A
DISSERTATION REPORT
ON

"STRUCTURE AND PROPERTIES OF MOLECULAR COMPOSITES OF POLY-p-PHENYLENE-TEREPHTHALAMIDE/ POLY-ETHER-ETHER-KETONE [PPTA/PEEK]

Submitted for partial fulfillment of the requirement for award of the degree of

INTEGRATED MASTER OF TECHNOLOGY
IN
POLYMER SCIENCE & TECHNOLOGY

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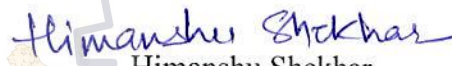**SAHARANPUR CAMPUS**
June 2014

CANDIDATE'S DECLARATION

I, Himanshu Shekhar, hereby declare that the work which is being presented in this dissertation report entitled "**Structure and Properties of Molecular Composites of Poly-p-Phenylene-Terephthalamide/Poly-Ether-Ether-Ketone   [PPTA/PEEK]**" in partial fulfillment of the requirements for the award of the degree of Integrated Master of Technology in Polymer Science and Technology, IIT Roorkee is an authentic record of my own work carried under the supervision of Dr. Sanjay Palsule, Associate Professor, Department of Polymer & Process Engineering, IIT Roorkee.

The matter presented in this report has not been submitted for the award of any other degree of this or any other institute.

Date: 27/06/14

Place: Saharanpur

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This is to certify that the above statement made by the candidate is correct to the best of our knowledge.

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And in the end I would like to thank my family and colleagues who stood by me and kept me motivated throughout the duration of the project.

Date:

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ABSTRACT

Molecular composites have been classified as the third generation of Polymers. The concept of Molecular Composite was first presented by Dr. T.E.Helminiak of USAF-WP-AFB. Molecular composite is defined as a miscible blend of a rigid rod macromolecule and a flexible polymer, in which the flexible polymer is molecularly reinforced by the rigid rod macromolecule.

In this project, the molecular composites of Poly-p-Phenylene-Terephthalamide/Poly-Ether-Ether-Ketone [PPTA/PEEK] have been processed by solution blending the components in sulphuric acid, and then co-precipitating the blend in water.

The glass transition temperatures of PEEK and the molecular composites have been recorded as PPTA does not show any glass transition temperature. The miscibility in PPTA/PEEK molecular composites has been established by observing that the molecular composite shows higher glass transition temperature as compared to the component flexible PEEK polymer and the glass transition temperature of the molecular composite increases with increasing amounts of PPTA in PPTA/PEEK molecular composites.

The specific interactions imparting miscibility have been recorded by Fourier Transform Spectroscopy and the role of similar solubility parameters in imparting miscibility has also been recorded.

Thermal degradation in PEEK and PPTA/PEEK molecular composites has been studied by TGA curves.

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ABBREVIATIONS

In alphabetical order

PEEK...Polyetheretherketone

PPTA...Poly-Para-Phenylene-Terephthalamide

LCST...Lower Critical Solution Temperature

UCST...Upper Critical Solution Temperature

DTA..Differential Thermal Analyzer

FTIR...Fourier Transform Infra Red Spectroscopy

FE-SEM...Field Emission-Scanning Electron Microscopy

TGA..Thermo-gravimetric Analyzer

T_g...Glass Transition Temperature
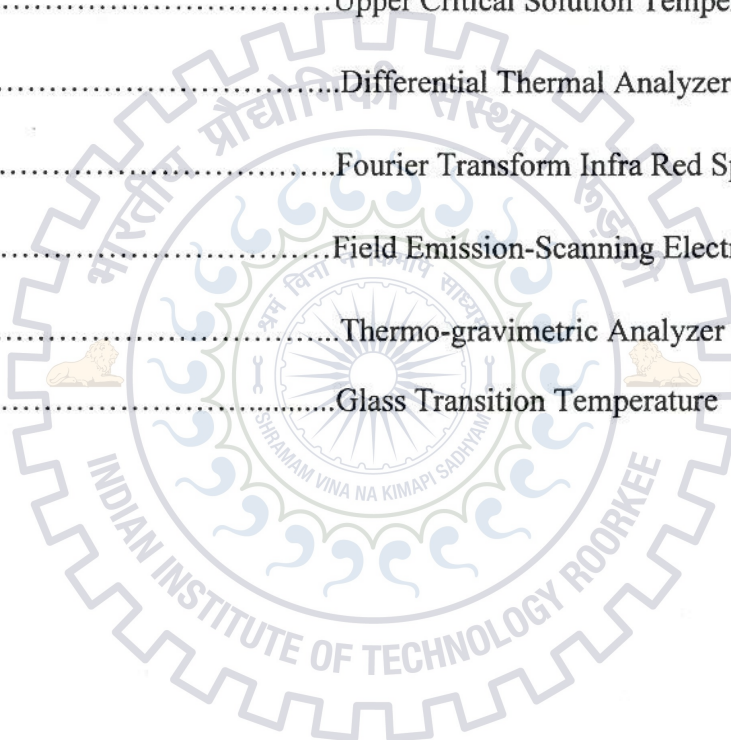
CHAPTER 1
INTRODUCTION

1.1 Classification of Polymeric Materials

Polymeric Materials have been categorized into three generations [1, 2]. The first generation of polymeric materials includes homopolymers and copolymers; thermoplastics, thermosets and elastomers. The second generation of polymeric materials includes particle reinforced and fiber reinforced polymer composites and polymer blends. The third generation of polymeric materials includes molecular composites based on rigid and flexible polymers.

1.2 Molecular Composites

The concept of a molecular composite – a flexible polymer reinforced by a rigid polymer- was first proposed by Helminiak [3 - 8] of the Wright Patterson Air Force Base of the US Air Force and by Takayanagi [9 - 12] who were working on high performance polymers. Helminiak [3-8] has defined molecular composites as a miscible blend of a rigid rod polymer and a flexible coil polymer where the rigid rod polymer is dispersed at the molecular level in the matrix of the flexible polymer. The role of the rigid rod polymer is to act as a reinforcing material, much like the way fiber acts in traditional fiber-filled polymer composite.

Molecular Composites are classified as third generation polymeric materials [1, 2]. Since dispersion of the rigid rod macromolecule happens at the molecular level in the matrix of the flexible polymer, molecular composites offer improved thermo-mechanical properties over the first and second generation polymeric materials.

1.3 Limitations of molecular composites

The premise of molecular composites as advanced engineering materials is definitely very promising but there are certain limitations to it. Some of these are:

1. Because of the combinatorial entropy of mixing between the rigid rod polymer and the flexible polymer and the tendency of the rigid rod polymer to align itself, it is difficult to achieve miscibility between the two.

2. Since rigid rod polymers cannot be melt processed, solution blending is the only way to process a molecular composite.

3. It is difficult to obtain miscible polymer composites, because of low miscibility between the constituent rigid and the flexible polymers, and high tendency of the phase separation of the blend of the rigid and the flexible polymers.

1.4 Objectives of the project

The objective of this project is to study the miscibility and structure of molecular composites of Poly-p-Phenylene-Terephthalamide / Poly-Ether-Ether-Ketone (PPTA/PEEK) with a view to successfully develop the same as advanced engineering materials for the future.

In particular, the objectives of the project are as follows:

1. To process the molecular composites of PPTA/PEEK by solution blending.

2. Establishing miscibility in molecular composites of PEEK/PPTA by Differential Scanning Calorimetry.

3. To study and analyze the thermodynamics and the reasons of miscibility in the molecular composites of PPTA/PEEK by establishing the solubility parameters and specific interactions of Hydrogen bonding type by Fourier Transform Infrared Spectroscopy (FTIR).

4. To study structure and morphology of the PPTA/PEEK molecular composites by FE-SEM.

The following studies have been performed for the miscibility and the structure of the molecular composites so that they can be developed as advanced engineering materials:

1. **Materials:** PPTA has been selected as the reinforcing rigid rod macromolecule. PEEK has been selected as the flexible matrix polymer.

2. **Processing:** The way a molecular composite is processed greatly affects its miscibility and structure. The miscibility between the component polymers also depends upon the processing method used. Processing of molecular composites of PPTA/PEEK by solution blending was investigated.

3. **Miscibility:** Establishing miscibility in molecular composites of PPTA/PEEK is the primary aim of this project. Miscibility between the component polymers greatly affects the nature of the composite. To study miscibility in molecular composites experiments have been performed by DSC and FTIR to establish the thermodynamics of miscibility and to investigate the specific interactions imparting miscibility; respectively.

4. **Morphology:** Palsule's "Molecular Theory of Solid State Thermodynamics" explains the amorphous nature of molecular composites. Scanning Electron Microscopy was used to study the morphology of the molecular composite of PPTA/PEEK.

CHAPTER 2

FUNDAMENTALS OF MOLECULAR COMPOSITES AND LITRATURE SURVEY

The fundamentals of thermodynamics of miscibility of polymer blends can be applied to study miscibility in molecular composites.

2.1 Thermodynamics of miscibility

A polymer blend [13 – 16] is basically a mixture of two or more polymers and/or copolymers. Polymer blends exhibit phase behavior. There can be different degrees of miscibility [17] in polymer blends in between the extremes (i.e. partial miscibility).

Miscibility is governed by the combinatorial entropy of mixing of the constituents. In cases where the constituents have low molecular weight, this combinatorial entropy of mixing is large and in turn the components are miscible. For example, owing to their low molecular weight hexane-ethanol mixtures are miscible. However, their analogs that have higher molecular weights like polyolefin and poly vinyl alcohol are highly immiscible. In polymer blends, since the component polymers have high molecular weight the resultant combinatorial entropy of mixing is very low (almost zero) and subsequently leads to immiscibility. This concept of combinatorial entropy of mixing explains the reason for why solvent-solvent mixtures show a broader range of miscibility when compared to polymer-solvent mixtures. The concept of miscibility in polymer blends was described by Cowie [17].

Thermodynamically, for a multi-component system to be miscible it is must that its Gibb's free energy of mixing (ΔG_m) is negative. The equation relating Gibb's free energy to other parameter is:

$$\Delta G_m = \Delta H_m - T\,\Delta S_m \tag{2.1}$$

Where, ΔG_m is the Gibb's free energy of mixing, T is temperature, ΔH_m represents enthalpy of mixing, and ΔS_m is for the entropy of mixing.

For the components to be miscible, $\Delta G_m < 0$ is a necessary but insufficient condition. For a polymer-polymer blend system, miscibility is also governed by the composition of the blend.

For miscibility in a blend system it is necessary that the below mentioned condition be satisfied, and the blend system will be miscible and stable only when equation (2.2) is satisfied

$$\left(\frac{\partial^2 \Delta Gm}{\partial \Phi i^2}\right)_{P,\ T} > 0 \qquad\qquad (2.2)$$

Where, Φi is the volume fraction of the component i.

Even if the Gibb's free energy is negative, a negative value of $\left(\frac{\partial^2 \Delta Gm}{\partial \Phi i^2}\right)_{P,\ T}$ will indicate that the system is immiscible and phase separation will take place, as explained through figure – 2.1
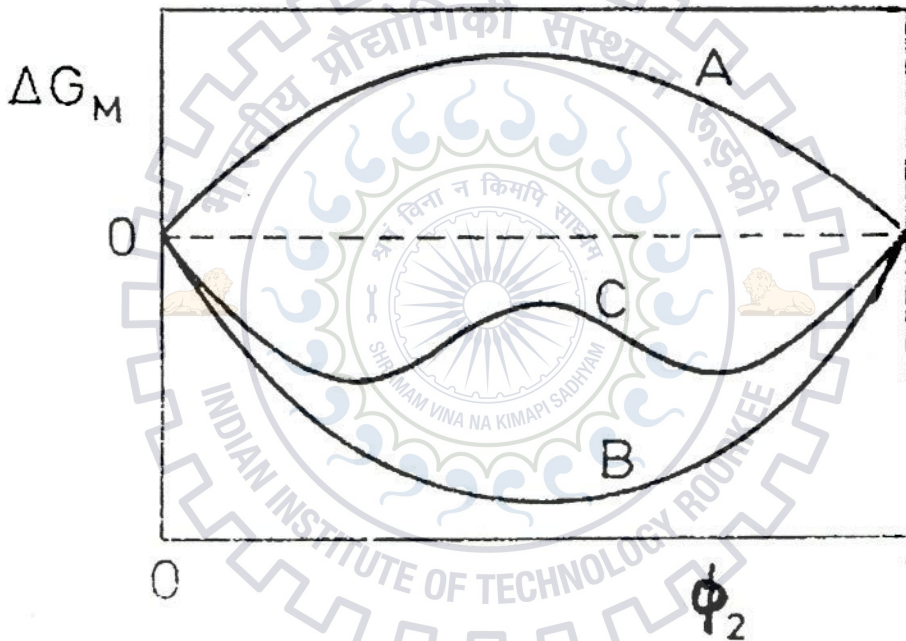
In the above figure, using equation (2.1) and (2.2), we can see that system A is an immiscible system, system B is completely miscible while system C is partially miscible.

It has been observed that in a system with low molecular weight components, an increase in temperature will drive the Gibb's free energy to more negative value which can even be verified using equation (2.1). This leads to increased miscibility in systems with low molecular weight components on increasing temperature. But for components with larger molecular weights the value of combinatorial entropy of mixing (ΔS_m) is almost zero and

hence the other factors which are mainly the non-combinatorial entropy and enthalpy dominates and hence increasing temperature can lead to decrease in miscibility.

It is observed that solvent-solvent and polymer-solvent systems generally show Upper Critical Solution Temperatures (UCST), while polymer-polymer systems usually show Lower Critical Solution Temperatures (LCST). [Figure 2.2]
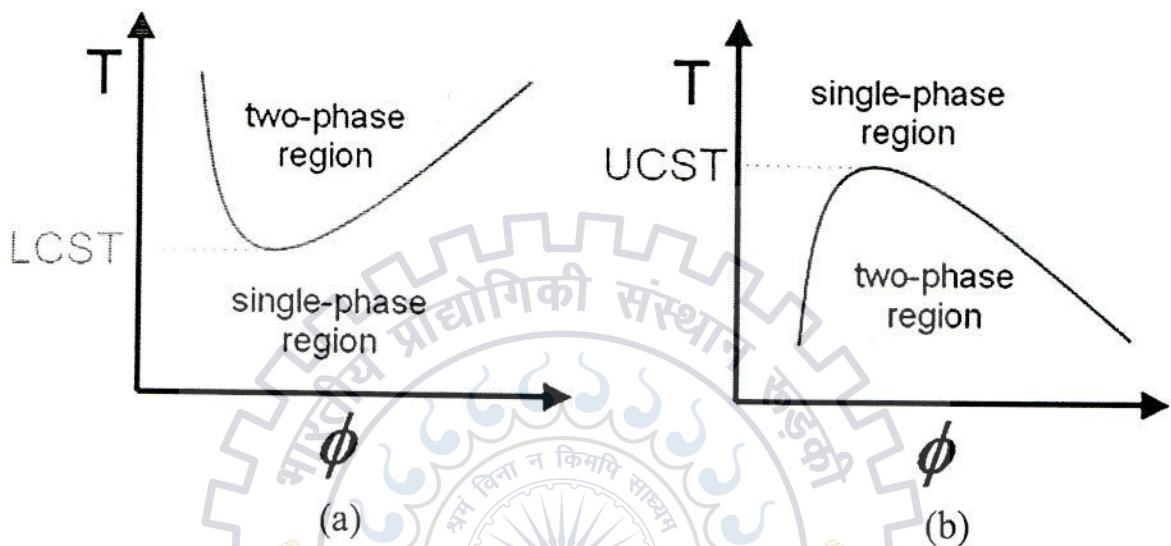
Fig 2.2: LCST and UCST behavior

2.2 Flory-Huggins theory

This theory was developed independently by Flory and Huggins [18 – 21]. This theory was initially developed to study the thermodynamics of polymer-solvent. It was Scott [22] and Tompa [23] who applied this theory to polymer-polymer system by introducing the concept of reference segment volume (V_r). Reference segment volume is considered as the smallest repeat unit.

According to Flory-Huggins theory, the entropy of mixing (ΔS_m) is given by the following relation:

$$\Delta S_m = -R \left(\frac{V}{V_R} \right) \left\{ \frac{\phi_1}{m_1} \ln \phi_1 + \frac{\phi_2}{m_2} \ln \phi_2 \right\} \quad (2.3)$$

Where, m_i is the molecular weight of the ith component, Φ_i is the volume fraction of the ith component, V_r is the reference volume. From equation (2.3) it can be observed that as the

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molecular weight becomes larger i.e. tends towards infinity 1/m tends towards zero and the entropy of mixing becomes zero.

The binary heat of mixing (ΔH_m) is given by the following equation:

$$\Delta H_m = RT \left(\frac{V}{V_R} \right) \chi_{12} \phi_1 \phi_2 \qquad (2.4)$$

Where, χ is the Flory-Huggins parameter, V is the total volume of the two components..

Substituting the values of ΔS_m and ΔH_m from equations (2.3) and (2.4) respectively in equation (2.1), we get

$$\Delta G_m = RT \left(\frac{V}{V_R} \right) \left\{ \frac{\phi_1}{m_1} \ln \phi_1 + \frac{\phi_2}{m_2} \ln \phi_2 + \chi_{12} \phi_1 \phi_2 \right\} \qquad (2.5)$$

χ_{12} takes into account all the non-combinatorial contributions and it has the nature of free energy term, i.e. it is dependent on both temperature and composition. χ can be written as the combination of non-combinatorial entropic term and the enthalpic term:

$$\chi = \chi_H + \chi_S \qquad (2.6)$$

In eqn.(2.5) the first two terms in the bracket represent the combinatorial entropy of mixing (ΔS_m) while the third term represents enthalpic correction that arises because of the non-ideal behaviour of the solution. χ is a temperature dependent term and its dependence on temperature is given by the following equation:

$$\chi = a + (b/T) \qquad (2.7)$$

Where, T stands for temperature.

For polymer-solvent mixtures, χ_{12} is dependent on temperature as well as concentration:

$$\chi_{12} = a + (b/T) + c\, \phi_1 + d\, \phi_1^2 \qquad (2.8)$$

2.3   Solubility Parameter Approach for miscibility

In cases where two non-polar liquids are mixed, the concept of solubility parameter is used. This concept was given by Hildebrad [24] wherein he applied the approach to calculate the Flory-Huggins interaction parameter and the values enthalpy of mixing (ΔH_m) which gives an indication about whether the two non-polar components being mixed are miscible or immiscible. The Solubility parameter is related to the cohesive energy density (δ), defined as the energy of vaporization (ΔE) per unit volume (V) of material, and expressed as:

$$\delta = \sqrt{\frac{\Delta E}{V}} \tag{2.9}$$

The equation for heat of mixing (ΔH_m) is as given by:

$$\Delta H_m = V (\delta_1 - \delta_2)^2 \, \Phi_1 \Phi_2 \tag{2.10}$$

Where, δi represents solubility parameter for each component, Φ_i is the component volume fraction.

On equating the expression of ΔH_m given by equation (2.10) with the ΔH_m expression given by Flory-Huggins theory, we get

$$\tag{2.11}$$

δ for each polymer is $\quad \chi_{1,2} = \frac{V_R}{RT} (\delta_1 - \delta_2)^2 \quad$ ntribution method. This method for calculating δ was given by Small. The equation for δ is given by:

$$\delta = \left(\frac{\rho \Sigma F_i}{M}\right) = \frac{\Sigma F_i}{\upsilon} \tag{2.12}$$

where, ρ is the density of polymer at the given temperature, M is the molecular weight of repeat unit, ΣF_i is the sum of all the molar attraction constant of all chemical groups in polymer repeat unit, υ is molar volume.

According to equation (2.10), if two substances have equal solubility parameters i.e. $\delta_1 = \delta_2$ then the enthalpy of mixing ΔH_m will be zero. As a result the small negative value of entropy of mixing will result in negative Gibb's free energy which implies that the substances will be miscible. This validates the general rule that chemically and structurally similar substances are generally miscible. The larger the difference in the solubility parameter, the higher will be the degree of immiscibility.

2.4   Specific interactions and miscibility

In cases involving chemically dissimilar pairs of polymers, a miscible blend may be possible if there is specific interaction occurring between the component polymers. Because of specific interaction there is negative heat of mixing i.e. $\Delta H_m<0$ or we can say that there is exothermic heat of mixing. Miscibility between two polymers can be enhanced by hydrogen bonding, ionic and dipole interactions, π electron interaction and charge transfer complex interaction. This concept can be used to enhance miscibility in polymer blends. For example:

in immiscible polymer blends, some chemical groups that can give rise to specific interactions can be incorporated into one or both of the component polymers, this will make the originally immiscible polymers miscible.

2.5 Selection of Rigid and Flexible Polymers for Molecular Composites by Predicting Miscibility.

Thermodynamics of polymer blends (where both the components are flexible polymers) has been described in the above sections. However, molecular composites unlike blends cannot be processed with the conventional processing techniques. The distinctive feature of molecular composites over blends is that in molecular composites there is dispersion of rigid rod macromolecules in the matrix of the flexible polymer unlike blends which is a mixture of two flexible polymers. The presence of rigid rod polymers imparts to the molecular composites its unique and improved thermo-mechanical properties. But, at the same time it imposes a few limitations too as far as processing of composites is concerned. It was Flory [25], Onsager [26], Ishihara [27] and Saiki [28] who first explained the thermodynamics of binary mixtures of rigid rod polymers and solvent. This concept was further extended by Flory to examine the thermodynamics of ternary system consisting of rid rod polymer/flexible polymer/solvent.

On the basis of Flory's theory [29], Hwang et al [8, 30-31] first examined the processing of molecular composites from a ternary blend of rigid rod polymer/flexible polymer/solvent. Before a molecular composite is processed, the following points must be taken care of:

1. A flexible polymer whose properties can be improved by molecular reinforcement should be selected.

2. An intrinsically rigid rod polymer should be chosen as the reinforcing material for the composite.

3. Utmost care should be taken for the uniform dispersion of rigid rod polymer in the matrix of the flexible polymer; and sufficient entanglement in the rigid-rod polymer and flexible polymer must be obtained so as to finally obtain miscible system. Rigid rod polymers cannot be melt processed as they degrade before melting. Hence, this is achieved through solution blending of the rigid and flexible polymers in a solvent and co-precipitating the solution in a non-solvent.

4. There should be complete miscibility between the rigid rod polymer and flexible polymer.

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2.6　Palsule theory of solid state thermodynamics of molecular composite

The thermodynamics of the dispersion of the rigid and the flexible polymer governs the amorphous solid state of a rigid molecular composite processed by co-precipitation of the ternary rigid rod/flexible coil/solvent system.

Palsule has proposed a 'Molecular Theory of Amorphous Solid Thermodynamics' [1] to explain the amorphous state of a molecular composite. A solid molecular composite may be treated as a solid solution of a flexible polymer acting as isodiametrical solvent and the reinforcing rigid rod polymer acting as solute. The repeat unit of rigid rod polymer is assumed to consist of m segments, all of the same length and the axis ratio x and the degree of polymerisation of such a polymer is assumed to be n. For such a polymer:

The aspect ratio (length to diameter) of the repeat unit, $\lambda = 2mx$.

The aspect ratio of the polymer, $\lambda_p = 2mnx$.

It is hoped that- (i) an ideal combination of solubility parameters and specific interactions between the rigid and the flexible polymer may result in exothermic heat of mixing and a miscible molecular composite. (ii) A miscible molecular composite system based on a rigid rod like polymer of known aspect ratio may undergo phase separation depending upon the relative amounts of the rigid polymer. Alternately, a miscible isotropic molecular composite may become anisotropic at higher concentrations of the rigid polymer due to orientation of the rigid polymer network.

In such cases a critical volume fraction of reinforcement (V_r^*) is defined as the maximum amount of reinforcement (rigid polymer) at which a molecular composite is isotropic and above which either a miscible anisotropic or a phase separated system is obtained.

The effect of finite chain length on thermodynamic properties decreases as the concentration is increased. At concentrations above the critical concentrations, the chemical potentials depend upon the concentration of the polymer and not upon the chain length.

Irrespective of the isotropic or anisotropic nature, in a miscible molecular composite, the chain segments of both the rigid and flexible polymers form 'molecular composite segments' and respond in unison to the thermal energy imparted to the molecular composite. Thus the potential energy barrier for vibrational, rotational, translational and diffusional motions of the

molecular composite chain segments is intermediate between the potential energy barrier for thermo-mechanical motions of individual rigid and flexible polymers.

It is a well established principle of polymer blends that miscible polymers have a single glass transition temperature and this temperature lies in between the glass transition temperatures of the component polymers of the blend. Thus irrespective of the isotropic or anisotropic nature, a miscible molecular composite will exhibit a single T_g intermediate between the glass transition temperatures of the two component polymers. Anisotropic molecular composite will show different moduli and strengths in longitudinal and transverse directions. Unlike anisotropic molecular composites, phase separated amorphous molecular composites will show two glass transition temperatures.

2.7 Literature Survey on PPTA and/or PEEK based Molecular Composites

Literature search has been performed to study the molecular composites developed using PPTA as a reinforcing rigid rod macromolecule, and also to study molecular composites developed using PEEK as the flexible polymer. Literature survey indicates that no molecular composite of PPTA/PEEK has been developed.

2.7.1 Molecular Composites of PEEK

The wet-state-consolidation technique is employed for the processing of molecular composites of poly (p-phenylene benzobisthiazole) / poly(ether ether ketone); i.e. PPBT/PEEK [32]. The morphology was studied by X-ray scattering and scanning electron microscopy. Mechanical properties of the molecular composites were studied and they were found to be similar to those of molecular composites made from other rigid rod/thermoplastic.

2.7.2 Molecular Composites of PPTA/PA-6, 6

Molecular composite [9] of poly (p-phenylene terephthalamide) / nylon-6,6 (PPTA/PA-6,6) have been processed by co-precipitation of ternary sulfuric acid solution of the components in water. In the molecular composite, crystallization of flexible polyamide was induced by the rigid PPTA. The molecular composite showed increased mechanical and viscoelastic properties, compared to that of the flexible polymer.

Miscibility and crystalline nature of molecular compsites of poly-*p*-phenylene terephthalamide (PPTA)/nylon 6,6 molecular composites [33]that were prepared by coagulatingthe ternary sulfuric acid solutions were studied. It was concluded that specific interaction between the macromolecules was the reason for miscibility.

2.7.3 Molecular Composites of PPTA/PA-6

Molecular composite [9] of poly (p-phenylene terephthalamide) / nylon-6 (PPTA/PA-6) have been processed by co-precipitation of ternary sulfuric acid solution of the components in water. In the molecular composite, crystallization of flexible polyamide was induced by the rigid PPTA. The molecular composite showed increased mechanical and viscoelastic properties, as compared to the flexible polymer.

Miscibility and crystallization of molecular composites of poly-*p*-phenylene terephthalamide (PPTA)/nylon 6 [33] that were processed by coagulating of the ternary sulfuric acid solution demonstrated the solvation of nylon 6 crystals in PPTA matrix if the composite had PPTA content in excess of 70 wt% due to cross-hydrogen bonding. Specific interaction was the reason for miscibility.

The effects of molecular weight of nylon 6 on the phase separation of nylon 6 in the molecular composites [34] of poly(*p*-phenyleneterephthalamide)/nylon 6 (PPTA/PA-6) kept at 240°C has been studied by preparing the material from ternary solution of the components in sulfuric acid and co-precipitating the solution in water. The crystallinity of nylon 6 was lost in the presence of PPTA when the PPTA content exceeds 50 wt% through all the range of molecular weight of nylon 6. The tensile modulus and strength increased if the molecular weight of nylon 6 and weight fraction of PPTA in the composites were also increased.

2.7.4 Molecular Composites of PPTA/PA-3

Molecular composites [35] of PPTA/Nylon-3 have been processed by *in situ* polymerization wherein the anion of the poly-(phenylene terephthalamide) (PPTA) was employed as the initiator during the polyerization. The materials exhibited improved mechanical properties compared to nylon 3.

2.7.5 Molecular Composites of PPTA and PVP

Molecular composites [36] were processed by dispersing the ionically-modified poly (p-phenylene terephthalamide) (PPTA anion) in the matrix of poly (4-vinylpyridine) (PVP). The resulting composite was transparent and exhibited a single T_g for upto 5% rigid rod macromolecule concentration. The mechanical properties were found to increase with increase in the concentration of PPTA and attained a maximum at 5% PPTA concentration.

2.7.6 Molecular Composites of PPTA and PVC

Solution blending was used to blend Poly (*p*-phenylene terephthalamide) (PPTA) with poly (vinyl chloride) (PVC). Dimethyl sulfoxide was used as the common solvent. In PPTA/PVC molecular composite [37], PPTA was found to enhance the thermal degradation of PVC. The molecular composite exhibited higher Young's modulus and yield stress compared to that of PVC. The mechanical properties of the composite were better than that of PVC.

2.7.7 Molecular Composites of PPTA and ABS Resin

Molecular composite [38] of poly(*p*-phenylene terephthalamide) (PPTA) and ABS resin were processed from ternary solution of *N*-sodium PPTA/ABS/ dimethylsulfoxide by co-precipitating the solution into acidic water. Transmission electron micrograph showed that PPTA was found to be dispersed in the matrix of ABS resin in microfibril form with diameter of 10–30 nm. The *Tg* of the resin component in ABS was found to increase upon increasing the PPTA content. Molecular composites showed higher values of tensile modulus and strength upon reinforcement with PPTA.

CHAPTER 3

MATERIALS AND PROCESSING FOR MOLECULAR COMPOSITES OF PPTA/PEEK

This study aims to develop molecular composites of PPTA/PEEK. Accordingly, Poly-Ether-Ether-Ketone (PEEK) has been selected as the flexible polymer. Poly-p-Phenylene-Terephthalamide (PPTA) has been selected as the reinforcing rigid rod macromolecule. These are described below:

3.1   Rigid Rod Macromolecule PPTA
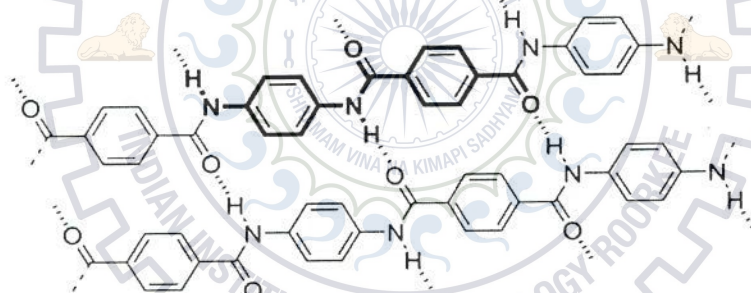
3.1.1   Structure of PPTA

Fig. 3.1: Structure of PPTA (Kevlar)

- Poly-para-phenylene Terephthalamide – (macromolecule used to process Du Pont's Kevlar® fiber) – is a para-aramid synthetic fibre of high strength.

- Formation of polyamides requires reaction of aromatic diamine and aromatic dichloride. For PPTA formation para-phenylene di amine as aromatic di amine and terephthaloyl chloride as aromatic di chloride is used. Polymerization is done by the poly - condensation reaction.
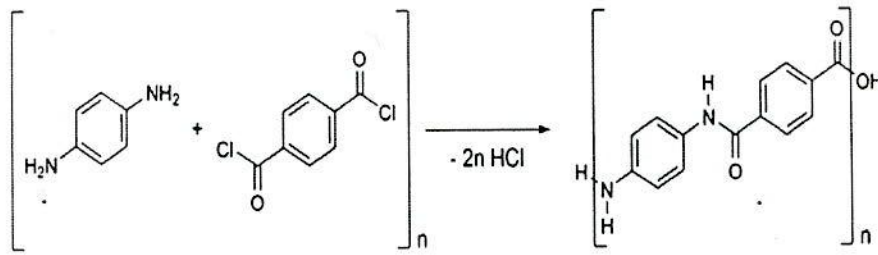
Fig 3.2: Synthesis of PPTA

3.1.2 Properties of PPTA

Tensile Strength	3620 MPa
Density	1.44
Glass Transition Temperature	Does not exist
Degradation Temperature	500 °C

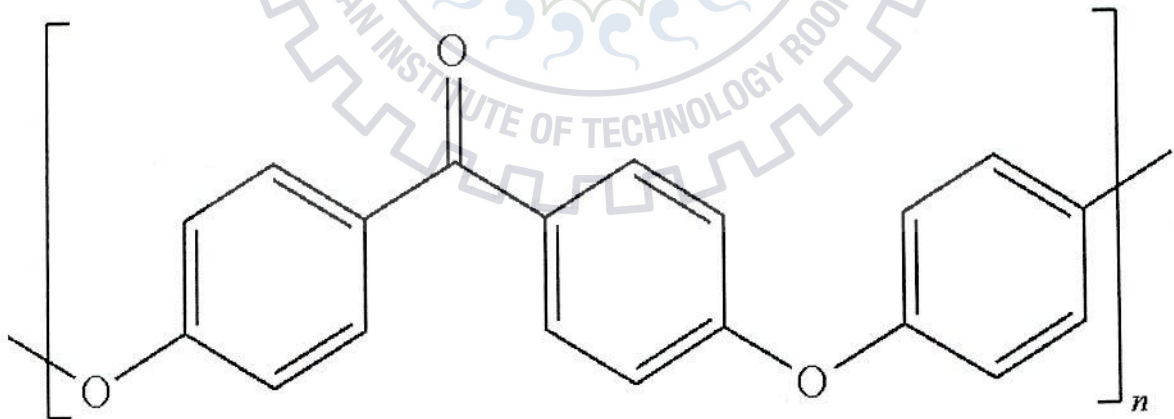## 3.2 Flexible Polymer PEEK

3.2.1 Structure of PEEK

Fig. 3.3: Structure of PEEK

- PEEK is colourless, thermoplastic and an organic polymer that is used for engineering purposes.

- PEEK is synthesized by using the step growth polymerization technique which involves the dialkylation of bisphenol salts. The reaction of 4,4-difluorobenzophenone with disodium salt of hydroquinone is used to obtain PEEK. The reaction temperature is around 300°C and diphenylsulphone is used as solvent.
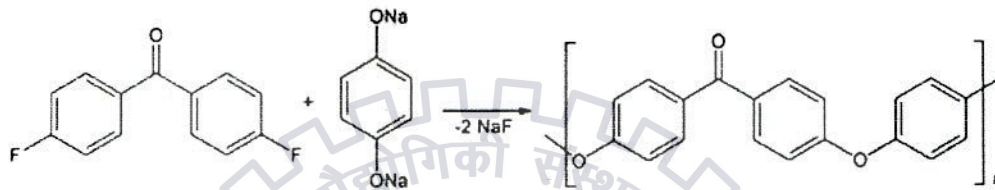

Fig 3.4: Synthesis of PEEK

3.2.2 Properties of PEEK

Density	1320 kg/m^3
Young's Modulus	3.6 GPa
Tensile Strength	90-100 MPa
Elongation at break	50%
Notch Strength	55 KJ/m^2
Glass Transition Temperature	143 °C
Melting Point	343 °C
Thermal Conductivity	0.25 W/m.K

3.3 Thermodynamics of Molecular Composite Processing

Molecular composites are processed from a ternary solution of a rigid rod polymer/flexible polymer/solvent. This solution is characterized by its critical concentration (C_r). The critical concentration is defined as the maximum concentration of polymers in the solution at which the solution still exists in the isotropic state. In case of dilute solutions, the concentration of

polymers is low (i.e. $C<C_r$) (shown in fig. 3.5a) and there is no polymer-polymer interaction. At this stage the solution is isotropic and the solution's viscosity starts to exhibit non-Newtonian nature. As the concentration of the polymer in the solution starts to increase and becomes equal to the critical concentration (i.e. $C=C_r$) (shown in fig 3.5b), the rigid rod polymers or small bundles of the rigid rod polymers get trapped in the highly elastic medium (matrix) of the entangled flexible polymer. On further increase in the concentration of the polymers ($C>C_r$) (shown in fig. 3.5c) phase separation takes place. At this stage, the rigid rod polymers segregate into liquid crystalline domains which are dispersed in an entangled flexible matrix. As there is phase separation at concentrations above the critical concentration, we cannot process molecular composites at concentrations above the critical concentration. So for processing of molecular composites the ideal condition is where the concentration is almost equal to the critical concentration ($C<C_r$).

Fig. 3.5 Structure of Phase of ternary mixture as function of composition

Molecular composites cannot be processed by the method of solvent casting. In solvent casting, slow evaporation of the solvent takes place and its concentration begins to increase and thus the originally isotropic solution with $C<C_r$ passed through the critical temperature and phase separation occurs. Hence to process molecular composites, co-precipitation in a non solvent is done.

3.4   Processing of PPTA/PA-6,6 Molecular Composites

PPTA is rigid rod polymer and can-not be melt processed. Consequently, processing of the molecular composites of PPTA/PEEK has been performed by solution blending by following the principles described earlier.

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Table 3.1   Composition of various PPTA/PEEK Molecular Composites

Molecular Composites	PPTA (gm)	PEEK (gm)
5/95 PPTA/PEEK	5	95
10/90 PPTA/PEEK	10	90
15/85 PPTA/PEEK	15	85

Detailed process is described below.

Following compositions of PPTA/PEEK molecular composites have been processed; 5/95 PPTA/PEEK, 10/90 PPTA/PEEK and 15/85 PPTA/PEEK as follows in the Table – 3.1

3.4.1   Processing of 5/95 PPTA/PEEK

Following steps were followed to process the PPTA/PEEK molecular composites –

- 5 gms PPTA was added to 50 ml sulphuric acid.
- The above solution was subjected to continuous stirring for 50 hours at room temperature.
- After 50 hrs, clear, translucent isotropic solution of PPTA/SA was obtained.
- 95 gms PEEK was added to 950 ml sulphuric acid.
- The above solution was subjected to continuous stirring for 75 hours at room temperature.
- After 75 hrs, clear, translucent isotropic solution of PEEK/SA was obtained.
- PPTA/SA and PEEK/SA were mixed and further diluted with 100 ml sulphuric acid
- The above solution was stirred for 50 hrs till clear, translucent isotropic ternary solution of PPTA/PEEK/SA was obtained.
- This final solution was then co-precipitated in non-solvent water to remove sulphuric acid by dissolving sulphuric acid in water.
- Coagulation of solutions resulted in precipitation of PPTA/PEEK molecular composite in water.
- The molecular composite was washed thoroughly with water and acetone to remove any traces of residual sulphuric acid and dried in air oven and then into the vacuum oven at 50°C for 50 hours.
- The dried flakes were then used for analyzing the structure and properties by various characterization methods.

3.4.2 Processing of 10/90 PPTA/PEEK

The steps listed above in 3.4.1 were followed to process 10/90 PPTA/PEEK molecular composites with appropriate amounts of PPTA and PEEK listed in Table 3.1.

3.4.3 Processing of 15/85 PPTA/PEEK

The steps listed above in 3.4.1 were followed to process 15/85 PPTA/PEEK molecular composites with appropriate amounts of PPTA and PEEK listed in Table 3.1

CHAPTER 4

TESTING AND CHARACTERIZATION OF MISCIBILITY AND MORPHOLOGY

4.1 Miscibility by Differential Thermal Analyzer

Thermal Analysis is a group of techniques that study the properties of a material as they change with temperature. In Differential Thermal Analysis (DTA) the material under study and an inert reference are made to undergo identical thermal cycles. Any temperature difference between the material and the reference is recorded. In this technique the heat flow to the sample and the reference remains the same instead of temperature. The differential temperature is then plotted against time or temperature (DTA curve or thermo-gram).

Fig 4.1: DTA equipment

Miscible polymer blends exhibit a T_g which lies in between the glass transition temperatures of the component polymers, while phase separated/immiscible blend shows two distinct glass transition temperatures correspond to individual components of polymer blends.

For a blend to be miscible it is required that the blend shows a single glass transition temperature (T_g) which is higher than the glass transition temperature (T_g) of the flexible polymer.

4.2   Morphology by Field Emission Scanning Electron Microscope FE-SEM

To study the morphology of the surface of the Molecular Composites of PPTA/PEEK, electron microscopy technique (FE-SEM) was used.

A FE-SEM is used to view minute details on the surface of materials (sample).It can be used to observe structures in the nanometer size range. In a FE-SEM, electrons emitted from a field emission source and accelerated through a high electrical field gradient are used to produce a narrow beam which bombards the object, this leads to emission of secondary electrons from the bombarded object. These secondary electrons' velocity and angle related to the surface of the object. These secondary electrons are then caught by a detector which then produces electronic signals which is used to generate an image of the surface of the object.
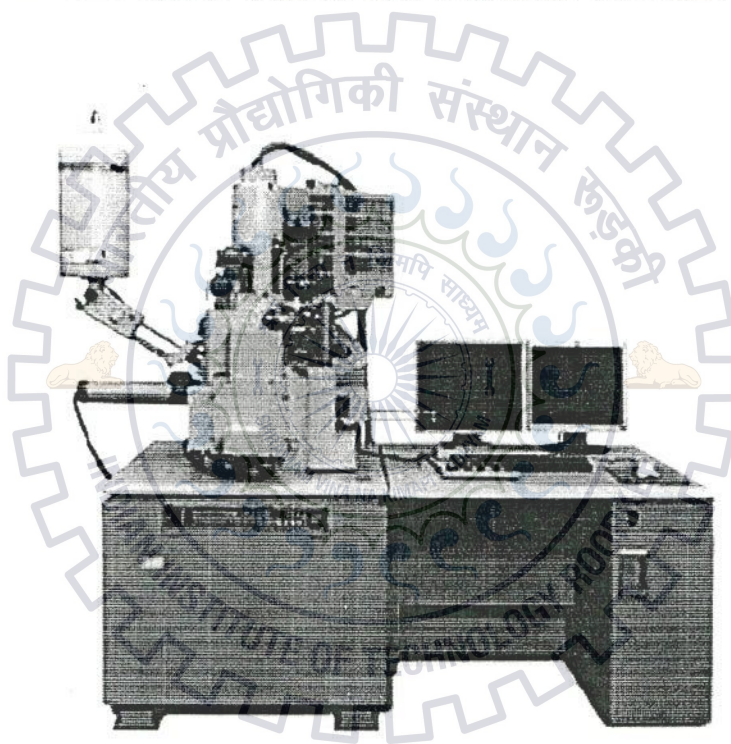
Fig. 4.2: FE-SEM equipment

To study the morphology of the Molecular Composites of PPTA/PEEK, FE-SEM images of these composites were studied. The FE-SEM analysis of the molecular composites of 5/95 PPTA/PEEK, 10/90 PPTA/PEEK, 15/85 PPTA/PEEK were carried under a magnification of 2000x, 5000x and 10000x magnifications.

4.3 Specific Interactions by FTIR Spectroscopy

Fourier Transform Infrared Spectroscopy was used to get the absorption spectra of the molecular composites. In this technique, a beam containing multiple frequencies of light is made to strike the sample at once. The amount of beam that is absorbed by the sample is measured. Another beam with a different set of frequencies is made to strike the sample; this gives another set of data. This process is repeated multiple number of times. From the data obtained by this process, a graph of % transmittance / % absorbance against wave number is plotted. Since, a Fourier Transform is employed to convert the raw data into a spectrum the technique is known as Fourier Transform Infrared Spectroscopy.
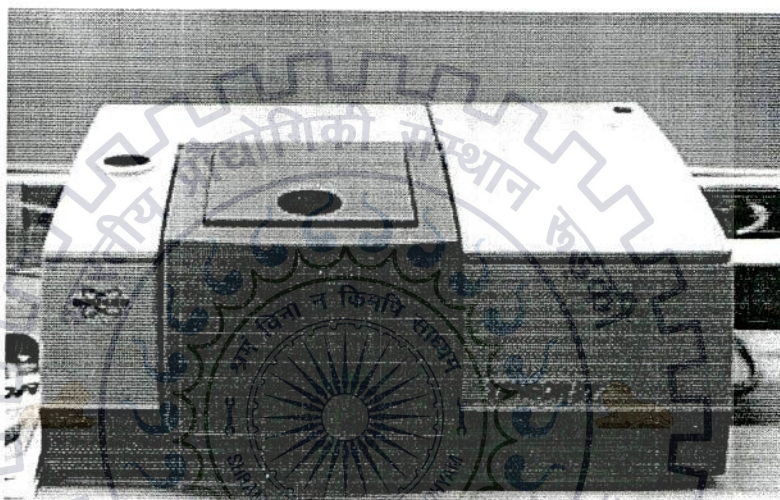
Fig 4.3: FTIR Spectrometer

FTIR produces an infrared spectrum of the sample which is used to identify the chemical bonds present in the sample. The spectra gives a profile of the sample being tested, this profile can be used as fingerprint for analyzing the presence of different groups in the sample. Polymer FTIR gives information about the presence of different groups as well as the bonding that is taking place.

The reason and thermodynamics of miscibility in molecular composites of poly-ether-ether-ketone and polyp-phenylene-terephthalamide has been evaluated by recording the Fourier transform infra red spectroscopy of the flexible PEEK polymer and the PPTA/PEEK molecular composites.

The role of specific interactions and solubility parameter in in determining the miscibility of a blend has been studied in detail. It can be concluded that the miscibility in molecular composites arise due to the similar solubility parameters of the component units in PPTA and PEEK and is further increased by intermolecular H-bonding between the N-H group of PPTA and C=O group of PEEK.

4.4 Thermal Stability and Degradation by DTA/TGA

Thermogravimetric Analysis is a technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere. TGA is a technique in which, upon heating a material, its weight increases or decreases. TGA measures a sample's weight as it is heated or cooled in a furnace. A TGA consists of a sample pan that is supported by a precision balance. That pan resides in a furnace and is heated or cooled during the experiment. The mass of the sample is monitored during the experiment. A sample purge gas controls the sample environment. This gas may be inert or a reactive gas that flows over the sample and exits through an exhaust.
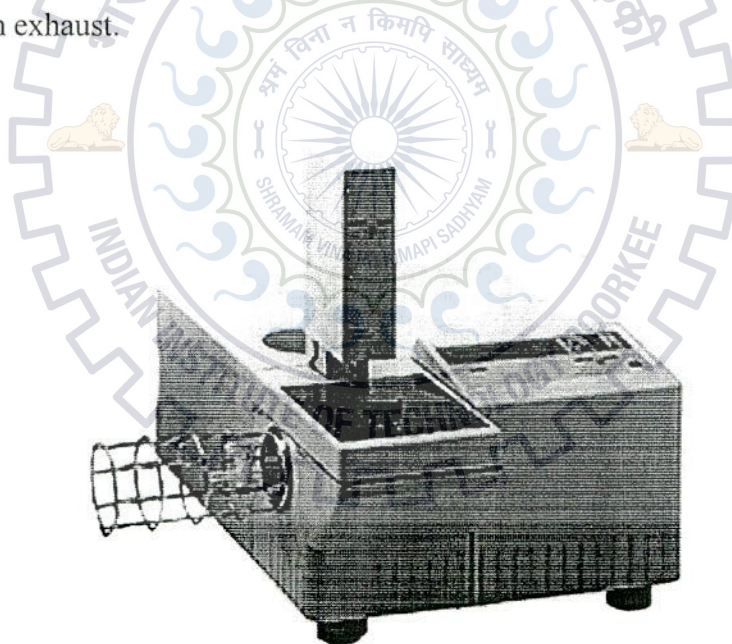
Fig: 4.4: TGA equipment

Thermo-gravimetric Analysis was used to analyze the thermal stability of PEEK and the molecular composites of PPTA/PEEK.

CHAPTER 5

MISCIBILITY IN MOLECULAR COMPOSITES
OF PPTA/PEEK

PEEK was characterized using DTA. The heating rate was maintained at 5K/min and the sample was heated from room temperature to 400°C. Miscibility in PPTA/PEEK molecular composites were established by determining their T_g using Differential Thermal Analyzer. Studies were performed by DTA operated at a heating rate of 5K/min from room temperature to 400 °C. All the three compositions of the PPTA/PEEK molecular composite, i.e. PPTA/PEEK- 5/95, PPTA/PEEK- 10/90 and PPTA/PEEK 15/85 were characterized using this technique.

5.1 Glass Transition Temperatures of Molecular Composites

Figures 5.1 to 5.4 show the DTA curves for PEEK, 5/95 PPTA/PEEK, 10/90 PPTA/PEEK and 15/85 and PPTA/PEEK respectively. The glass transition temperature (T_g) for PEEK and PPTA/PEEK composites have been obtained from their respective DTA curves.
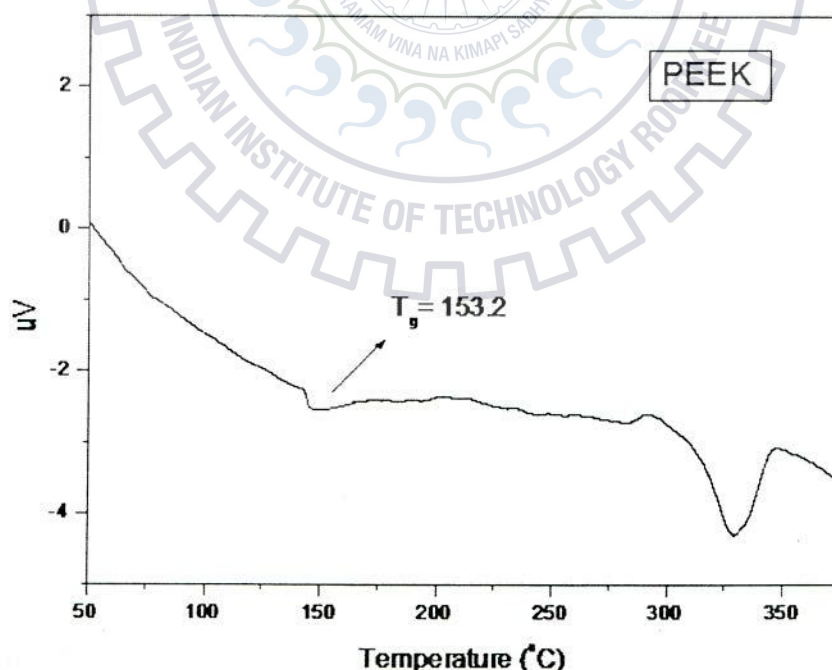
Fig. 5.1: DTA curve of PEEK
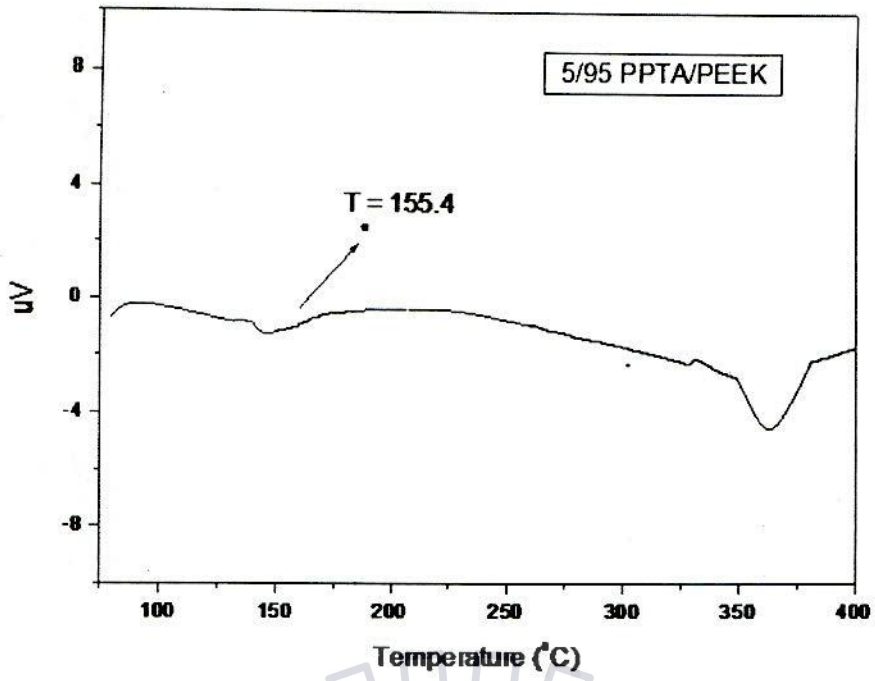
Fig: 5.2 DTA curve of 5/95 PPTA/PEEK
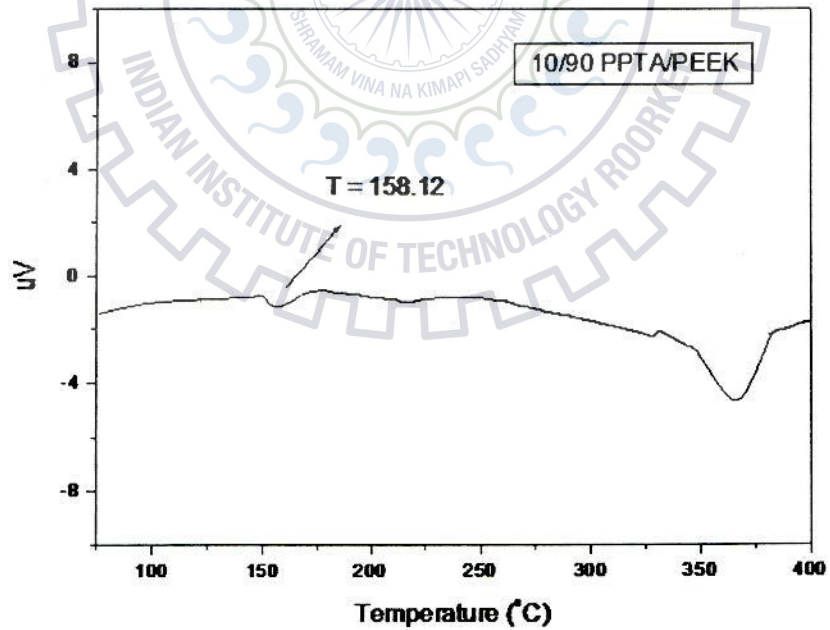
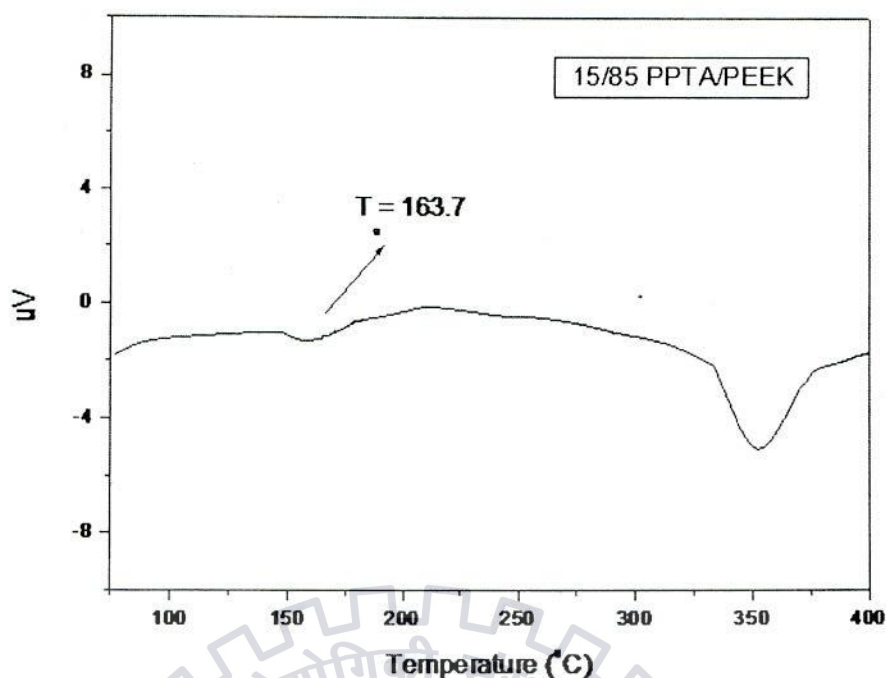Fig: 5.3: DTA curve of 10/90 PPTA/PEEK

Fig: 5.4: DTA curve of 15/95 PPTA/PEEK

5.2 Increase in Glass Transition Temperature with Increasing PPTA

Table 5.1: Tg of PPTA/PEEK molecular composites

Molecular Composite	Glass Transition Temperature	% increase in Tg
PEEK	153.2 $^{\circ}$C	-
5/95 PPTA/PEEK	155.4 $^{\circ}$C	1.43
10/90PPTA/PEEK	158.12 $^{\circ}$C	3.2
15/85 PPTA/PEEK	163.7 $^{\circ}$C	6.85

The gradual increase in the T_g values of the molecular composites upon increasing the amounts of the rigid rod macromolecule in the molecular composite is evident from the above table. Addition of 5%, 10% and 15% PPTA leads to an increase of 1.43%, 3.2% and 6.85% in the glass transition temperature of the composite as compared to glass transition temperature of PEEK. The glass transition temperatures of PEEK, 5/95 PPTA/PEEK, 10/90 PPTA/PEEK and 15/85 PPTA/PEEK were recorded at 153.2°C, 155.4°C, 158.12°C, 163.7°C respectively.

This also shows that reinforcement of flexible polymer with rigid rod polymer leads to improvement in the thermal property of the composite.

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5.3 Miscibility in PPTA/PEEK

It is now an established practice to establish miscibility in molecular composites by establishing that the Tg of the molecular composite is higher than that of the flexible polymer and increases with increasing amounts of reinforcing rigid rod macromolecules in the molecular composites.

As stated earlier, for a molecular composite to be miscible it has to exhibit a single glass transition temperature which is greater than the glass transition temperature of the flexible polymer. From the above DTA curves of PEEK and various PPTA/PEEK molecular composites it is clear that the molecular composites exhibit single glass transition temperature which is greater than the glass transition temperature of PEEK. The establishment of a single glass transition temperature which is greater than the glass transition temperature of the flexible polymer (PEEK in this case) confirms miscibility.
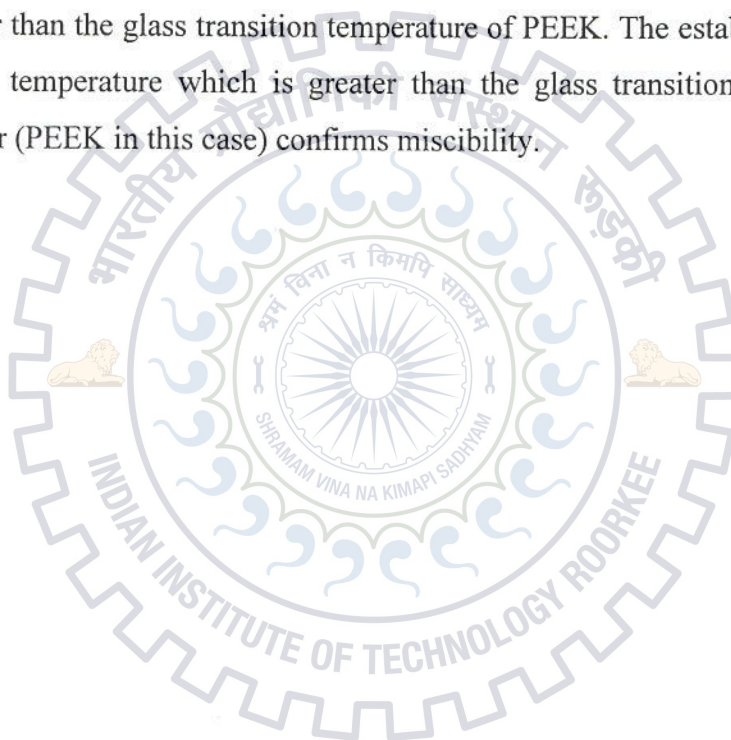
CHAPTER 6

SPECIFIC INTERACTIONS IMPARTING MISCIBILITY IN PPTA/PEEK MOLECULAR COMPOSITES BY FTIR

6.1   Hydrogen Bonds by FTIR

The reason and thermodynamics of miscibility in molecular composites of poly-ether-ether-ketone and polyp-phenylene-terephthalamide has been evaluated by recording the Fourier transform infra red spectroscopy of the flexible PEEK polymer and the PPTA/PEEK molecular composites.

The role of specific interactions and solubility parameter in determining the miscibility of a blend has been studied in detail. It can be concluded that the miscibility in molecular composites arise due to intermolecular H-bonding between the N-H group of PPTA and C=O group of PEEK. This intermolecular hydrogen bonding is evident in FTIR spectra recorded in figures 6.1, 6.2 and 6.3 and 6.4 respectively.
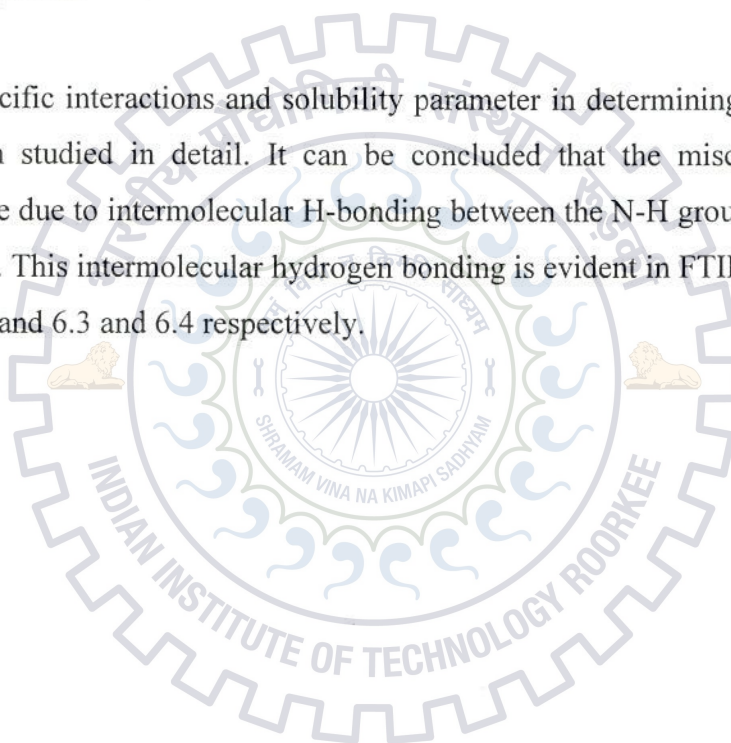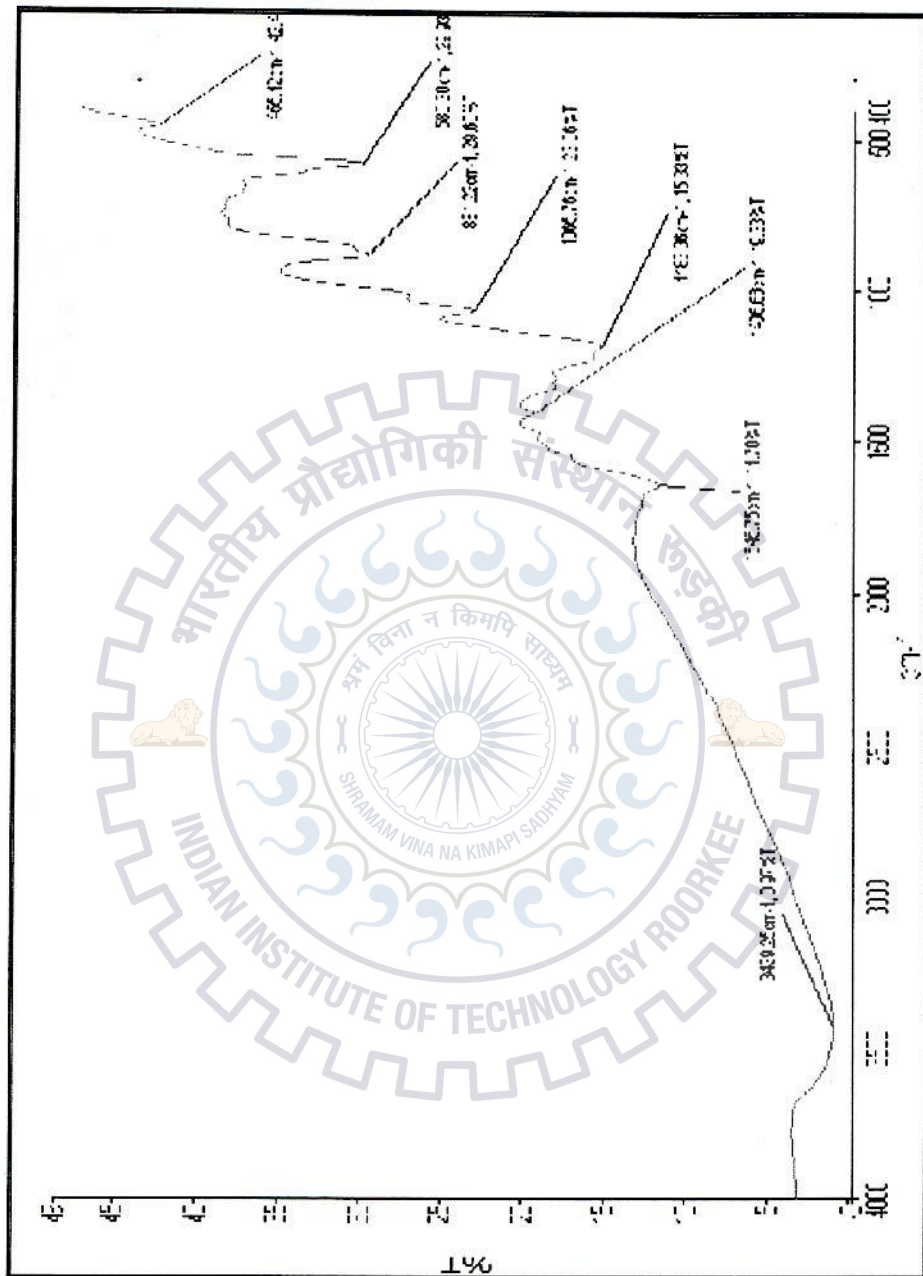
Fig 6.1: FTIR spectrum of PPTA/PEEK- 5/95
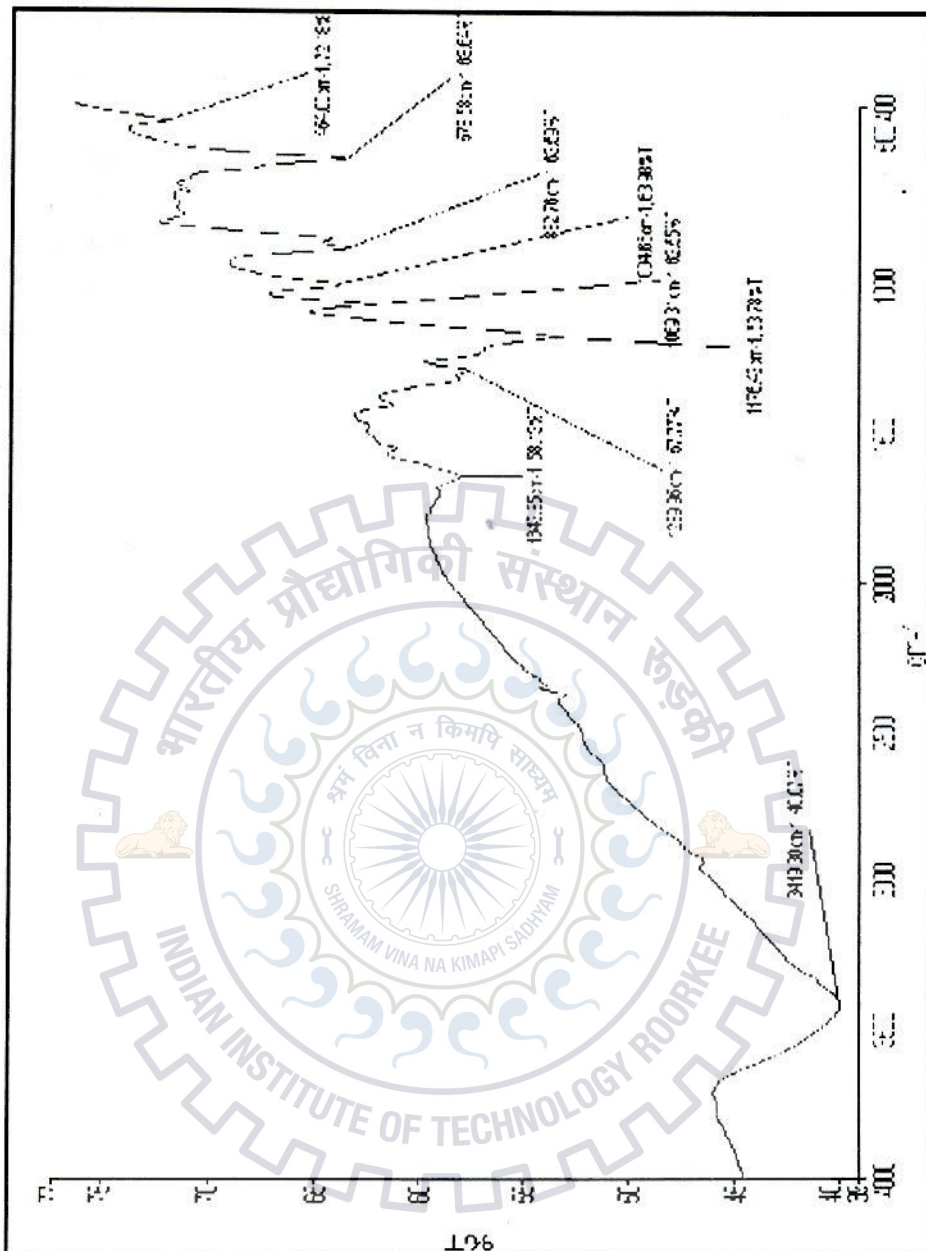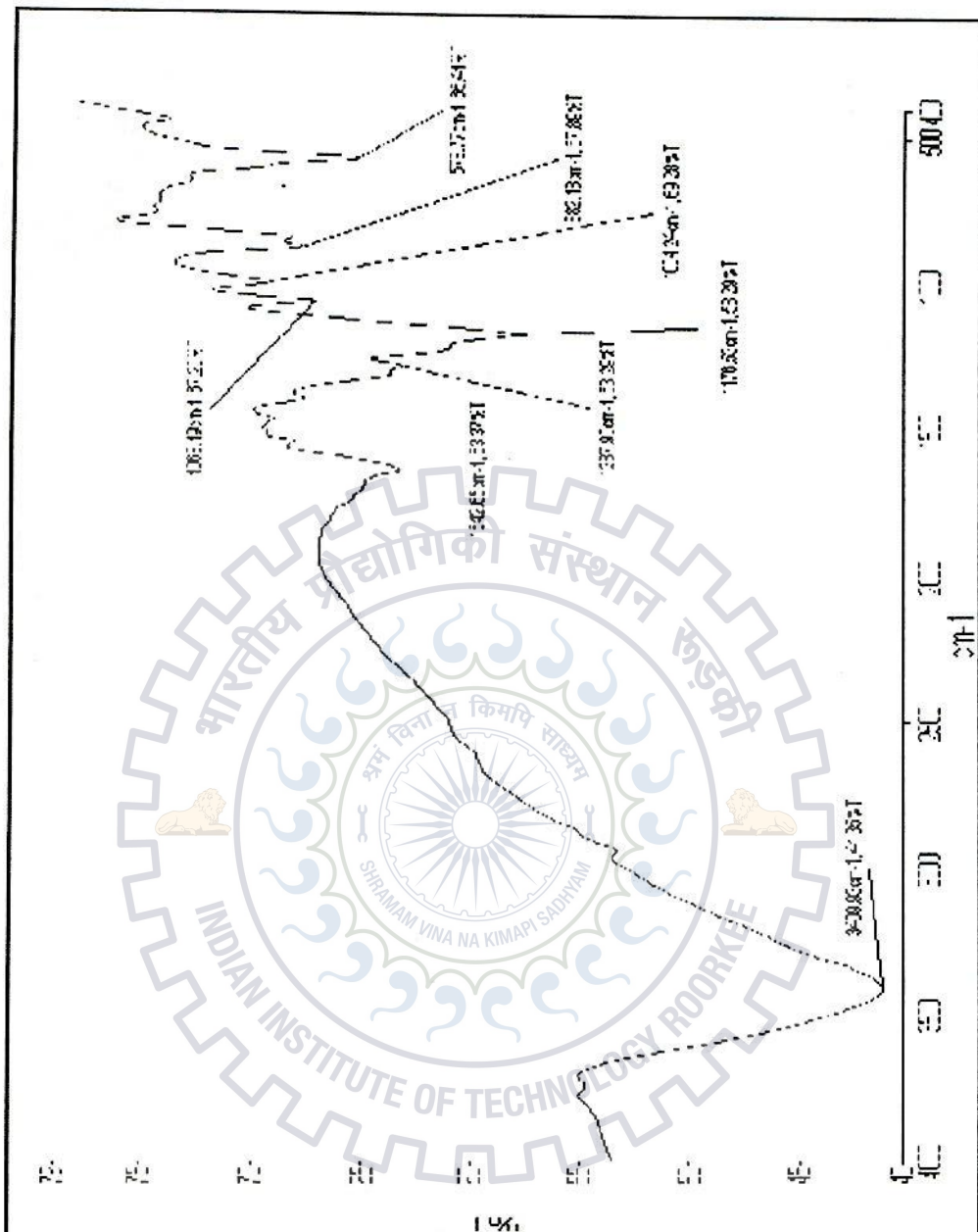
Fig 6.2: FTIR spectrum PPTA/PEEK- 10/95

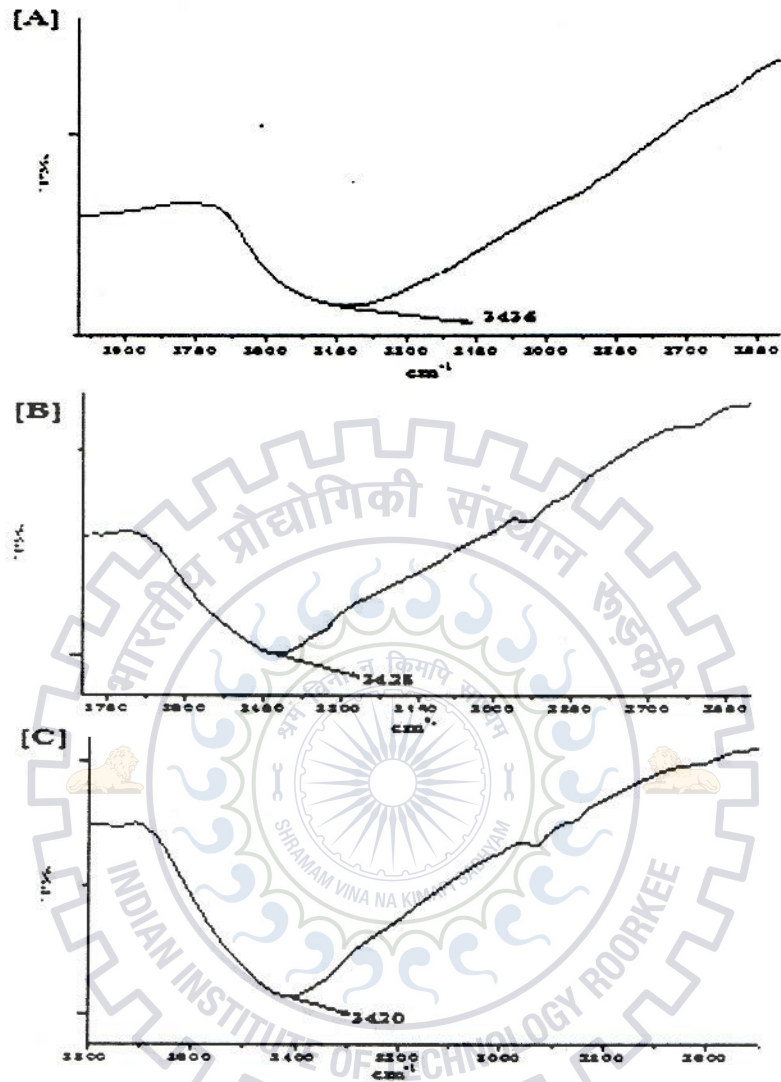Fig 6.3: FTIR spectrum PPTA/PEEK- 15/85

Fig: 6.4: FTIR spectra of showing formation of H-bond

[A] 5/95 PPTA/PEEK, [B] 10/90 PPTA/PEEK, [c] 15/85 PPTA/PEEK

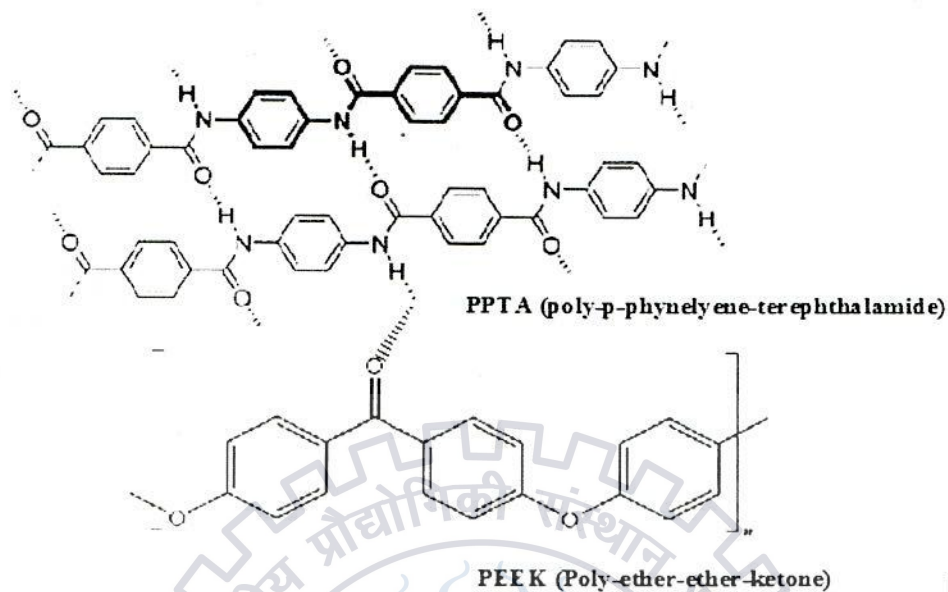## 6.2 Role of Hydrogen Bonds in Imparting Miscibility in PPTA/PEEK

Fig: 6.5: Hydrogen bonding between PPTA and PEEK

PPTA and PEEK are miscible because of their similar solubility parameters. Due to the presence of similar chemical units in their repeat unit they both have similar solubility parameter. But miscibility between the two polymers is further enhanced by specific interactions mainly of the Hydrogen bonding type. The H-bonding occurs between the H-atom from the NH group of PPTA and the O atom from the CO group of PEEK. This H-bonding as evident from the FTIR spectra (at around 3420 cm^{-1}) of the molecular composites of PPTA/PEEK makes the two polymers miscible and hence phase separation in the molecular composite does not occur.

CHAPTER 7

MORPHOLOGY OF
PPTA/PEEK MOLECULAR COMPOSITES

To study the morphology of the surface of the Molecular Composites of PPTA/PEEK, electron microscopy technique (FE-SEM) was used.

7.1 Uniform Homogeneous Morphology of PPTA/PA-6,6 Molecular Composites

To study the morphology of the Molecular Composites of PPTA/PEEK, FE-SEM images of these composites were studied. The FE-SEM analysis of the molecular composites of PPTA/PEEK- 5/95, PPTA/PEEK- 10/90, PPTA/PEEK-15/85 were carried under a magnification of 2000x, 5000x and 10000x magnifications. Fig. 8.2 to 8.10 shows the FE-SEM images.

7.1.1 Morphology of 5/95 PPTA/PEEK

Figures 7.1 (a to c) show the FE-SEM micrographs of 5/95 - PPTA/PEEK molecular composite at x2000, x5000 and x10,000. The analysis of these micrographs follows after the figures / images.
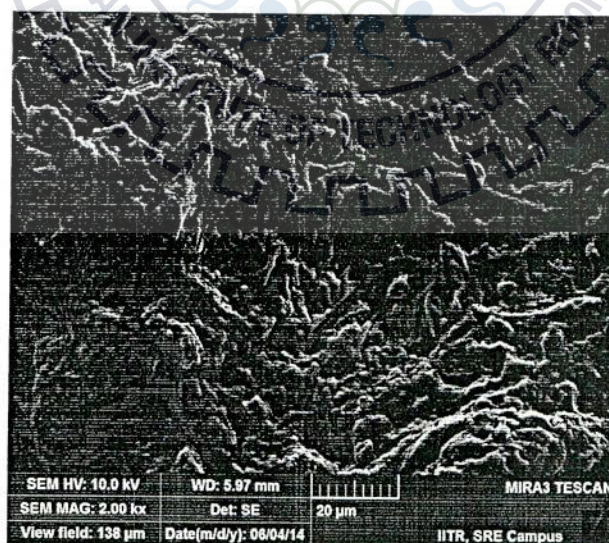

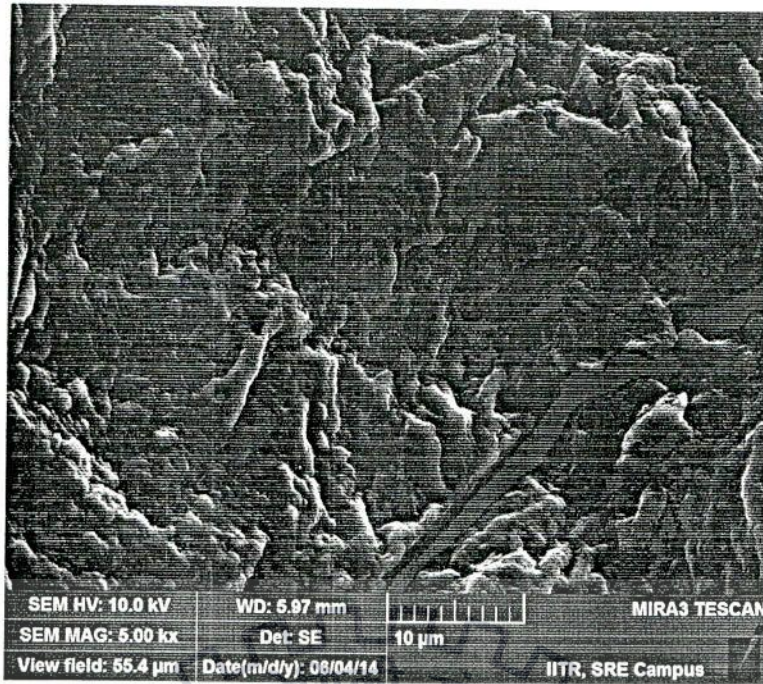Fig. 7.1 (a): FE-SEM image of PPTA/PEEK- 5/95 at 2000x magnification

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Fig. 7.1 (b) : FE-SEM image of 5/95 PPTA/PEEK at 5000x magnification
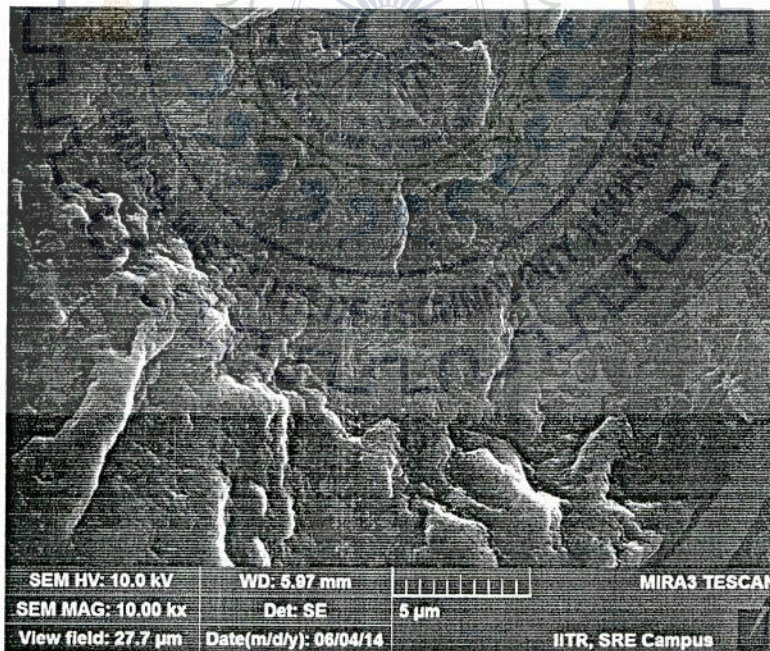

Fig. 7.1 (c): FE-SEM image of 5/95 PPTA/PEEK- at 10000x magnification

From the micrographs, it is evident that the constituent rigid PPTA and the flexible PEEK are uniformly dispersed in the molecular composites, with no phase separation and without formation of any second phase and thereby confirming the formation of homogeneous, single phase molecular composite of 5/95 PPTA/PEEK.

7.1.2 Morphology of 10/90 PPTA/PEEK

Figures 7.2 (a to c) show the FE-SEM micrographs of 10/90 - PPTA/PEEK molecular composite at x2000, x5000 and x10,000. The analysis of these micrographs follows after the figures / images.
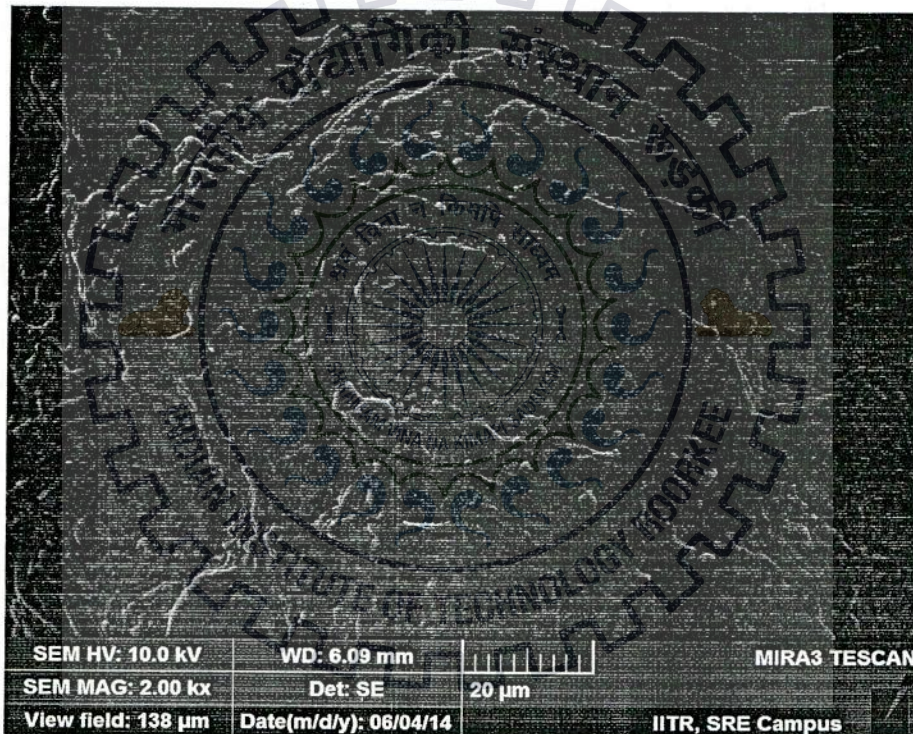

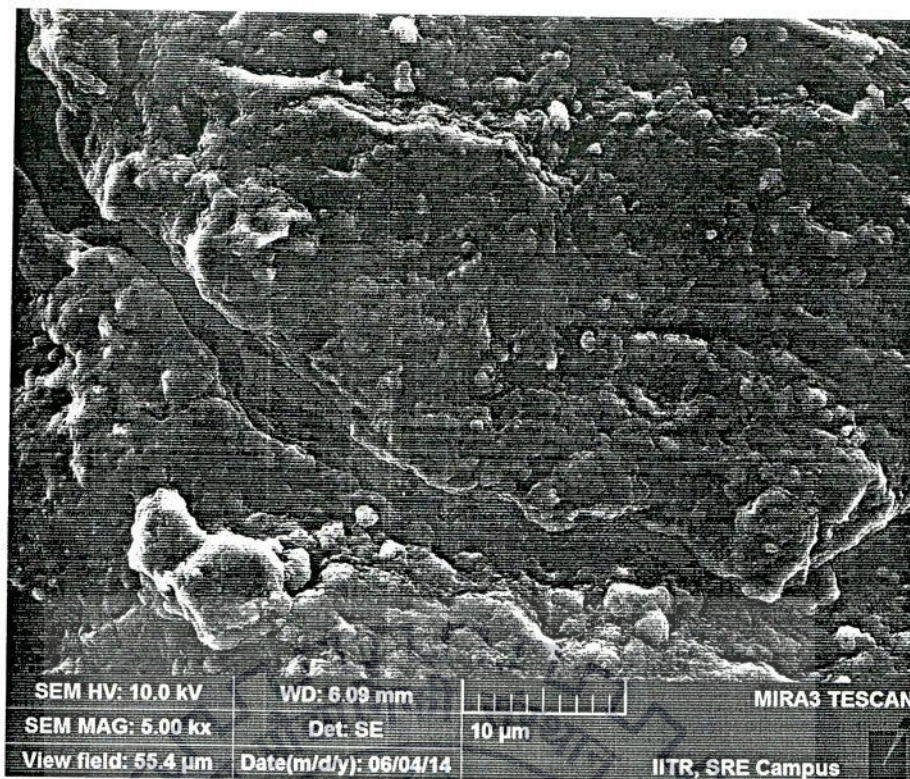**Fig. 8.2 (a): FE-SEM image of 10/90 PPTA/PEEK at 2000x magnification**

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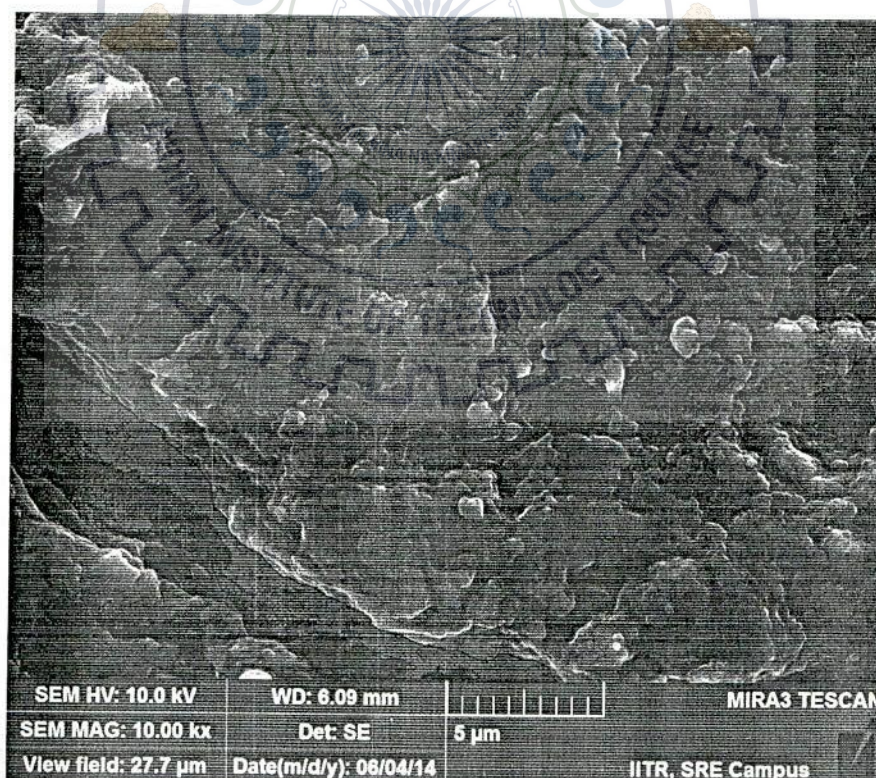**Fig. 7.2 (b):** FE-SEM image of 10/90 PPTA/PEEK at 5000x magnification

Fig. 7.2 (c): FE-SEM image of 10/90 PPTA/PEEK at 10,000x magnification

The above photographs [fig 7.2 (a to c)] show the FE-SEM micrograph of 10/90 PPTA/PEEK molecular composite. From the micrograph, it is evident that the constituent rigid PPTA and the flexible PEEK are uniformly dispersed in the molecular composites, with no phase separation and without formation of any second phase and thereby confirming the formation of homogeneous, single phase molecular composite of 10/90 PPTA/PEEK.

8.1.3 Morphology of 15/85 PPTA/PEEK

Figures 7.3 (a to c) show the FE-SEM micrographs of 15/85 - PPTA/PEEK molecular composite at x2000, x5000 and x10,000. The analysis of these micrographs follows after the figures / images.
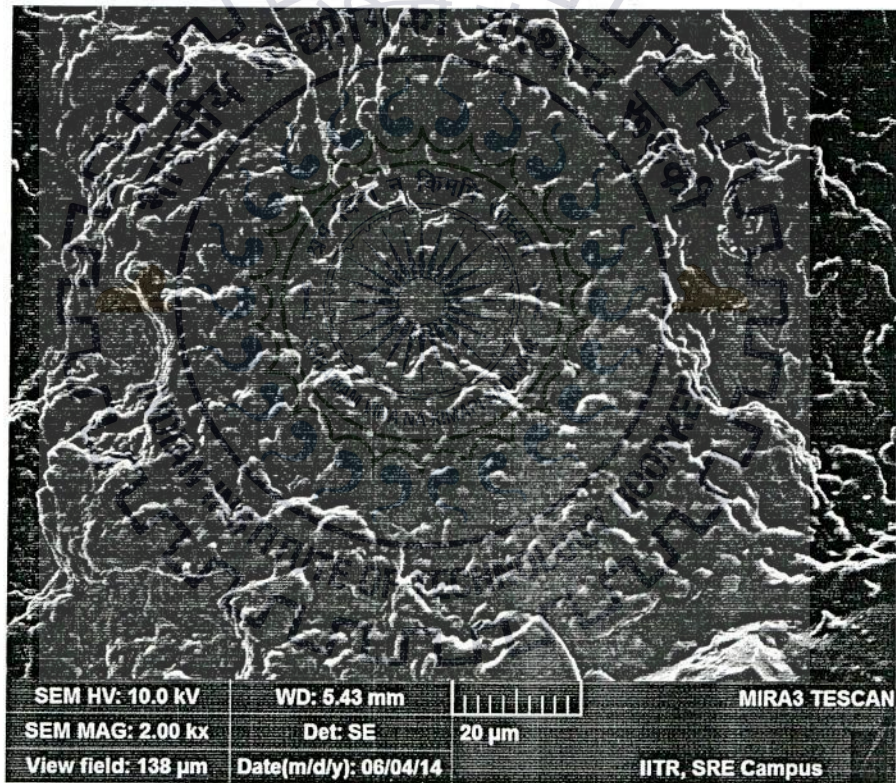

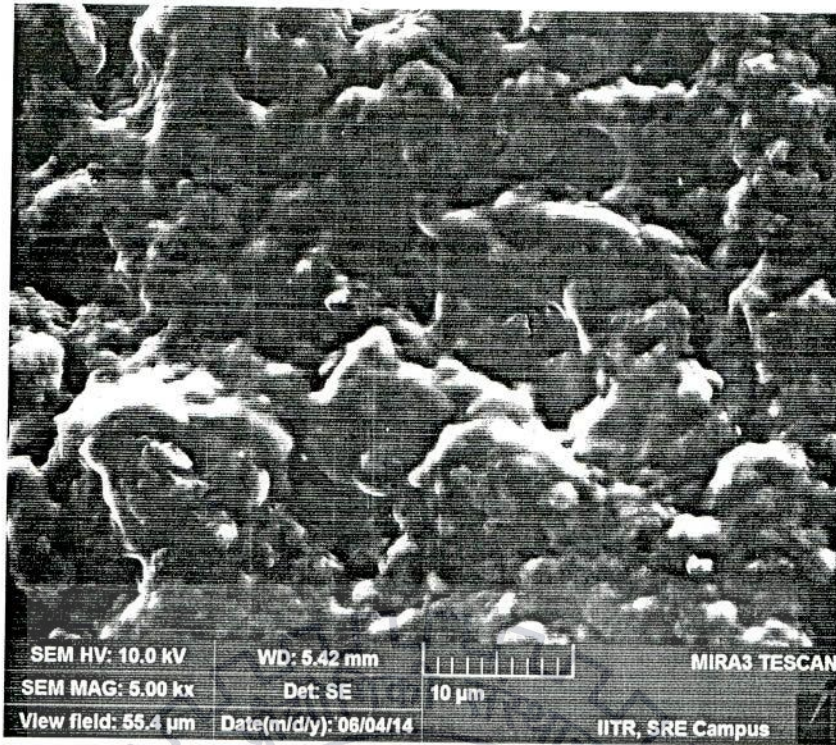**Fig. 7.3 (a): FE-SEM image of 15/85 PPTA/PEEK at 2000x magnification**

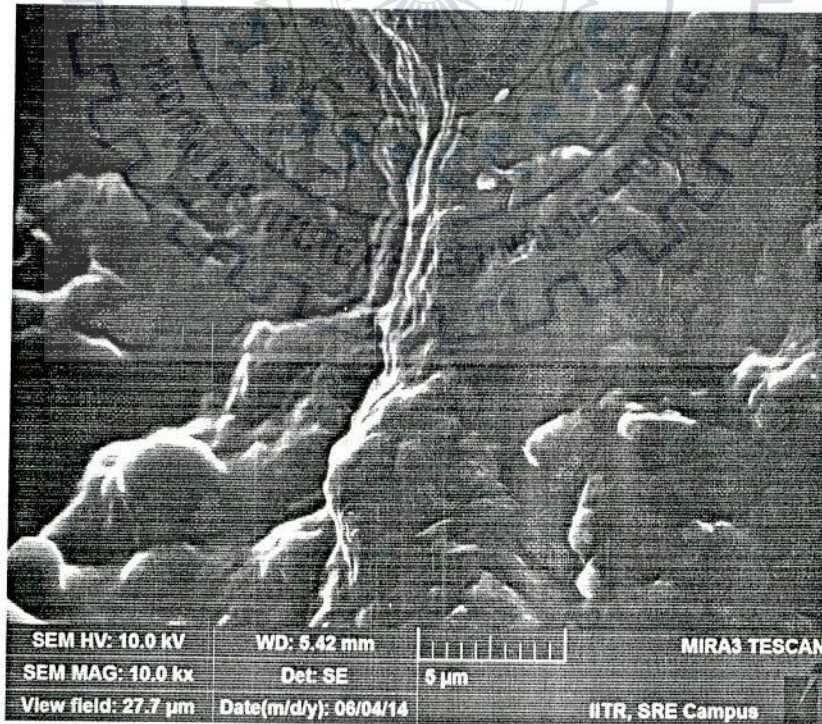Fig. 7.3 (b): FE-SEM image of 15/85 PPTA/PEEK at 5000x magnification

Fig. 7.3 (c): FE-SEM image of 15/85 PPTA/PEEK at 10,000x magnification

The above photographs [figure 7.3 (a to c)] show the FE-SEM micrograph of 15/85 PPTA/PEEK molecular composite. From the micrograph, it is evident that the constituent rigid PPTA and the flexible PEEK are uniformly dispersed in the molecular composites, with no phase separation and without formation of any second phase and thereby confirming the formation of homogeneous, single phase molecular composite of 15/85 PPTA/PEEK.

CHAPTER 8

THERMAL STABILITY AND DEGRADATION

Thermal stability of PEEK and PPTA/PEEK molecular composites were studied by Therogravimetric analyzer. PEEK and PPTA/PEEK molecular composites were heated from room temperature to 800 ^{o}C. The TGA curve for PEEK is shown below:
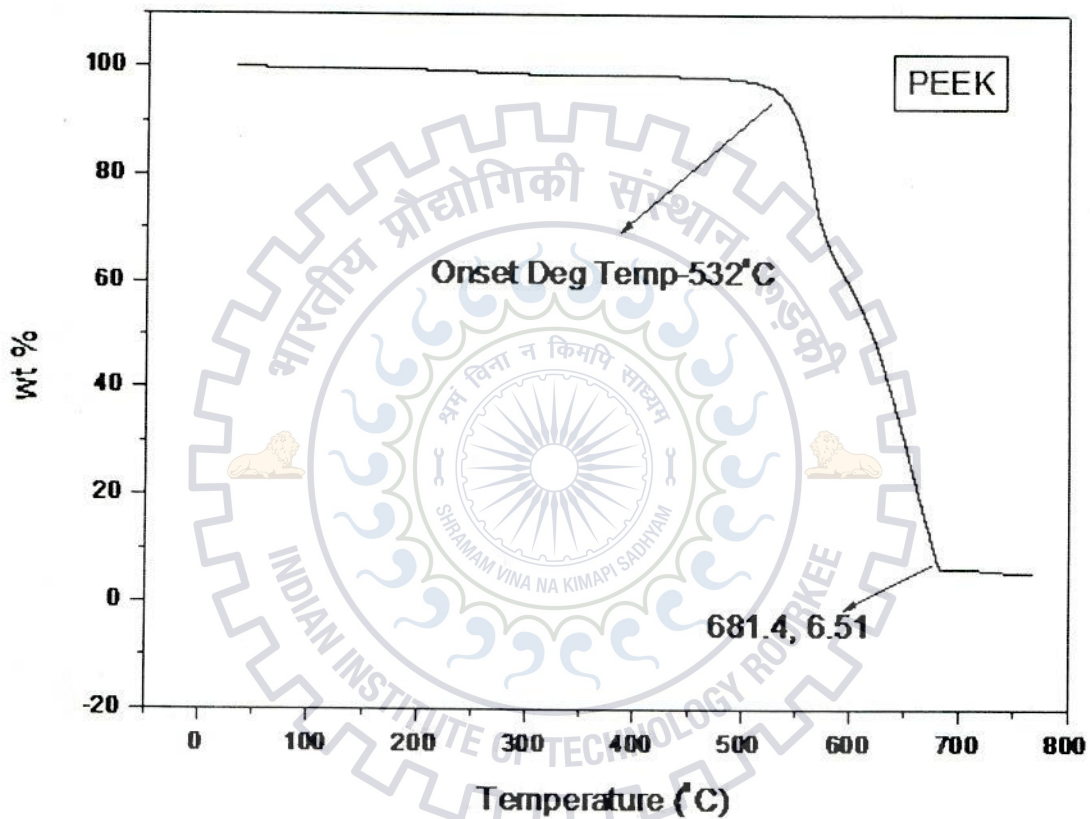

Fig. 8.1: TGA curve for PEEK

The Onset degradation temperature is 532°C and the residual weight percentage is about 6.51%.

8.1 Thermal Stability and Degradation of 5/95 PPTA/PEEK

The TGA curve for 5/95 PPTA/PEEK is given below:

Fig: 8.2: TGA curve of 5/95 PPTA/PEEK

The above TGA curve for 5/95 PPTA/PEEK shows the onset degradation temperature to be 561°C. The residual weight percentage is 10.97%.

The enhancement of onset degradation temperature and the increase in the residual weight percentage upon addition of rigid rod polymer PPTA indicates enhancement in thermal properties of the composite.

8.2   Thermal Stability and Degradation of 10/90 PPTA/PEEK

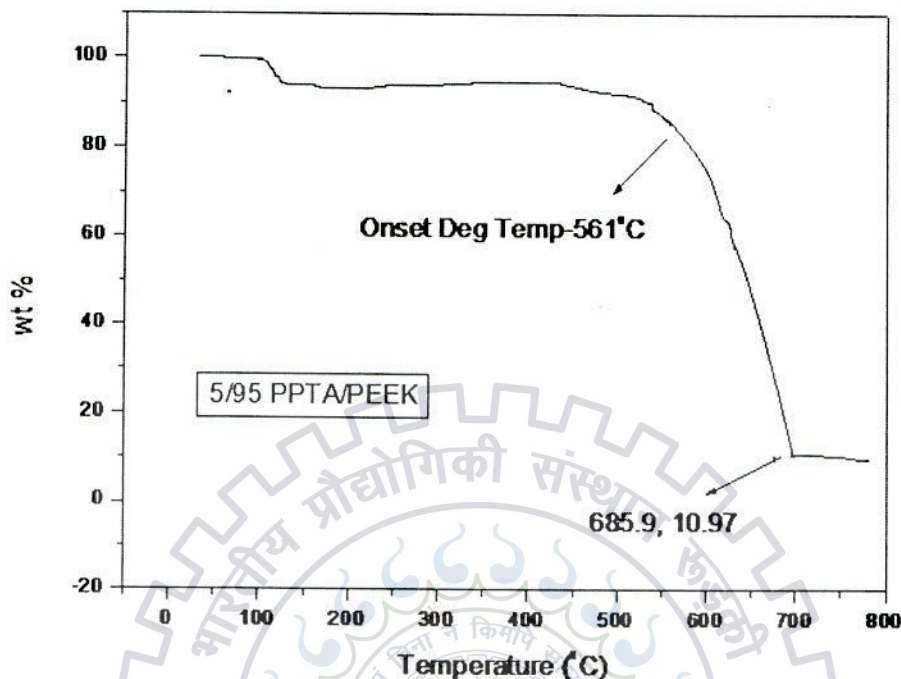The TGA curve for 10/90 PPTA/PEEK is given below:
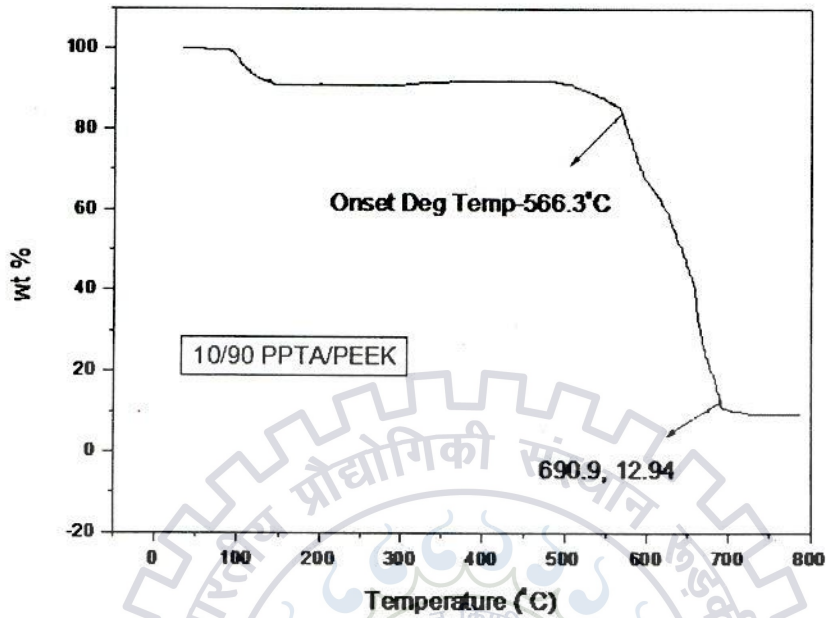
Fig. 8.3: TGA curve of 10/90 PPTA/PEEK

The above TGA curve for 10/90 PPTA/PEEK shows the onset degradation temperature to be 566.3°C. The residual weight percentage is 12.94%.

The enhancement of onset degradation temperature and the increase in the residual weight percentage upon addition of rigid rod polymer PPTA indicates enhancement in thermal properties of the molecular composite.

8.3 Thermal Stability and Degradation of 10/90 PPTA/PEEK

The TGA curve for 10/90 PPTA/PEEK is given below:
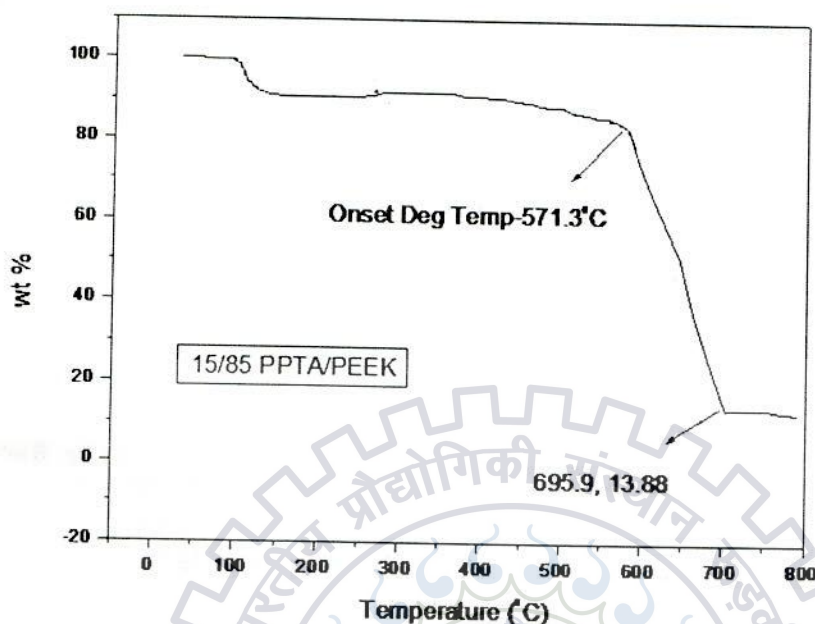
Fig. 8.4: TGA curve of 15/85 PPTA/PEEK

The above TGA curve for 15/85 PPTA/PEEK shows the onset degradation temperature to be 571.3°C. The residual weight percentage is 13.88%.

The enhancement of onset degradation temperature and the increase in the residual weight percentage upon addition of rigid rod polymer PPTA indicates enhancement in thermal properties of the composite.

8.4 Thermal Stability and Degradation of PPTA/PA-6,6 Molecular Composites

Table 8.4: Thermal degradation of PEEK and PPTA/PEEK molecular composites

Material	Onset Degradation Temperature	Residual Weight (%)
PEEK	532 °C	6.51
5/95 PPTA/PEEK	561 °C	10.97
10/90 PPTA/PEEK	566.3 °C	12.94
15/85 PPTA/PEEK	571.3 °C	13.98

It is evident from the above table that upon reinforcing PEEK with the rigid rod polymer PPTA the thermal stability is enhanced. The molecular composites of PPTA/PEEK show higher onset degradation temperature than that of PEEK. The residual weight percentage also increases.

CHAPTER 9

CONCLUSIONS

After carrying out the project work, the following conclusions were drawn:

- Molecular Composites can be processed by solution blending process.

- Molecular Composites of Poly-p-Phenylene-Terephthalamide/Poly-Ether-Ether-Ketone [PPTA/PEEK] are miscible at various compositions of the constituent polymers

- The Molecular Composites of Poly-p-Phenylene-Terephthalamide/Poly-Ether-Ether-Ketone [PPTA/PEEK] exhibit a single glass transition temperature higher than that of PEEK which the flexible polymer component of the Molecular Composite. This confirms miscibility and indicates that using Poly-p-Phenylene-Terephthalamide/Poly-Ether-Ether-Ketone (PPTA) as reinforcer helps improve the thermal properties of the Molecular Composite.

- The reasons for miscibility in the Molecular composites are:

  I. Similar solubility parameters of the constituent polymers because of the presence of similar structures.

  II. Intermolecular H-bonding between the constituent polymers. This is evident from the FTIR graph obtained.

- There is no phase separation in the Molecular Composites of Poly-p-Phenylene-Terephthalamide/Poly-Ether-Ether-Ketone [PPTA/PEEK]. This is evident from the FE-SEM images of the Molecular Composites.

- The molecular composites of PPTA/PEEK exhibit enhanced onset degradation temperature and residual weight percentage. This indicates improvement in thermal properties.

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