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FTIR and Thermal Studies on Polyethylene Terephthalate and Acrylonitrile Butadiene Styrene

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The present study deals with the characterization of the polymeric materials *viz.*, polyethylene terephthalate (PET) and acrylonitrile butadiene styrene (ABS) by employing FTIR and thermal measurements. The complete vibrational band assignment made available for PET and ABS using FTIR spectra confirms their chemical structure. FTIR spectroscopy provides detailed information on polymer structure through the characteristic vibrational energies of the various groups present in the molecule. The thermal behaviour of PET and ABS essential for proper processing and fabrication was studied through TGA and DTA thermograms. The thermal stability of the polymers was studied from TGA and the activation energy for the degradation of the polymeric materials was calculated using Murray-White plot and Coats-Redfern plot. The polymer with high activation energy is more thermally stable. Polyethylene terephthalate is found to be more thermally stable than ABS. The major thermal transitions such as crystalline melting temperature (T_m) and degradation temperature (T_d) of the polymers were detected from DTA curves. The melting behaviour of the polymer depends upon the specimen history and in particular upon the temperature of crystallization. The melting behaviour also depends upon the rate at which the specimen is heated. The various factors such as molar mass and degree of chain branching govern the value of T_m in different polymers.

Key Words: Polyethylene terephthalate, Acrylonitrile butadiene styrene, FTIR, Thermal stability, Activation energy, Molecular symmetry.

INTRODUCTION

Polymer characterization is an essential step in working with polymers. As a rule such efforts are directed towards a specific purpose. The structure and organization of the macromolecules ultimately determine the mechanical, physical and chemical properties of polymers[1,2]. Thus the precise characterization of molecular order is a primary prerequisite to understanding the macroscopic properties of polymeric materials[3,4]. The polymeric materials such as polyethylene terephthalate (PET) and acrylonitrile butadiene styrene (ABS) are studied here by FTIR and thermal studies. Polyethylene terephthalate is one of the important thermoplastic polyester. This resin is used extensively in three major product types-fibers, films and molding

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resins. The polyester gives wrinkle resistance, permanent pleat capability and staining resistance to the fabric[5]. Hollow PET fibers are used as insulative material in sleeping bags and winter coats. Polyethylene terephthalate films are used in a high proportion because of their ruggedness and clarity. The use of PET for soft-drink bottles requires that the resin be tough and inexpensive and have a low permeability to carbon dioxide. Polyethylene terephthalate is a reasonable compromise and has performed well in this application.

The combination of three monomers in acrylonitrile butadiene styrene (ABS) gives a family of materials that are strong, stiff and abrasion resistant with notable impact-resistance properties and ease of processing[6]. Many applications include pipes, refrigerator liners, car-instrument surrounds, radiator grills, telephones, boat shells and radio and television parts. Acrylonitrile butadiene styrene is an ideal material wherever superlative surface quality, colourfastness and luster are required. Acrylonitrile butadiene styrene is readily modified both by the addition of additives and by variation of the ratio of the three monomers-acrylonitrile, butadiene and styrene: hence grades available include medium, high and very high impact. Acrylonitrile butadiene styrene is readily blended or alloyed with other polymers further increasing the range of properties available.

EXPERIMENTAL

The pure samples of PET and ABS were obtained from Central Institute of Plastic Engineering and Technology (CIPET), Chennai, India. The FTIR spectra have been recorded in the range 4000-400 cm^{-1} using Bruker IFS 66V spectrophotometer at Indian Institute of Technology (I.I.T), SAIF, Chennai, India. The standard sample preparation technique involves making KBr discs, with finely ground polymer samples dispersed in the discs at concentrations of less than 1 %. They are prepared by compressing in a pellet-making press. The KBr discs with the polymer sample were placed in the IR cell and the spectrum was recorded. Whether to identify the chemical nature of the polymer or to determine its composition, IR is a useful highly specific tool[7]. For quantitative analysis of microstructure, stereoregularity, branching or crosslinking, in many cases, IR analysis is the simplest and most sensitive method.

Thermoanalytical techniques are used for characterization of glass transition and melting temperatures, thermal stability and other properties as a function of temperature of polymers and fibres[8]. Thermogravimetric analysis was carried out in a high-resolution thermobalance (NETZSCH STA 409 C/CD instrument) at Indian Institute of Technology, Chennai, India. Thermogravimetric analysis is a technique whereby the weight of a substance in an environment is recorded when the sample is heated or cooled at a controlled rate and change of weight is measured as a function of temperature or time. Approximately 5-6 mg of sample was heated from room temperature to 1400 ºC at a heating rate of 20 ºC/min with a continuous nitrogen gas flow. The sample weight and its rate of weight loss were continuously measured as a function of temperature. The thermal stability of the selected polymeric materials was studied from TGA curves.

Differential thermal analysis (DTA) involves heating or cooling a test sample and an inert reference under identical conditions, while recording any temperature difference between the sample and reference. This differential temperature is then plotted against time or against temperature. Differential thermal analysis curves are recorded simultaneously with TGA curves. In the DTA trace, the baseline remains unchanged so long as there is no thermal transition in the sample. First-order transitions, namely crystallization (T_c) and melting (T_m), appear as peaks in the exothermic and endothermic directions, respectively. After melting the material may undergo decomposition reactions at higher temperatures (T_d) which give broad peaks. These may be generally exothermic, but are sometimes more complex in shape[9]. The major transition temperatures T_m and T_d were detected from the DTA thermograms of PET and ABS.

RESULTS AND DISCUSSION

IR spectroscopy has been usefully applied for identification of the basic structural units present in the chemical configuration of PET and ABS. The complete vibrational band assignment is made available for the selected polymeric materials, thereby confirming their molecular structure[10,11]. The vibrational frequencies of all the fundamental bands along with their relative intensities and probable assignments are given in Tables 1 and 2. The primary motivation for determining the molecular structure of a polymer using FTIR spectroscopy is to relate the structures to the performance properties of the polymer in end use. If the polymer chains are completely characterized and the structural basis of its properties are known, the polymerization reaction can be optimized and controlled to produce the optimum properties from the particular chemical system.

TABLE-1
FTIR SPECTRA (cm^{-1}) AND ASSIGNMENT OF PET

Frequency (cm^{-1})		Assignment
FTIR	Intensity	
3065	ms	C-H asymmetric stretching/C-H aromatic stretching
2976	m	C-H symmetric stretching
2926	m	CH_2 asymmetric stretching
2815	mw	CH_2 symmetric stretching
1730	vs	C-C ring stretching/C=O stretching
1474	vs	CH_2 scissoring
1344	s	CH_2 wagging
1235	s	CCH asymmetric bending/C-O-C asymmetric stretching
1161	s	C-O-C symmetric stretching/CH_2 twisting/CCH symmetric bending
1120	s	C-O stretching
1062	vs	C-C stretching
810	m	OCH asymmetric bending
770	m	OCH symmetric bending
677	m	CH_2 rocking
518	mw	C-C bending/CCO asymmetric bending
475	vw	C-O-C deformation/CCO symmetric bending

TABLE-2
FTIR SPECTRA (cm^{-1}) AND ASSIGNMENT OF ABS

Frequency (cm^{-1})		Assignment
FTIR	Intensity	
3065	vs	C-H asymmetric stretching/C-H aromatic stretching
3002	vs	C-H symmetric stretching
2919	vs	CH$_2$ asymmetric stretching
2860	vs	CH$_2$ symmetric stretching
2238	s	C $\equiv$ N stretching
1635	s	C=C stretching
1603	s	C-C ring stretching
1490	vs	CH$_2$ asymmetric deformation
1454	vs	CH$_2$ scissoring
1352	vs	CH$_2$ wagging
1261	s	CCH asymmetric bending
1156	s	CCH symmetric bending/CH$_2$ twisting
1070	vs	C-C stretching
708	vs	CH$_2$ rocking
552	vs	C-C bending

One of the important properties of polymeric materials is its thermal behaviour. Thermogravimetric analysis is a thermo-analytical method used to study the thermal properties of elastomers. In this procedure, the weight of a sample is continuously monitored as the sample temperature increases. When a sample decomposes or degrades, normally the decomposition components volatilize off, resulting in a change in weight. The continuous weight loss curves for the thermal degradation of PET and ABS are presented in Figs. 1 and 2. The thermal stability of the chosen rubber samples was studied from TGA. These thermograms suggest that the samples are thermally stable upto 389 °C. Thermal stability refers to the ability to maintain required mechanical properties such as strength, toughness and elasticity at a given temperature. It is also used to determine the kinetic parameters of degradation of rubber materials. The thermal stability of the selected rubber materials at different temperatures are presented in Table-3.

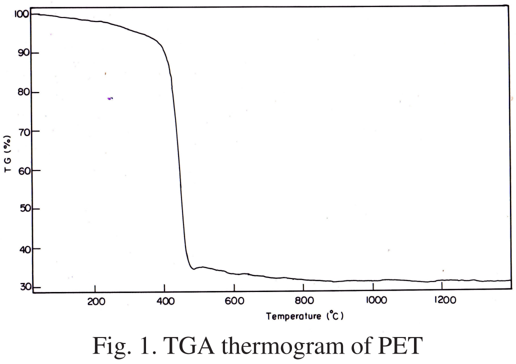


Fig. 1. TGA thermogram of PET

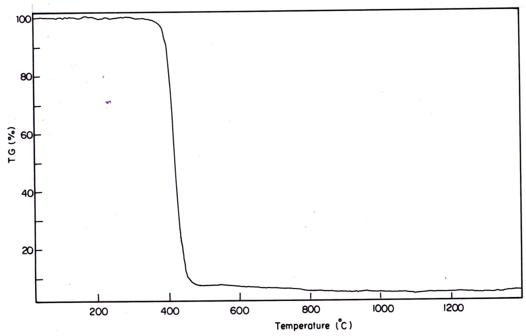


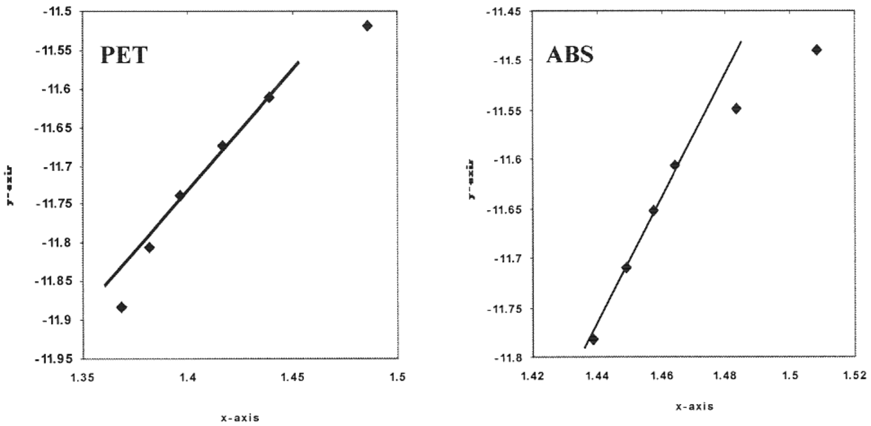
Fig. 2. TGA thermogram of ABS

TABLE-3
THERMAL STABILITY OF POLYMERIC MATERIALS

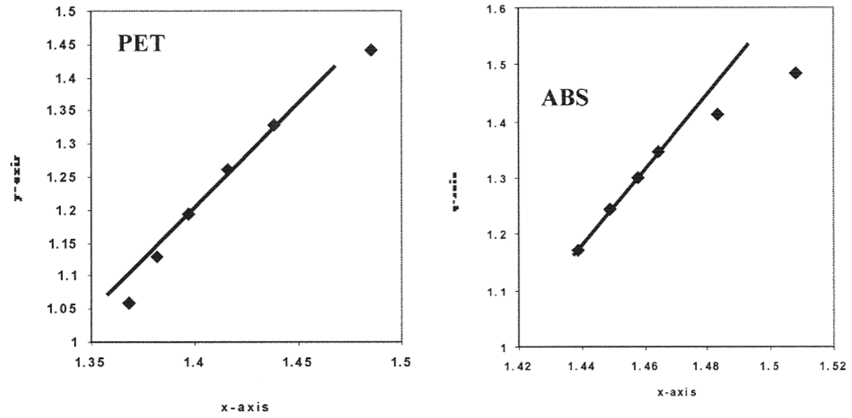
Sample	Temperature (°C) corresponding to weight loss								
	10%	20%	30%	40%	50%	60%	70%	80%	90%
PET	400	422	433	443	451	458	–	–	–
ABS	390	401	410	413	417	422	429	436	455

The thermal degradation of PET is a single stage process[12]. Around 60 % of the sample gets degraded in this stage between 340 °C and 516 °C. Table-3 shows that PET is thermally stable as 10 % of the sample gets decomposed at 400 °C and 60 % degradation of the sample requires 458 °C. The TGA curve of ABS shows that the degradation process is single stage[13,14]. About 92 % of the polymeric material was degraded in this stage between 348 to 482 °C. Acrylonitrile butadiene styrene has undergone 50 % degradation at 417 °C and 90 % degradation at 455 °C. On comparing the TGA curves of PET and ABS, it is seen that ABS decomposes at a relatively lower temperature than PET. This means that PET is more thermally stable than ABS. Moreover 30 % of PET remains as a residue material *i.e.*, remains undegraded at 1400 °C whereas only 5 % of ABS remains undegraded at this temperature. This further implies that PET is more thermally stable polymer than compared with ABS.

Activation energies of degradation of polymeric materials: Activation energy is the minimum amount of energy that is required to activate atoms or molecules to a condition in which they can undergo chemical transformation or physical transport. Activation energy calculations for the degradation of PET and ABS were made from TGA curves using Murray-White plot[15] and Coats-Redfern plot[16]. A linear correlation was obtained by plotting the logarithm of heating rate against the reciprocal of the absolute temperature. In Murray-White method, a linear correlation was obtained by plotting $T^{-1} \times 10^{-3}$ (K^{-1}) against [ln (ln (1-C)-2 ln T]. In Coats-Redfern method, a linear correlation was obtained by plotting $T^{-1} \times 10^{-3}$ (K^{-1}) *vs.* log [ln (1-C)]/T^2. The method of calculating activation energy[17,18] for the degradation of PET and ABS are given in Tables 4 and 5. The Arrhenius plot for degradation of PET and ABS using Murray-White plot and Coats-Redfern plot is presented in Fig. 3. Activation energy calculated from TGA curve using the two methods is presented in Table-6.



Murray and White method: $T^{-1} \times 10^{-3}$ (K^{-1}) *vs.* ln [ln (1-C)] -2 ln T



Coats and Redfern method: $T^{-1} \times 10^{-3}$ (K^{-1}) *vs.* log [ln (1-C)] / T^2

Fig. 3. Arrhenius plot of degradation of polymer materials

TABLE-4
CALCULATION OF ACTIVATION ENERGY FOR THE DEGRADATION OF PET

Degradation (%)	T (K)	$T^{-1} \times 10^{-3}$ (K^{-1})	1-C	2 ln T	T^2	ln [ln (1-C)]- 2 ln T	log [ln(1-C)] / T^2
10	673	1.4858	90	13.0234	452929	-11.5194	1.441×10^{-6}
20	695	1.4388	80	13.0878	483025	-11.6103	1.328×10^{-6}
30	706	1.4164	70	13.1192	498436	-11.6727	1.260×10^{-6}
40	716	1.3966	60	13.1473	512656	-11.7378	1.193×10^{-6}
50	724	1.3812	50	13.1695	524176	-11.8055	1.129×10^{-6}
60	731	1.3679	40	13.1888	534361	-11.8835	1.060×10^{-6}

TABLE 5
CALCULATION OF ACTIVATION ENERGY FOR THE DEGRADATION OF ABS

Degradation (%)	T (K)	$T^{-1} \times 10^{-3}$ (K^{-1})	1-C	2 ln T	T^2	ln [ln (1-C)]- 2 ln T	log [ln(1-C)] / T^2
10	663	1.5082	90	12.9935	439569	-11.4895	1.485×10^{-6}
20	674	1.4836	80	13.0264	454276	-11.5489	1.412×10^{-6}
30	683	1.4641	70	13.0529	466489	-11.6064	1.346×10^{-6}
40	686	1.4577	60	13.0617	470596	-11.6522	1.300×10^{-6}
50	690	1.4492	50	13.0733	476100	-11.7093	1.244×10^{-6}
60	695	1.4388	40	13.0878	483025	-11.7825	1.173×10^{-6}

TABLE-6
ACTIVATION ENERGY FOR THE DEGRADATION OF POLYMER MATERIALS

Sample	Activation energy E_a in KJ/mol	
	Murray-White Method	Coats-Redfern Method
PET	0.4046	0.4716
ABS	0.0768	0.0911

From Table-6, it is observed that PET has high decomposition activation energy than ABS. Acrylonitrile butadiene styrene is found to have low activation energy of degradation[13]. Hence PET is thermally stable polymer than ABS which is confirmed in the TGA curves. Thus, PET with high activation energy is more thermally stable and the extent of polymerization, the chain length and hence the molecular weight will be more for ABS that is less stable[19,20].

Differential thermal curves for PET and ABS are shown in Figs. 4 and 5. The major transition temperatures such as crystalline melting temperature (T_m) and degradation temperature (T_d) were identified from DTA curves of polymers. There are several characteristics of the melting behaviour of polymers which distinguishes them from other materials. It is not possible to define a single melting temperature for a polymer sample as the melting generally takes place over a range of temperature. The melting behaviour depends upon the specimen history and in particular upon the temperature of crystallization and the rate at which the specimen is heated[21]. There is found to be a strong dependence of the observed melting temperature of a polymer crystal, T_m, upon the crystal thickness, l. A process which affects the melting behaviour of crystalline polymers and is of interest in its own right is annealing. It is found that when crystalline polymers are heated to temperatures just below the melting temperature, there is an increase in lamellar crystal thickness. The driving force is the reduction in free energy gained by lowering the surface area of a lamellar crystal when it becomes thicker and less wide. The lamellar thickening only happens at relatively high temperatures when there is sufficient thermal energy available to allow the necessary molecular motion to take place. A certain amount of annealing usually takes place when a crystalline polymer sample is heated and melted. The increase in lamellar thickness, l, causes an increase in T_m. This means that the measured melting temperature will depend upon the heating rate because annealing effects will be lower for more rapid rates of heating.

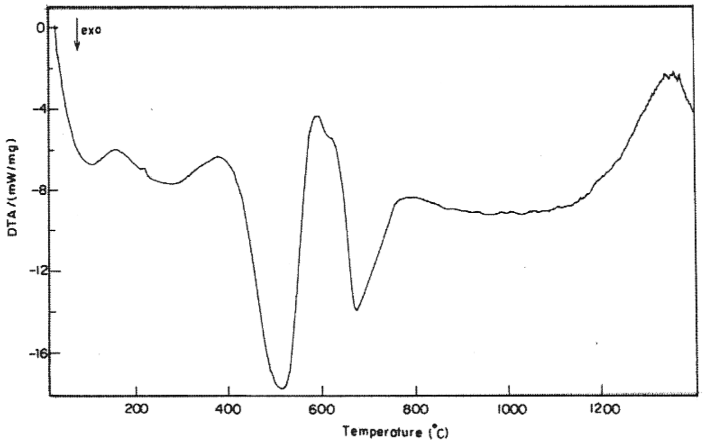


Fig. 4. DTA thermogram of PET

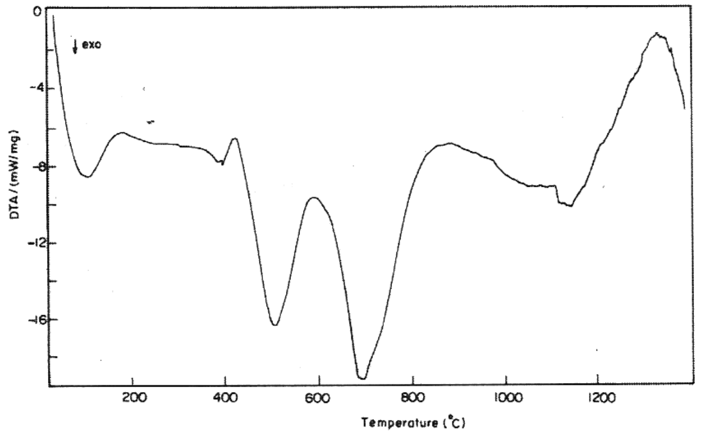


Fig. 5. DTA thermogram of ABS

The important thermal transitions such as T_m and T_d detected from DTA curves are presented in Table-7. The use of polymers in many practical applications is often limited by their relatively low melting temperatures. Because of this there has been considerable interest in determining the factors which control the value of T_m and in synthesizing polymers which have high melting temperatures[22]. For a particular type of polymer the value of T_m depends upon the molar mass and degree of chain branching. Chain ends and branches can be thought of as impurities which depress the melting points of polymer crystals. Carnelley[23] observed that high molecular symmetry is associated with high melting point. Symmetrical molecules in crystalline form have higher melting temperatures and exhibit lower solubility compared with molecules of similar structure but with lower symmetry. Symmetry in a molecule imparts a positive amount of residual entropy in the solid phase. This means that the entropy of a substance of symmetric molecules is greater than the entropy of substance of a similar, but non-symmetric molecule. Hence, it is concluded from Table-7 that PET with high melting point has high molecular symmetry, low solubility and high entropy. Acrylonitrile butadiene styrene does not exhibit crystalline melting temperature due to its amorphous nature. It is not possible for ABS to form crystallites due to the lack of compositional uniformity along polymer chains.

TABLE-7
THERMAL TRANSITION OF POLYMERS

Sample	Peak temperature (°C)	
	T_m	T_d
PET	158.7	340 477
ABS	–	381 448

Conclusion

The characterization studies on PET and ABS have been carried out using important experimental techniques. Their molecular structure was confirmed using FTIR spectroscopic technique. Once the molecular structure of a polymer is understood using FTIR spectroscopy, it becomes easy for a polymer scientist to relate the polymer structure to its performance properties in end use. The thermal stability of the polymeric materials was studied using TGA thermograms. The thermal study shows that PET is more thermally stable than ABS. The activation energy was calculated in KJ/mol for the degradation of polymers using Murray-White method and Coats-Redfern method. PET is found to have high activation energy calculated using both the methods. Since high decomposition activation energy is associated with high thermal stability, PET is considered to be more thermally stable than ABS. Finally, the major transition temperatures T_m and T_d were identified from DTA curves. The higher Tm value indicates the crystalline nature of the polymer. This means that PET is a crystalline polymer at room temperature. Acrylonitrile butadiene styrene, being amorphous does not exhibit T_m value. Thus it is concluded that the elastomers with high melting point have high molecular symmetry, low solubility and high entropy.

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