conclusion regarding the mechanical and thermal properties without performing the actual mechanical or thermal studies. The enhancement of these properties is related to the blue shift of the prominent peaks in FTIR and Raman spectrum and the red shift indicates decline in the properties. Thus we are correlated mechanical and thermal properties of polymer blends with spectroscopic investigation by FTIR and Raman spectral studies.

From UV-VIS absorption spectra, weak absorption peaks corresponds to $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ transition of different carbonyl group are considered as interaction peak marker. So we can predict the carbonyl group interaction by noticing this peak. And also correlate it with FTIR and

Raman spectroscopy. By noting down blue shift or red shift of carbonyl peak we will be able to conclude about bond interaction in two or more polymers.

7.2. Future Work

In conclusion, the present work has clearly shown that a careful combination of results from different experimental methods and theoretical calculations can help to explain interfacial phenomena and to give valuable information concerning the inter-phase properties like intermolecular interaction of polymer blends.

Bio-based polymers are attracting increased attention due to environmental concerns. Bio-based polymers not only replace existing polymers in a number of applications but also provide new combinations of properties for new applications. Polymer blending offers time and cost effective method to develop materials with desirable properties like polymer membrane. Therefore preparation of polymer membrane and effect of blending of polymer (polyacrylamide) with other bio-polymer (chitosan, Sodium Alginate, guar gum etc.) in different concentration will be studied. Main objective of study is to improve the Sorption, diffusion, and pervaporation separation ability of the membrane. The membrane has the capability to separate out water from water mixture. Membranes have improved flexibility, reduced cost, improved process ability, and enhanced selectivity and/or permeability compared to a single polymer.

Objectives to identify the blending behavior of polymer membrane with bio-polymer are as follows:

- To characterize the developed membrane in order to find its Structural, chemical, mechanical and thermal properties using spectroscopic techniques.

- To evaluate the performance of the developed membrane in terms of selectivity and permeability for the separation of water and chemical mixture.
- In the future work we also add the inorganic fillers in blend, which further enhances the different properties of the polymeric blend membrane.

Generalized two-dimensional (2D) correlation spectroscopy, proposed by Noda in 1986, has lately attracted considerable attention for its wide application compared with conventional one-dimensional spectra. Vibrational spectroscopic studies on polymer blends usually require hydrogen bonds as miscibility enhancers in blends, and IR and Raman spectroscopy to investigate hydrogen bonds. Generalized 2D IR correlation spectroscopy may identify various intra- and intermolecular interactions between polymer and its surrounding, either organic or inorganic, through specific correlation of bands.

Generalized 2D FTIR and Raman correlation spectroscopy will be applied to the study:

- The conformational changes and specific interactions in blends of any polymers.
- Simplification of complex spectra consisting of many overlapped peaks, and enhancement of spectral resolution by spreading peaks over the second dimension
- Establishment of explicit assignments through correlation of bands
- Measure the specific sequential order of spectral intensity of the polymer peaks which changes with different concentration of blend sand composites.
- Direct correlation between FTIR and Raman bands
- It may utilize with a number of different spectroscopy, e.g., FTIR, Raman, NIR, fluorescence, UV, and X-ray, and combining this spectroscopic measurement with

various physical perturbations, e.g., mechanical, thermal, chemical, optical, and electrical stimuli, to investigate a very wide area of applications.

Bio based polymer membrane will be characterized in order to find its structural, chemical, mechanical and thermal properties which may correlate with 2D FTIR and Raman spectroscopic results by measuring the various peak shifting.