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CHARACTERIZATION OF MULTIPHASE POLYMER SYSTEM
Nylon 6/ABS blends

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Seven different ratios of blends from nylon 6 and acrylonitrile - butadiene - styrene (ABS) were prepared by melt blending. Thermal analysis of these blends was carried out by DSC and TG. It has been observed that blend ratios such as 50/50, 40/60, 25/75 and 15/85 of nylon 6/ABS were having more compatibility in comparison with other blends. It is evident from the study of glass transition temperature, melting point, heat of fusion, change of crystallinity and activation energy values. Thermogravimetric analysis shows a decreasing trend of pyrolysis temperature of these blends with the increase in ABS concentration. Melt flow index and density data are found to indicate better physical and flow characteristics in blends compared to pure nylon 6.

Polymer blends are being developed in order to improve some specific properties of the finished products. Various aspects relating to high product performance, rheology and economics of polymer blends have been discussed by many researchers [1-2]. Certain polymers like PPS, PEEK etc. which are processed at high temperature, can be processed at lower temperature by blending/alloying with other polymers having lower melt temperature [3]. In general, the potentiality of polymers can be improved by blending and excellent thermal, mechanical, electrical and chemical properties can be achieved [4-5]. To evaluate the optimum blend composition, it is required to study the thermal behaviour which helps in evaluating the properties and morphology [6-7] of polymeric blends such as melt temperature range [8], heat of fusion, crystallinity and rate of crystallization [9].

In this investigation, it has been attempted to evaluate the compatibility of blends of nylon 6 and acrylonitrile-butadiene-styrene (ABS) and optimize the blend composition by determining the glass transition temperature, melting point, heat of fusion, crystallinity and heat of crystallization using

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differential scanning calorimetry (DSC) and nature of degradation and activation energy by thermogravimetric analysis (TG).

Experimental

Nylon 6 (S13XX) and ABS (Polylac 100 Gp-1) from M/s.Shriram Fibres Limited, India and M/s. Polychem Limited, India respectively were used in the investigation.

The melt blending was carried out at 235° and 35 rpm in the mixer unit (50H) fitted to Brabender Plasticorder (Model PLV 330). Seven compositions of blends were prepared in the ratios of 85/15, 75/25, 60/40, 50/50, 40/60, 25/75, and 15/85 of nylon 6/ABS by weight.

The density of each composition was measured as per ASTM D792-1966. The melt flow index (MFI) of all blends was measured at 235° and 2.16 Kg. load as per ASTM D1238-1970 in order to determine the melt flow characteristics of the blends.

A DuPont thermal analyser (Model 1090) with differential scanning calorimeter (Model 910) and thermogravimetric analyser (Model 951) were used to study the thermal behaviour of the blends. For calorimetric analysis, the heating rate was maintained as 10° min^{-1} upto 250° under nitrogen blanket and crystallization curves were obtained by subsequently cooling samples at a rate of 10 deg min^{-1} to 60°.

From the above calorimetric analysis, the parameters such as glass transition temperature (*Tg*), the onset melting, melting peak temperature, the heat of fusion, onset crystallization, heat of crystallization and change of crystallinity were obtained. Thermogravimetric analysis was carried out in nitrogen atmosphere at a heating rate of 10 deg min^{-1} to evaluate the degradation behaviour. The energy of activation was calculated by Broido method [10].

Results and discussion

The density and melt flow index of all blends as well as Nylon 6 and ABS materials are mentioned in Table 1. It reveals that the density of nylon 6 and ABS are 1.143 and 1.045 g cc^{-1} respectively and on blending the density decreases from 1.131 to 1.055 g cc^{-1} while changing the blend ratio from 85/15 to 15/85 of nylon 6/ABS. Nylon 6 material is having the melt flow index 14.3 g/10 min which shows high flow characteristics and it decreases by blending with ABS which is having melt flow index of 5.0 kg/10 min. It has bee observed that the value of melt flow index decreases from 13.3 g/10 min to 7.0 g/10 min with the change in blend ratio from 85/15 to 15/85 of nylon 6/ABS.

Table 1 Density and melt flow index

Blend composition % Nylon 6/ABS	Density, (g cc^{-1})	MFI, (235°C and 2.16 kg load) g/10 min
100/0	1.143	14.3
85/15	1.131	13.3
75/25	1.110	12.4
60/40	1.106	10.7
50/50	1.102	9.88
40/60	1.094	8.4
25/75	1.065	7.6
15/85	1.055	7.0
0/100	1.045	5.0

A consistent change in density and melt flow index value with increase in concentration of ABS in the blends clearly shows the compatibility of nylon 6 over a wide range of proportions.

The data obtained from differential scanning calorimetry are shown in Table 2. It has been observed that endotherm for nylon 6 in the glass transi-

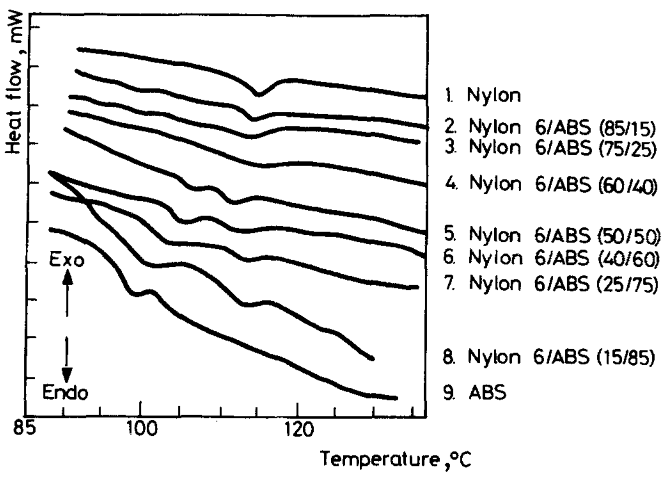

Fig. 1 DSC curve of nylon 6/ABS blends in *Tg* region

tion region is dominant when percentage of nylon 6 in blends is varying from 100 to 60 and the *Tg* endotherm of ABS is found to be suppressed due to its lower concentration (Fig. 1), whereas in other blends having ABS more than 50%,*Tg* endotherm of nylon 6 and ABS are observed and their shift towards each other clearly indicates higher miscibility and improved ductility with higher percentage of ABS. However, it has been observed that the *Tg* endotherm of ABS i.e. 94.4^0 and nylon 6, i.e. 113.5^0 have shifted maximum to 110^0 and 102.5^0 respectively in the case of 50/50 of nylon 6/ABS blend. This may be due to maximum polymer-polymer interaction in this composition. Moreover, the suppression of glass transition temperature of nylon 6 in blends indicates the improved toughness of the blend.

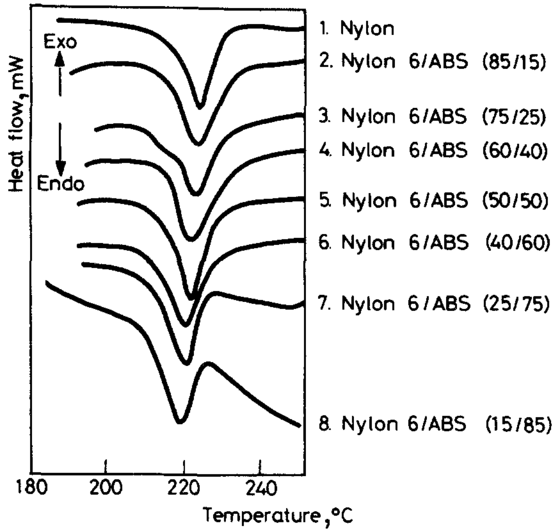

Fig. 2 DSC curve of melting temperature of nylon 6 in nylon 6/ABS blends

It has been observed that onset melting temperature and melt endotherm peak temperature decrease from 213.8^0 to 208.2^0 and 224.0^0 to 217.0^0 respectively by increasing the percentage of ABS in blends (Fig. 2, Table 2). This decrease in melting point may be due to better compatibility of polymer in blends. The shifting of melt endotherm peak of blend towards lower temperature is more in higher concentration of ABS which may be due to polymer-polymer interaction [11-12]. This compatible nature has also been observed from shifting of endotherm in the region of glass transition temperature.

Table 2 Thermal behaviour of Nylon 6/ABS blends

Sr.No.	Blend Composition Nylon 6/ABS, %	*Tg* of Nylon 6, °C	*Tg* of ABS, °C	Melting		Heat of Fusion ΔHf, Jg^{-1}	Decrease in crystallinity, %	Crystallization		Heat of Crystallization ΔHc Jg^{-1}
				Onset, °C	Peak, °C			Onset, °C	Peak, °C	
1	100/0	113.5	–	213.8	224.0	43.2	–	198.5	192.8	46.6
2	85/15	113.0	–	212.8	223.7	37.1	8.4	195.4	192.4	42.7
3	75/25	112.6	–	212.3	223.4	28.6	26.4	195.2	192.2	34.3
4	60/40	112.0	–	212.4	222.9	27.3	26.6	194.9	192.2	34.2
5	50/50	110.0	102.5	209.9	221.3	21.9	47.0	194.2	191.2	24.7
6	40/60	110.5	101.0	209.7	220.8	14.6	61.6	193.3	190.3	17.9
7	25/75	111.0	99.5	209.0	219.7	6.14	80.1	193.2	189.7	9.26
8	15/85	112.0	97.5	208.3	217.2	4.58	85.2	192.9	188.6	6.90
9	0/100	–	94.4	–	–	–	–	–	–	–

The shifting of onset melting temperature and melt temperature peak towards lower side along with decrease in melt flow index with the increase in concentration of ABS upto 85 percent shows that material can be easily processed at lower temperature with better melt stability.

The heat of fusion ($\Delta\ Hf$) was determined from area under fusion endotherm peak. The heat of fusion of blends decreases compared to that of pure nylon 6 indicating the decrease in crystallinity of blends. The drop in crystallinity of blends was calculated by using the following Eq. (8).

Percentage drop in crystallinity of nylon 6 in blends ($\Delta Xc.$)

$$\frac{\Delta Hf(\text{nylon } 6) - \Delta Hf(\text{in blends})}{\Delta Hf(\text{nylon } 6)} \text{x} \, 100$$

The data obtained from DSC cooling scan reveal that onset crystallization temperature, crystallization endotherm peak temperature and heat of crystallization decrease from 195.4^{0} to 192.9^{0}, 192.4^{0} to 188.6^{0} and 42.7 to 6.90 J g^{-1} respectively with increase in the percentage of ABS in blend. This

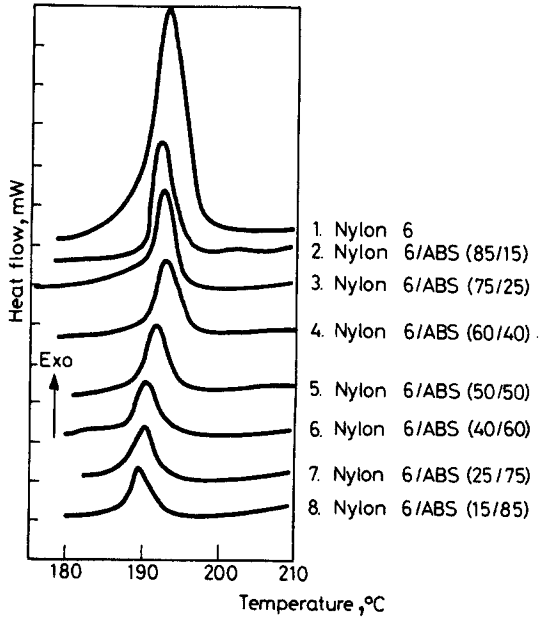

Fig. 3 DSC curve of crystallization of nylon 6 in nylon 6/ABS blends

indicates that homogeneous nucleation process of nylon 6 has been retarded during its crystallization in blends.

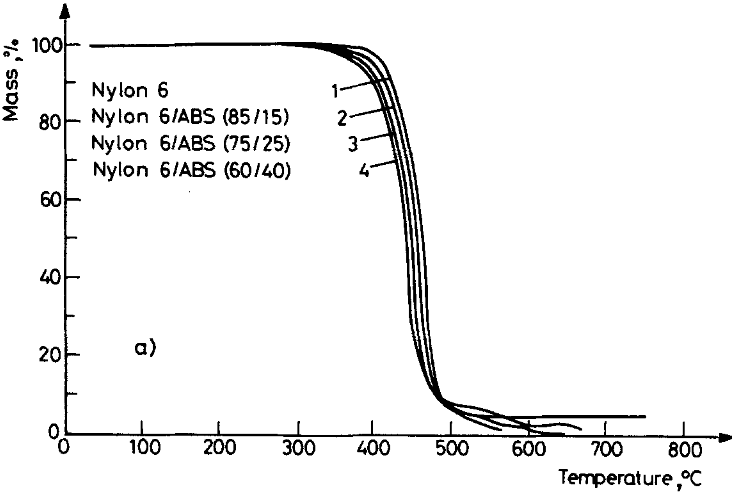

Fig. 4a Thermogravimetric curves of nylon 6, ABS and their blends

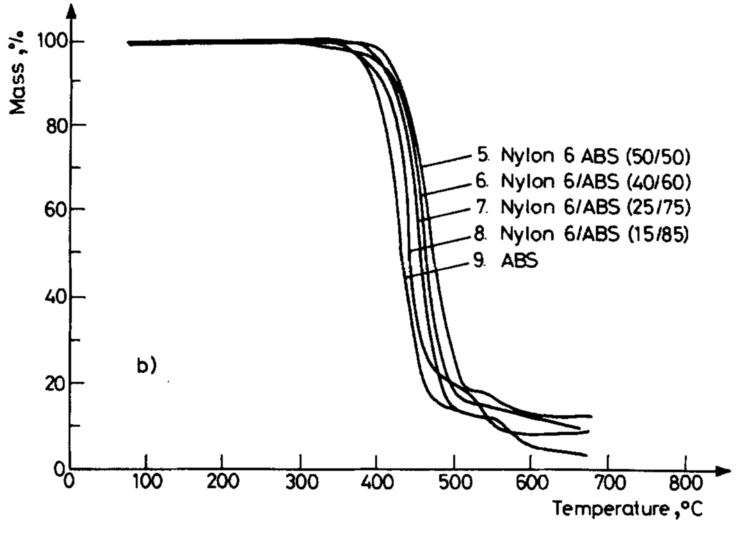

Fig. 4b Thermogravimetric curves of nylon 6, ABS and their blends

The study of thermogravimetric analysis (Fig. 4 and Table 3) reveals that initial decomposition temperature of nylon 6 is 375°, and it decreases in a uniform order upto 335° with the increase in concentration of ABS, supporting better interaction of the two polymers in the system.

Table 3 Thermogravimetric analysis

Blend Composition Nylon 6/ABS, %	Initial decomposition temp., °C	Activation energy (E) (kcal.mol^{-1})
100/0	375.0	12.51
85/15	365.0	11.60
75/25	350.0	10.5
60/40	345.0	9.53
50/50	342.0	5.04
40/60	340.0	5.17
25/75	338.0	5.38
15/85	335.0	5.49
0/100	300.0	8.14

Newkirk [13] and Smith [14] developed methods for kinetic analysis based on the assumption that the mechanism of thermal decomposition may be a first order reaction. The appropriate Arrhenious Plot was made and examined for linearity from the thermogravimetric data and approximate linearity over wide range of weight loss has been taken as evidence for first order kinetics. Hence, activation energy was calculated from the following equation applicable for first order reaction [10].

$$\log [\ln(1/y)] = -E^*/2.303RT + \text{Constant}$$

$Y = Wt / Wo$ and the ratio is termed as normalised weight, where Wt and Wo are the weights of material not decomposed at time 't' and initial weight of material respectively. The activation energy (E^*) has been computed from the slope of the plot of log [ln(1/y)] *vs.* 1/T, (Table 3). It has been found that four blend compositions of nylon 6/ABS (i.e. 50/50, 40/60, 25/75 and 15/85) are having lower activation energy when compared with other blends which indicates that these compositions are optimum in terms of interaction and miscibility of two components. This reinforces the observation of calorimetric data for compatibility, homogeneity and improved flow of blends in molten state.

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Zusammenfassung – Durch Mischschmelzen wurden Gemische aus Nylon 6 und Acrylnitril-Butadien-Styrol (ABS) mit sieben verschiedenen Zusammensetzungen hergestellt. Mittels DSC und TG wurde eine Thermoanalyse dieser Gemische durchgeführt. Es konnte festgestellt werden, daß Gemische mit Nylon 6/ABS Verhältnissen von 50/50, 40/60, 25/75 und 15/85 im Vergleich zu anderen Gemischen eine größere Kompatibilität besitzen, was aus der Betrachtung von Schmelzpunkt, Schmelzwärme und der Veränderung der Kristallinität und der Aktivierungsenergiewerte eindeutig hervorgeht. TG zeigt für die Pyrolysetemperatur dieser Gemische mit zunehmendem ABS-Gehalt eine sinkenden Tendenz an. Der festgestellte Schmelzindex und die gefundenen Dichtewerte weisen im Vergleich zu reinem Nylon 6 auf bessere physische und Fließeigenschaften hin.