CHAPTER - V

RESULTS AND DISCUSSION

5.1. Instrumental Analysis :

**SEM, FTIR, DSC and XRD Studies:**

Various analytical techniques such as Scanning Electron Microscopy (SEM), Fourier Transform Infra Red Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC) and X-Ray Diffraction (XRD) were used to study the effect of azeotropic solvent mixture treatment on 100%PETY, 100%PETF, 80:20 PCY and 80:20 PCF materials in comparison with untreated materials. The results obtained and discussions on the observed results will be presented in the foregoing sections.

5.1.1. Scanning Electron Microscopic studies (SEM)

In order to study the impact of azeotropic solvent mixture treatments on the surface of textile materials used in the current study, Scanning Electron Micrographs were recorded. The results obtained are shown in Figs.5.1-5.28.

The surface of untreated yarns and fabrics are found to have a smooth appearance while the samples treated with azeotropic mixture of solvents have a rough surface, indicating solvent-fiber interaction. Etching or erosion of surface of treated materials are observed due to interaction of solvent mixtures with the treated fiber materials. With increase in pretreatment durations, erosion was found to propagate inside the fiber resulting in formation of elongated pits or cavities on the surface of the fiber materials. Such observations have been reported in earlier studies [1-3]. As the duration of solvent mixture treatment increased, both the depth and frequency of occurrence of pits increased. The weight loss of such treated materials was found to be more.
Many reports are available on the fact that the surface of polyester, and polyester/ cotton blended yarns and fabrics show cavitated and porous surface structures after treating with organic solvent systems. The extent of cavities and porosity increased with increase in duration of treatment with non-aqueous solvent systems used [4-6]. Similar observations were made in the current study as well.

The extent of interactions of different solvent systems used in the present study on 100% PET, 80:20 PET/cotton blended yarns and fabrics were found to follow the following order,

\[ \text{W-FA-PA} > \text{W-NM-nP} > \text{W-CTC-sBA} \]

Among the three different solvent systems used, the extent of attack of W-FA-PA solvent system on the yarn and fabric materials was found to be maximum and least in the case of samples treated with W-CTC-sBA. Among the textile materials used the effect of solvent treatment is more pronounced in the case of 100% PET yarns than 100% PET fabric and 80:20 PCY and PCF. Among 80:20 PCY and PCF samples the effect on yarn samples was more pronounced. The reason has been discussed under section 4.1.1 in this thesis. The results of FTIR Spectral studies, XRD, DSC and dyeing provide further support the above observations and are discussed in detail under appropriate sections in this thesis.
SEM photographs of untreated and solvent treated 100% PETY

Fig. 5.1 untreated (100% PETY)

Fig. 5.2. 100% PETY treated with W-FA-PA – 2 mins pretreatment

Fig. 5.3. 100% PETY treated with W-FA-PA – 20mins pretreatment
Fig. 5.4. 100% PETY treated with W-NM-nP– 2 mins pretreatment

Fig. 5.5. 100% PETY treated with W-NM-nP– 20mins pretreatment

Fig. 5.6. 100% PETY treated with W-CTC-sBA – 2 mins pretreatment

Fig. 5.7. 100% PETY treated with W-CTC-sBA – 20mins pretreatment
SEM photographs of untreated and solvent treated 100% PETF

Fig 5.8 100% PETF - Untreated

Fig. 5.9. 100% PETF treated with W-FA-PA - 2 mins pretreatment

Fig. 5.10. 100% PETF treated with W-FA-PA – 20 mins pretreatment
Fig. 5.11. 100% PETF treated with W-NM-nP – 2 mins pretreatment

Fig. 5.12. 100% PETF treated with W-NM-nP – 20 mins pretreatment

Fig. 5.13. 100% PETF treated with W-CTC-sBA – 2 mins pretreatment

Fig. 5.14. 100% PETF treated with W-CTC-sBA – 20 mins pretreatment
SEM photographs of untreated and solvent treated 80:20PCY

Fig 5.15. 80:20 PCY - Untreated

Fig 5.16. 80:20 PCY treated with W-FA-PA – 2 mins pretreatment

Fig 5.17. 80:20 PCY treated with W-FA-PA – 20mins pretreatment
Fig. 5.18. 80:20 PCY treated with W-NM-nP – 2 mins pretreatment

Fig. 5.19. 80:20 PCY treated with W- NM-nP – 20 mins pretreatment

Fig. 5.20. 80:20 PCY treated with W-CTC-sBA – 2 mins pretreatment

Fig. 5.21. 80:20 PCY treated with W-CTC-sBA - 20 mins pretreatment
SEM photographs of untreated and solvent treated 80:20PCF

Fig. 5.22. 80:20 PCF - Untreated

Fig. 5.23. 80:20 PCF treated with W-FA-PA – 2 mins pretreatment

Fig. 5.24. 80:20 PCF treated with W-FA-PA – 20mins pretreatment
Fig. 5.25. 80:20 PCF treated with W-NM-nP – 2 mins pretreatment

Fig. 5.26. 80:20 PCF treated with W- NM-nP – 20mins pretreatment

Fig. 5.27. 80:20 PCF treated with W-CTC-sBA – 2 mins pretreatment

Fig. 5.28. 80:20 PCF treated with W- CTC-sBA – 20mins pretreatment
5.2. Fourier-Transform Infra-Red Spectroscopic Study

Untreated and solvent treated 100% PET yarn and fabric 80:20 PCY and PCF were subjected to FTIR spectroscopic studies to analyze changes if any caused by solvent treatment on these materials to assess any structural change, creation of any new functional groups or the alteration of existing groups in these materials as a consequence of solvent treatments. The spectra obtained are presented in Figs.5.29-5.44. The spectra of samples treated for 4 minutes and 20 minutes were taken for comparison with the spectrum of untreated sample.

Fig. 5.29 shows the FTIR spectrum of 100% PET Yarn before and after treatment with three different azeotropic mixtures of solvents used in the present study in the range of 400 cm$^{-1}$ – 4000 cm$^{-1}$. The absorption spectral pattern obtained for both treated and untreated samples was found to be almost same without any additional peaks. However there was a slight shift in the position of the observed peaks in the case of samples treated with all the three different solvent systems used in the present study towards higher wave number. The extent of shift in absorption peaks depends on treatment duration as well as the type of solvent systems used (Figs. 5.30-5.32). The same trend was observed in the case of 100% PETF samples (Figs. 5.33-5.36). However the extent of shift in absorption peaks were found to be more in the case of 100% PCY samples as the penetration of solvent into the interior of the fibersamples were easy compared to 100% PETF samples wherein the tightness of packing of fibersamples is more in comparison to yarn samples. A broad peak at 1720 cm$^{-1}$ is characteristic of carbonyl stretching of $\alpha$ - $\beta$ unsaturated ester. In the case of solvent treated samples the width of the peak had reduced and the peak value is shifted to higher wave number, i.e. 1740 cm$^{-1}$. A small peak in the region between
800-850 cm\(^{-1}\) can be accounted for out of plane bending of aromatic ring system. The peak at 1250 cm\(^{-1}\) and 1300 cm\(^{-1}\) may be due to C-O stretching of the polymer backbone. An intense peak at 2350 cm\(^{-1}\)- 2360 cm\(^{-1}\) can be attributed to methylene C-H stretching. The peak height for this peak has increased with solvent treatment in all the cases indicating the strong interaction of solvent mixtures with the treated material. The small peak close to 3000 cm\(^{-1}\) can be correlated to C-H stretching of aromatic ring.

The extent of shift in position of the absorption peaks to higher wave numbers was found to be more in the case of samples treated with W-FA-PA and least in the case of W-CTC-sBA which is in conformity with their polarity index values [6]. The solvent system having highest polarity index was found to have greatest interaction while the solvent system with lowest polarity index was found to have lowest interaction. The trend in extent of interaction and shift in position of absorption peaks is found to follow the order,

\[ \text{W-FA-PA > W-NM-nP > W-CTC-sBA} \]

The extent of shift of absorption peaks was also found to be dependent on the duration of solvent treatment. As the duration of solvent treatment increased the extent of shift to higher wave number increased.

Similar studies were carried out for 80:20 PCY and 80:20 PCF samples and the spectral pattern obtained are shown in figs.5.37-5.44. Analysis of the spectra obtained showed that there is an interesting feature in all the spectra was that an additional sharp small peak observed at around 3600 cm\(^{-1}\) corresponds to free –OH groups of cellulose component in comparison to 100% PETY and 100% PETF samples studied. This peak indicates that solvent treatment had increased the extent
of amorphous region in the cotton component of the material. The interaction of azeotropic solvent mixture can be attributed to water being present as one of the component of the solvent mixture. This trend was further been supported by the results of strength measurements and SEM studies. The observed small peaks between the region 1110 cm\(^{-1}\) - 1150 cm\(^{-1}\) were due to cellulosic component of the fiber materials [7].

The extent of shift in absorption peaks were found to be more in the case of 80:20 PCY samples as the penetration of solvent into the interior of the fibersamples were easy compared to fabric samples wherein the tightness of packing of fibersamples is more in comparison to yarn samples. The effect of solvent treatment was found to follow the same order as mentioned above which can be attributed to their polarity index and hence the variation in the extent of interaction with the fibermaterials.
Fig. 5.29. FTIR spectra of untreated and solvent treated 100% PETY (Treatment time-20 min.) (a) untreated (b) W-CTC-sBA (c) W-NM-nP (d) W-FA-PA

Fig. 5.30. FTIR spectra of 100% PETY treated with W-FA-PA for different durations (a) untreated (b) treated for 4 min. (c) treated for 20 min.
Fig. 5.31. FTIR spectra of 100% PETY treated with W-NM-nP for different durations (a) Untreated (b) treated for 4 min. (c) treated for 20 min.

Fig. 5.32. FTIR spectra of 100% PETY treated with W-CTC-sBA for different durations (a) untreated (b) treated for 4 min. (c) treated for 20 min.
Fig. 5.33. FTIR spectra of untreated and solvent treated 100% PETF (Treatment time-20 min.) (a) untreated (b) W-CTC-sBA (c) W-NM-nP (d) W-FA-PA

Fig. 5.34. FTIR spectra of 100% PETF treated with W-FA-PA for different durations (a) untreated (b) treated for 4 min. (c) treated for 20 min.
Fig. 5.35. FTIR spectra of 100% PETF treated with solvent W-NM-nP for different durations (a) untreated (b) treated for 4 min. (c) treated for 20 min.

Fig. 5.36. FTIR spectra of 100% PETF treated with solvent W-CTC-sBA for different durations (a) untreated (b) treated for 4 min. (c) treated for 20 min.
Fig. 5.37. FTIR spectra of untreated & Solvent treated 80:20 PCY (Treatment time - 20 min) (a) untreated (b) W-CTC-sBA (c) W-NM-nP (d) W-FA-PA

Fig. 5.38. FTIR spectra of 80:20 PCY treated with solvent W-FA-PA for different durations (a) untreated (b) treated for 4 min. (c) treated for 20 min.
Fig. 5.39 FTIR spectra of 80:20 PCY treated with solvent W-Nm-nP for different durations (a) untreated (b) treated for 4 min. (c) treated for 20 min.

Fig. 5.40 FTIR spectra of 80:20 PCY treated with solvent W-CTC-sBA for different durations (a) untreated (b) treated for 4 min. (c) treated for 20 min.
Fig. 5.41. FTIR spectra of untreated & Solvent treated 80:20 PCF (Treatment time-20 min) (a) untreated (b) W-CTC-sBA (c) W-NM-nP (d) W-FA-PA

Fig. 5.42. FTIR spectra of 80:20 PCF treated with W-FA-PA for different durations (a) untreated (b) treated for 4 min. (c) treated for 20 min.
Fig. 5.43. FTIR spectra of 80:20 PCF treated with W-NM-nP for different durations (a) untreated (b) treated for 4 min. (c) treated for 20 min.

Fig. 5.44. FTIR spectra of 80:20 PCF treated with W-CTC-sBA for different durations (a) untreated (b) treated for 4 min. (c) treated for 20 min.
5.3. DSC studies of 100% PET and PET/Cotton blended fabrics and yarns

Differential Scanning Calorimetry (DSC) can be used to measure the extent of crystallinity and molecular orientation within the fibers. This type of analysis is based on distinctly different values of the heats of fusion for crystalline and non-crystalline forms of the polymer.

Differential Scanning Calorimetric studies were made for 100% PETY, 100% PETF, 80:20 PCY and 80:20PCF samples before and after solvent pretreatments with the azeotropic solvent mixtures used in the present study. The DSC curves obtained are presented in Figs.5.45-5.60. In each case the starting temperature, peak melting temperature and maximum heat flow were noted. The starting temperature is the starting of the melting endotherm and can be regarded as the melting of the smallest crystallite in the sample. The DSC thermograms of solvent pretreated samples obtained were found to have appreciable changes in terms of starting temperature, peak temperature and melting temperature in comparison to untreated samples. The considerable increase in maximum heat flow for solvent pretreated samples can be attributed to solvent induced crystallization. During the interaction of the polymer with the solvent, the solvent enters into the amorphous region of polymer structure, weakens polymer-polymer interaction, replaces it with polymer-solvent interaction, induces extensive segmental motion and lowers the effective glass transition temperature of fiber material. The polymer chain rearranges themselves into a lower free energy state. This induces crystallization even in the swollen state. The interaction of solvent with the polymer is of two types viz., inter-crystalline interaction and intra-crystalline interaction. In the case of inter-crystalline interaction, the solvent penetrates inside the amorphous region only. The polymer chains within this region are under lower stress and generally results in the rearrangement of
molecular chains [8-10]. In this case, crystallization takes place in the swollen state and crystalline areas of the sample increases. On the other hand, in the case of intra-crystalline interaction the interacting solvent penetrates inside the crystalline region, de-crystallizes the sample and affects higher lateral order parts of the fiber.

In the present study, the interaction of solvent with the fiber material is found to be inter-crystalline in nature. This is evident from the considerable increase in the melting heat for solvent treated samples due to solvent induced crystallization. It is further supported by the observed small increase in starting temperature, peak temperature and melting temperature of the treated samples. The extent of increase melting temperature and melting heat was found to be more in the case of samples treated with W-FA-PA and least in the case of W-CTC-sBA, which is in conformity with their polarity index values. The solvent system having highest polarity index was found to induce more crystallization to the polymer matrix while the solvent system with lowest polarity index was found to have lower impact in inducing crystallization. The trend in inducing crystallization assisted by the solvent is found to follow the order,

**W-FA-PA> W-NM-nP > W-CTC-sBA**

It was also observed that the extent of increase in melting temperature and melting heat was dependent on duration of solvent treatment and type of sample. As the duration of solvent treatment increased the extent of increase in melting temperature and melting heat got increased. The trend in the increase of melting temperature and melting heat was found to increase in the following order for the samples used in the study.

**100% PETY > 100% PETF > 80:20 PCY > 80:20 PCF**
Fig. 5.45 DSC of 100% PETY treated with W-FA-PA different durations

UT=untreated, $T_1=4$ min. and $T_2=20$ min.

Fig. 5.46 DSC of 100% PETY treated with W-NM-nP for different durations

UT=Untreated, $T_1=4$ min. and $T_2=20$ min.
Fig. 5.47 DSC of 100% PETY treated with W-CTC-sBA for different durations
UT=untreated, $T_1=4$ min. and $T_2=20$ min.

Fig. 5.48 DSC of 100% PETY treated with three different azeotropic solvents
UT=Untreated, $S_1= W$-CTC-sBA , $S_2= W$-NM-nP, $S_3= W$-FA-PA
Fig. 5.49 DSC of 100% PETF treated with W-FA-PA for different durations

UT=untreated, $T_1=4$ min. and $T_2=20$ min.

Fig. 5.50 DSC of 100% PETF treated with W-NM-nP for different durations

UT=untreated, $T_1=4$ min. and $T_2=20$ min.
Fig. 5.51 DSC of 100% PETF treated with W-CTC-sBA for different durations

$UT=untreated, T_1=4 \text{ min. and } T_2=20 \text{ min.}$

Fig. 5.52 DSC of 100% PETF treated with three different azeotropic solvents

$UT=Untreated, S1= W-CTC-sBA, S2= W-NM-nP, S3= W-FA-PA$
Fig. 5.53 DSC of 80:20 PCY treated with W-FA-PA for different durations
UT=untreated, T₁=4 min. and T₂= 20 min.

Fig. 5.54 DSC of 80:20 PCY treated with W-NM-nP for different durations
UT=Untreated, T₁=4 min. and T₂= 20 min.
Fig. 5.55 DSC of 80:20 PCY treated with W-CTC-sBA for different durations
UT=untreated, $T_1=4$ min. and $T_2=20$ min.

Fig. 5.56 DSC of 80:20 PCY treated with four different azeotropic solvents
UT=Untreated, S1=W-CTC-sBA, S2=W-NM-nP, S3=W-FA-PA
Fig. 5.57 DSC of 80:20 PCF treated with W-FA-PA for different durations
$UT=\text{untreated}, T_1=4 \text{ min. and } T_2=20 \text{ min.}$

Fig. 5.58 DSC of 80:20 PCF treated with W-NM-nP for different durations
$UT=\text{untreated}, T_1=4 \text{ min. and } T_2=20 \text{ min.}$
**Fig. 5.59** DSC of 80:20 PCF treated with W-CTC-sBA for different durations
UT=untreated, $T_1=4$ min. and $T_2=20$ min.

**Fig. 5.60** DSC of 80:20 PCF treated with four different azeotropic solvents
UT=Untreated, S1= W-FA-PA, S2= W-NM-nP, S3= W-CTC-sBA
5.4. XRD studies of 100% PET and PET/Cotton blended fabric and yarns

X-ray diffraction (XRD) studies is a unique method in determining the crystallinity of a compound. XRD studies is mainly used for study of crystalline, amorphous and semi-crystalline region/ phases of polymeric materials which are responsible for the observed electrical and mechanical properties of polymeric materials. X-ray diffraction pattern of most polymers contain sharp as well as broad and diffused peaks. The sharp peaks correspond to crystalline regions, the diffused and the broad ones refer to amorphous regions [11].

When polymers are subjected to solvent treatments, the solvent molecules penetrate into the interior of the polymeric material and interact with polymeric material. Three different types of interactions such as physical, chemical and physicochemical are possible. As a result of physical interaction of solvent molecules re-crystallization and de-crystallization of the corresponding polymer takes place.

Solvents differ in their solubility and compatibility with the polymers which depends on their molecular size and in turn their solubility parameter. The diffusion of solvent molecules follow a transport mechanism. Transport of solvents into the interior of the polymer depends on the free volume that is available in the amorphous region of the polymers which play a major role in the dye uptake process.

Polymers differ in the extent of their crystalline and amorphous content, which results in changes in physical characteristics of polymers. Polyester fibers are usually composed of both crystalline and non-crystalline regions, imparted during the drawing process. The physical properties of PET fiber mainly depend on its draw ratio and heat set process which disturbs its crystallinity, segmental motion, side chain motion, viscosity and the mechanical properties such as tensile strength and shrinkage which are the dependent of the ratio of amorphous content over crystalline content of the polymer. XRD finds application in the determination of percentage crystallinity and molecular orientation[12-14].
XRD studies of 100% PETY, 100% PETF, 80:20 PCY, 80:20 PCF samples used in the current study were made before and after solvent pretreatments involving W-FA-PA, W-NM-nP, W-CTC-sBA azeotropic solvent systems. XRD patterns obtained are presented in Figs.5.61-5.72. XRD patterns of 100% PETY treated with three different azeotropic solvent systems for two different time intervals viz. 4 min. and 20 min. are presented along with the pattern for untreated samples in Figs.5.61-5.63. The diffraction pattern of untreated fabric samples show low to medium sharp peaks in (010), (110) and (100) planes indicating the presence of crystalline as well as amorphous regions. The peak height was less pronounced in (010) plane.

The peak intensities of untreated 100% PET yarns were observed at 2θ values 17.5, 23 and 27 corresponding to (010), (110) and (100) planes. The first peak is diffused and other two peaks were sharp compared to the first peak due to polycrystalline nature of the material.

Analysis of XRD pattern of the pretreated samples show that the peaks became sharper and the intensity counts increased compared to untreated samples. These observations can be accounted for the fact that the solvents acted as plasticizer in the non-crystalline region of the polymeric material breaking intermolecular bonds and enhancing the segmental mobility of the polymer matrix. The segmental mobility of polymer matrix led to induced crystallization leading to the formation of crystallites.

The above observation is found to be similar to the observations reported in many earlier reports available in the literature [15-20]. In the case of samples treated for 20 minutes duration, intensity (counts) for the corresponding peaks further increased. Among the different solvents used in the present study W-FA-PA, is found to have much pronounced effect on the crystal structure of the polymer, while W-
CTC-sBA is having the least impact among the three solvents used. The effect of solvent treatment follow the following order

\[ \text{W-FA-PA} > \text{W-NM-nP} > \text{W-CTC-sBA} \]

XRD patterns obtained for 100% PET fabric samples before and after solvent treatments are given Figs.5.64-5.66. A comparison of the effect of solvent treatment among the three solvent mixtures showed the same trend as shown above which can be attributed to their solubility parameter.

A Comparison of the effect of solvent treatment on the crystal structure of 100% PET yarn and fabric samples show that the effect is much pronounced in the case of yarns samples than fabric samples due easy penetration of solvent into the yarn samples.

Figs. 5.67-5.70 show the XRD pattern obtained for 80:20 PCY treated with three different solvents for two different durations viz 4 and 20 min. Similar observations were found in the case of 80:20 PCF samples studied with and without solvent pretreatments(Figs.5.71-5.73). The only difference between yarn and fabric samples is the extent of variation in the peak heights of the treated samples as observed in the case of 100% PETY and 100% PETF samples . The variation is due to the fact that the penetration being much easier in the yarns, the effect was much more pronounced in the case of yarns compared to the fabric samples.

In all the treated samples, the observed changes in fiber characteristics can be attributed to greater interaction of solvent mixture with the polyester component of the blends, since the organic solvents interact only with PET component of the bends and not with the cotton component.
The observed XRD results can be correlated with the fact that the solvent treatments have resulted in more open structure and greater chain mobility in the non-crystalline region of the polymers and created more voids in the fiber structure. The solvents caused swelling in the fiber matrix, an increase in the segmental mobility of the polymer leading to structural rearrangement. This type of structural rearrangement of polymer matrix is known as ‘solvent induced crystallization’ as discussed in chapter- II of this thesis. Many reports are available on this observation in the case of PET fibers. During this process cavitations were produced on the surface as well as interior of the polymer due to crystallization [19-25]. Solvent treatments have been reported to produce polymer crystallites. The crystallites tend to stabilize the polymer structure by preventing its complete collapse upon subsequent solvent removal [26]. Creation of micro-voids cracks etc in the polymer structure due to solvent treatment which was clearly seen in SEM photographs is further supported by this XRD studies.
Fig 5.61 XRD of 100% PETY treated with W-FA-PA for different durations UT=untreated, T1=4 min. and T2= 20 min.

Fig 5.62 XRD of 100% PETY treated with W-NM-nP for different durations UT=untreated, T1=4 min. and T2= 20 min.
Fig 5.63 XRD of 100% PETY treated with W-CTC-sBA for different durations
UT=untreated, T1=4 min. and T2= 20 min

Fig 5.64 XRD of 100% PETF treated with W-FA-PA for different durations  UT=untreated, T1=4 min. and T2= 20 min
Fig 5.65 XRD of 100% PETF treated with W-NM-nP for different durations
UT=untreated, $T_1$=4 min. and $T_2$=20 min.

Fig 5.66 XRD of 100% PETF treated with W-CTC-sBA for different durations
UT=untreated, $T_1$=4 min. and $T_2$=20 min.
Fig 5.67 XRD of 80:20 PCY treated with W-FA-PA for different durations
UT=untreated, T₁=4 min. and T₂=20min.

Fig 5.68 XRD of 80:20 PCY treated with W-NM-nP for different durations
UT=untreated, T₁=4 min. and T₂=20min.
Fig 5.69 XRD of 80:20 PCY treated with W-CTC-sBA for different durations
UT=untreated, T₁=4 min. and T₂=20 min.

Fig 5.70 XRD of 80:20 PCF treated with W-FA-PA for different durations
UT=untreated, T₁=4 min. and T₂=20 min.
Fig 5.71 XRD of 80:20 PCF treated with W--NM-nP for different durations
UT=untreated, T₁=4 min. and T₂=20 min.

Fig 5.72 XRD of 80:20 PCF treated with W-CTC-sBA for different durations
UT=untreated, T₁=4 min. and T₂=20 min.