Thermal behaviour and fibre studies of certain new aromatic - aliphatic polyamides

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ABSTRACT

Thirteen polyamides were synthesized by polycondensation using phosphorylation, low temperature solution and interfacial solution methods from 2, 2'-Dichloro-4, 4'-diaminoazobenzene condensed with different aliphatic diacids. These were characterised by inherent viscosity, solubility and spectral studies like UV-visible and IR. Moisture regain and dyeing properties have also been studied. TGA and DTA were reported. X-ray and mechanical properties of the fibres extruded were also studied.

Key words: Polyamides-synthesis-characterization-thermal and fibre properties.

INTRODUCTION

Among the various classes of thermally stable polymers, polyamides[1], polyimides[2], polyhydrazides[3], poly (1, 3, 4-oxadiazoles)[4], polybenzimidazoles[5], polyoxadiazoles[6] and poly quinoxalines[7] are of great importance. They are currently applied in many areas such as aerospace, microelectronic, automotive and gas separation industries as high temperature coatings, structural adhesives, matrix resins, films, interlayer dielectrics, wire insulation and semi-permeable membranes. Wholly aromatic polyamides are thermally stable but with poor solubility. Solubility and tractability are found to be greatly enhanced in aromatic-aliphatic polyamides which are important in polymer processing. The incorporation of halogen atom into the polymer backbone is known to improve flame resistance. Attempts have, therefore, been made to prepare such polyamides with high solubility and polymer melt temperatures.

EXPERIMENTAL

2,2'-Dichloro-4,4'-diaminoazobenzene was synthesised[8] from 2-chloro-4-nitroaniline (m.p. 320°C) adopting selective reduction using NaSH in EtOH.

Malonic acid was recrystallised from ether (m.p. 136-137°C). Succinic acid (m.p. 186-187°C), Azelaic acid (m.p. 107-108°C) and Sebacic acid (m.p.133-134°C) were recrystallised from aqueous ethanol. Glutaric acid was recrystallised from chloroform using a soxhlet extractor (m.p. 97-98°C). Chorosuccinic acid (Puriss, Fluka) was used after drying in a vacuum desicator, (m.p.150-151°C). N,N'-Pyromellitoyl diglycine diacid (Koch-light, GR) was dried over P_2O_5 at 100°C..

Polymerisation

Phosphorylation method, low-temperature solution method and interfacial polycondensation methods were followed[8].

Characterisation

Viscosity measurements were carried out in conc. sulphuric acid (98%) using Ubbelhode viscometer.

UV-visible spectra of the polymers in conc. H_2SO_4 were recorded with a CARL-ZEISS spectrophotometer employing a closed cell. FT-IR spectra of the polymers were recorded using KBr pellets with a Perkin-Elemer 257 spectrometer.
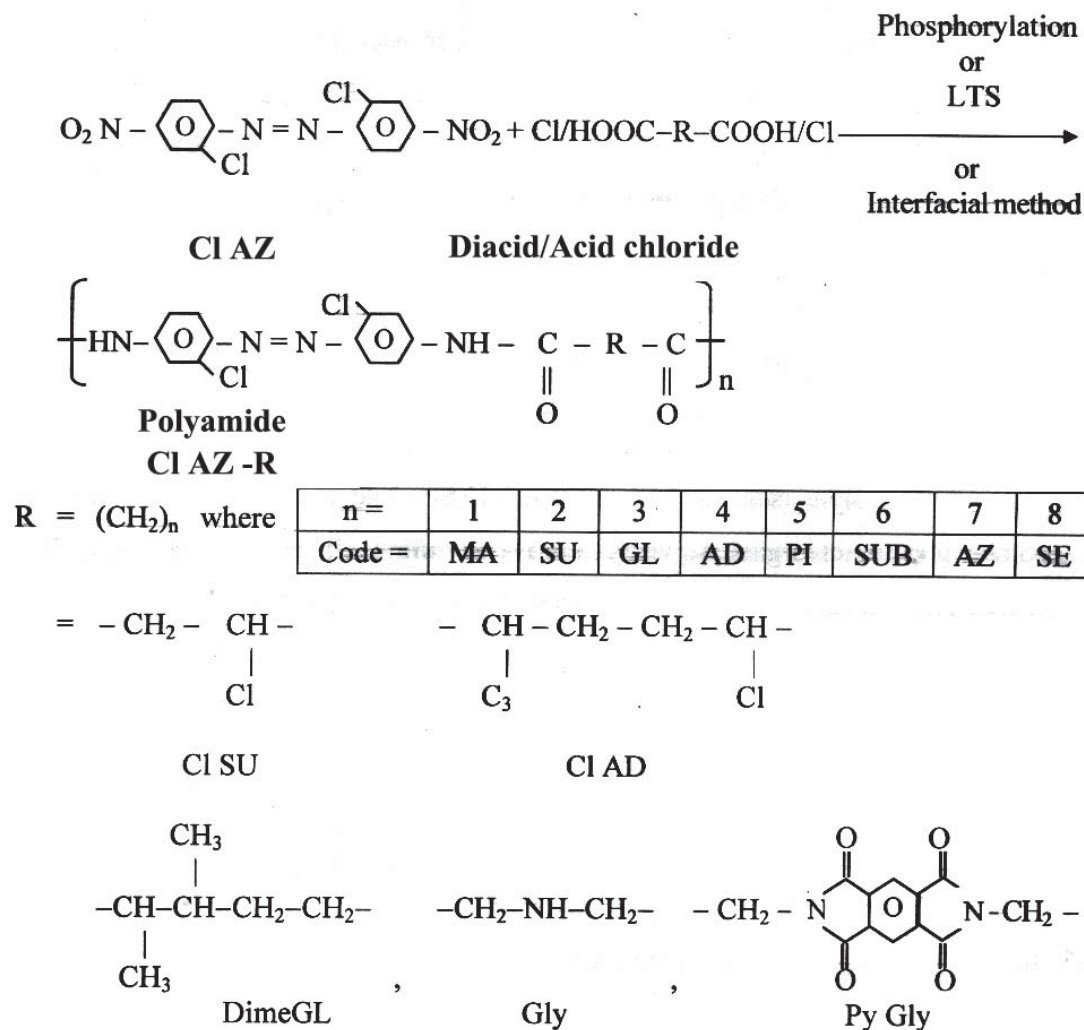
TGA and DTA studies were carried out for all the polymers in nitrogen atmosphere using Stanton-Redcraft simultaneous TG-DTA recorder.

Wide angle x-ray diffraction patterns were recorded. A nickel filtered CuK_a radiation (1.541°A) of powder 30KV and 10mA was employed.

Fibres were spun using a laboratory scale dry jet - wet spinning process[8]. The tensile properties were determined on an Instron 1112 model instrument.

RESULTS AND DISCUSSION

The scheme of the polymerisation reaction can be given as:

$$O_2N - \langle O \rangle - N = N - \langle O \rangle - NO_2 + Cl/HOOC-R-COOH/Cl \xrightarrow[\text{or}\ \text{Interfacial method}]{\text{Phosphorylation or LTS}}$$

Cl AZ   **Diacid/Acid chloride**

$$\left\{ HN - \langle O \rangle - N = N - \langle O \rangle - NH - \underset{O}{C} - R - \underset{O}{C} \right\}_n$$

Polyamide
Cl AZ -R

$R = (CH_2)_n$ where

n =	1	2	3	4	5	6	7	8
Code =	MA	SU	GL	AD	PI	SUB	AZ	SE

$= -CH_2 - \underset{Cl}{CH} -$ $-\underset{C_3}{CH} - CH_2 - CH_2 - \underset{Cl}{CH} -$

Cl SU   **Cl AD**

$-\underset{CH_3}{\overset{CH_3}{CH}} - CH - CH_2 - CH_2 -$, $-CH_2 - NH - CH_2 -$, $-CH_2 - N \langle O \rangle N - CH_2 -$

DimeGL   **Gly**   **Py Gly**

Phosphorylation

Studies were carried out to investigate the role played by pyridine and also to determine the optimum composition of the solvent. A mixture of CaCl$_2$ and LiCl in NMP/Py was also tried as solvent. An analysis of Table 1 shows that a smaller proportion of pyridine slightly decreases the viscosity. Since the azo polyamides are comparatively more rigid and less soluble in NMP / pyridine mixture, they are more easily precipitated and hence further growth is curtailed, resulting in a low molecular weight. Thus, the tolerance for pyridine is less for azopolyamides.

The inherent viscosity data are presented in Table 2 appear to depend on (i) the basicity of the diamine (ii) nature of the diacid (iii) initial insolubility of the growing polymer chain in the reaction medium and (iv) on the rigidity of the polyamide. Higher homologues series of substituted diacids give higher viscosities in the solution method than the phosphorylation method. This may be due to the initial insolubility of the diacids compared to the diamines in phosphorylation conditions. It is appropriate to compare the present work with methyl or methoxy substituted diamine based polymers synthesised in this laboratory. Table 3

shows that introduction of chlorine group enhances the viscosity and thermal stability when compared to unsubstituted one. However, the effect of CH$_3$ group is more than chlorine since – I effect of CH$_3$ group facilitates diamine to be more basic.

All the polymers are soluble in conc. H$_2$SO$_4$ and in trifluoroacetic acid, but insoluble in common organic solvents such as chloroform, ethanol and THF. In solvents like DMAc, DMF, DMSO and NMP, polyamides are partially soluble. In addition to this, polyamides derived from aliphatic diacids containing odd number of methylene units have significantly higher solubility than those derived from even - numbered straight chain diacids.

UV-visible spectral data are presented in Table 2. The bands in visible region (λ_{max} about 500 nm) are due to n $\rightarrow$ π* transitions in the - N = N - group whereas those in the UV region (λ_{max} about 263nm) are associated with π $\rightarrow$ π* transitions[8].

IR spectra of polyamides shows amide band at 3300 cm^{-1} characteristic of N-H stretching. Carbonyl stretching at 1630-1680 cm^{-1}, N-H in-plane deformation and C-N stretching at 1515-1570 cm^{-1}, in-plane combination of C-N stretching and

Table 1: Effect of solvent compqsition on the phosphorylation reaction

Polymer	Solvent composition in the reaction mixture	Yield	η_{inh}(dlg $^{-1}$)
CIAZ-MA	i. 25ml NMP + 18 ml LiCl	95	0.22
	ii. 23ml NMP + 2 ml Pyridine + Ig LiCl	92	0.24
	iii. 20 ml NMP + 5 ml Pyridine + Ig LiCl	60	0.10
CIAZ-SU	i. 25ml NMP + 18 ml LiCl	93	0.26
	ii. 23ml NMP + 2 ml Pyridine + Ig LiCl	90	0.26
	iii. 20 ml NMP + 5 ml Pyridine + Ig LiCl	84	0.18
CIAZ-GL	i. 25ml NMf + Ig LiCl	95	0.28
	ii. 23ml NMP+ 2 ml Pyridine + Ig LiCl	94	0.38
	iii. 20 ml NMP + 5 ml Pyridine + Ig LiCl	90	0.22
	iv. 65 ml NMP + 10ml Pyridine + 3g CaCh + 19 LiC1	92	0.18
CIAZ-AD	25ml NMP + 19 LiCl	98	0.44
	23ml NMP + 2 ml Pyridine + 19 LiCl	98	0.48
	20 ml NMP + 5 ml Pyridine + 19 LiCl	97	0.48
	65 ml NMP + 10 ml Pyridine + 3g CaCh + 19 LiCl	95	0.45
CIAZ-AZ	25ml NMP + Ig LiCl	98	0.35
	23ml NMP + 2 ml Pyridine + 19 LiCl	98	0.45
	20 ml NMP + 5 ml Pyridine + 19 LiCl	98	0.09

N-H deformation at 1200-1310 cm^{-1}, N-H out-of-plane deformation at 620-770 cm^{-1} are some of the important assignments made.

Thermal Studies

TG curves (Table 4) show three stages of weight loss. In the first stage (Fig.1), a weight loss of 1-5 percent occurs which is accompanied by a small endotherm in the temperature range 100-145°C in the DTA curves. This can be attributed to the removal of water or entrapped solvents. There is also a sharp endotherm in the temperature range 145-290°C which may be due to change in structural pattern of the polymers. The second stage corresponds to a steep fall in the TG curves. The weight loss in this portion is about 20 percent evidenced by the derivative curves. In the third stage, the TG curve is steady. The DTA portion corresponding to this shows a number of broad exothermic peaks. These exotherms may arise due to decomposition reactions like bond scissons, cyclisations and cross-linking reactions which are quite complex[10].

Chloro substituted polymers are found to be thermally more stable than the corresponding unsubstituted polymers AZ-R or methyl substituted polymer CH$_3$ AZ-R (Table 3). The introduction of chlorine group on the polymer backbone increases the chain stiffness and enhance the interchain

Table 2: Properties of Polymides

S. No.	Polymer	Polymerization method	% yield	çinh (d1g^{-1})	Colour	UV – Visible λ$_{max}$ in nm		Moisture regain (g kg^{-1})
1	CIAZ-MA	P	92	0.24	Dark brown	263.0	508.2	4.00
2	CIAZ-SU	P	94	0.26	Brown	264.2	501.0	3.55
3	CIAZ-GL	P	98	0.38	Reddish Brown	259.5	496.5	2.58
4	CIAZ-AD	I	I 90	0.30	Brown	255	483	2.30
		P	96	0.48				
		LTS	40	0.15				
5	CIAZ-PI	P98	98	0.49	Yellow	251	488	1.42
6	CIAZ-SUB	P	98	0.62	Light yellow	249.5	470	3.90
7	CIAZ-AZ	P	95	0.45	Dark yellow	249	473	3.95
8	CIAZ- SE	I	85	0.16	Light yellow	249.5	470	3.98
		P	97	0.20				
		LTS	30	0.50				
9	CIAZ-CISU	P	98	0.42	Light Brown	248	501	2.55
10	CIAZ-CIAD	P	98	0.54	Brown	242	394	2.60
11	C1AZ-DimeGL	P, LTS	92	0.62	Dark Brown	253	473	3.90
12	CIAZ-Gly	P, LTS	96	0.60	Brown	242	460	3.95
13	CIAZ-PyGly	P, LTS	90	0.80	Dark Brown	230	458.6	2.80

*Inherentviscosities measured at concentration of 0.5 g d1^{-1} in concentrated sulphuric acid at 25°C.

P -Phosphorylation method   I - Interfacial method.

LTS -Low temperature solution, method   # Measured at RH 65%

hydrogen bonding. Among the three substituents (CH_3, Cl and OCH_3), on the basis of 20% decomposition and T_{max} values, the following order can be given.

AZ - R < OCH_3 AZ - R < CH_3 AZ - R < Cl AZ - R

comparison can also be made with TG and DTA curves of polyglutaramides and polyadipamides which were derived in this laboratory from 4,4' - Diamino azo benzene condensed with glutaric acid / adipic acid[14]. From considerations of crystallinity (evidenced from x-ray studies) and viscosity, the

Table 3: Comparison of ciaz – R with CH_3 AZ – R, OCH_3 AZ- R, OCH_3 AZ-R and AZ_R [206]

S No.	Polyamide code	Viscosity (d1 g -1) ηinh	UV – Visible λ_{max}		TGA 20% (°C) decomp-osition	T_{max} (°C)	DTA Exotherm (°C)
1	CIAZ-MA	0.24	263	508.2	420	295	298
	CH3AZ- MA	0.32	255.5	495	400	270	270
	AZ-MA	0.22	253	487	311	292	295
2	CIAZ-SU	0.26	264.2	501.0	400	270	290
	CH3AZ- SU	0.34	255.5	488.0	380	255	210,255
	AZ - SU	0.23	253.5	473.5	304	309	325
3	CIAZ - GL	0.38	259.5	496.5	360	295	305
	CH3AZ-GL	0.44	252.0	484	340	370	370,410
	AZ-GL	0.34	238.4	432.9	345	370	-
4	CIAZ-AD	0.78	255	483	380	390	390
	OCH3AZ-AD	0.80	245.5	470	365	360	360,455
	CH3AZ- AD	0.53	245.5	470	305	390	370,450
	AZ-AD	0.26	247	457	361	340	355
5	CIAZ-PI	0.49	251	488	-	-	-
	CH3AZ- PI	0.62	242	474	360	340	335,355
	AZ - PI	-	-	-	-	-	-
6	CIAZ-SUB	0.62	258.8	490	-	-	-
	CH_3AZ- SUB	0.36	250.8	476	360	330	330,340
	AZ- SUB	0.36	250.8	476	302	305	230,265
		0.64	242	455	-	-	-
7	CIAZ- AZ	0.45	249	473	375	360	365
	CH_3AZ- AZ	0.60	241	460	260	255	210,250
	AZ - AZ	0.19	246	356	369	289	-
8	CIAZ - SE	0.20	249.5	470	-	-	-
	CH_3AZ- SE	0.63	241	457	350	320	320,330
	AZ- SE	0.22	246	453	369	336	-
9	CIAZ- CISU	0.22	248	501	-	-	-
	OCH_3AZ- CISU	0.80	240	488	390	265	215, 330
	AZ- CISU	0.21	237	474	265	260	27-
10	CIAZ - CIAD	0.36	242	394	380	290	305
	OCH_3AZ - CIADAZ- CIAD	0.80-	234-	381-	380-	370-	375,360-
11	CIAZ-DimeGL	-	253	473	375	410	415
	CH_3AZ- DimeGL	0.68	245	460	370	340	360, 415
	AZ - DimeGL	-	249	480	-	-	

Table 4: Thermal properties of azopolyamidesinn in nitrogen

Polymer	ηinh (d1 g-1)	Temperature (°C) at which the following % weight loss occur						T max (°C)	No. of Phases	
		10	20	30	40	50	60			
CIAZ-MA	0.24	280	420	460	490	570	-	295	2	295
CIAZ- SU	0.26	275	400	445	470	540	-	270	3	230,270
CIAZ-GL	0.38	335	360	405	470	550	-	295	3	390,435
CIAZ-AD	0.48	340	380	440	485	560	-	390	3	380,460
CIAZ-AZ	0.45	335	375	435	490	540	-	360	2	365, 455
CIAZ-CIAD	0.24	260	380	410	480	505	-	360	2	305,505, 335
CIAZ-DimeGL	0.45	340	375	445	440	580	-	290	3	415,515
CIAZ- Gly	0.65	340	370	440	510	575	-	410	2	408-548
CIAZ-PyGly	0.80	340	370	455	505	585	680	405	6	415 - 538

Heating rate: 2°C / min

Table 5: Mechanical Properties of Polyamide Fibres

Blend composition% of clAZ - PyGly	Jet stretch Initial	Bath composition	Tem °C	Draw ratio	Devices	Mechanical Properties		
						Tenacity g/denier	% Elongation	Initial modulus g/denier
Effect of Stretch								
F_{60} *	24.00	80:20	25°		45.0	2.91	180	14.2
F_{50}	20.00	80:20	25°		70.0	3.45	171	16.0
F_{25}	12.00	80:20	25°		79.0	3.80	162	20.4
Effect of hot-drawing								
F_{50}	. .	Not used	30	0	70	3.45	171	16.0
F_{50}	. .	Not used	150	2.0	46	3.80	80	24.5
F_{50}	. .	Not used	250	2.5	38	4.15	56	38.8
Effect of Blend composition (Dope concentration)								
F_{60}	. .	80:20	25°	0	45	2.91	140	14.2
				2.5	42	3.54	61	18.6
F_{50}	. .	80:20	25°	0	70	3.45	171	16.0
				2.5	38	4.15	56	38.9
F_{25}	. .	80:20	25°	0	29	3.80	162	20.4
				2.5	32	4.15	74	36.0
Effect of composition of coagulation bath								
F_{60}	. .	80:20	25°	0	. .	2.91	140	14.2
				2.0		3.54	61	18.6
F_{60}	. .	70:30	25°	0	. .	2.75	154	13.9
				2.0		3.33	52	14.5
F_{60}	. .	60:40	25°	0	. .	2.62	162	12.6
				2.0		2.95	74	18.0

*F_{60} =   clAZ – PyGly : LDPE   60%   40%

thermal stability of polyglytaramides are lower than those of the corresponding polyadipamides. It is found that chlorine substituted polymers are having higher T_{max} values as well as 20% decomposition temperatures.

DTA curves do not show any melting or glass transitions. Glass transition either occurs in a wide temperature range or masked by the broad endotherms due to the escape of volatile impurities[11]. The difference in thermal stability of these polyamides seem to depend on the number of carbon atoms in the aliphatic moiety. Those with an even number of aliphatic carbon atoms (methylene units) are more stable than the next higher odd numbered homologues since the odd number of methylene units possess only longitudinal order. i.e. odd-even alternation[12,13] effect.

Moisture regain

The tensile properties of fibres are affected significantly by the water it absorbs. Elongation at break is also increased on water absorption. T h e moisture regain values obtained at RH 65% for the polyamides are presented in Table 2. The moisture regain decreases with increase in the number of methylene groups in the polymer backbone and hence a decrease in the incidence of - NHCO -

groupings which are responsible for hydrogen bonding with water. The chlorine substituted polymers have slightly greater moisture values than the unsubstituted azopolyamides since low molecular weight polymers facilitate the penetration of water molecules in addition to bonding.

Dyeing

In order to assess the dyeability of the polymers, two anionic dyes Viz. (i) CI Acid Red 88 (Naphthalene red JS) and (ii) CI Acid Red 18 (Naphthalene Scarlet 4R) having similar structural features were chosen. The dyeing was carried out for the light coloured polyamides viz. ClAZ - PI, ClAZ - SE and ClAz - ClSU and the dye absorption was found to be 8.0, 8.75 and 6.50g Kg^{-1} in former and 2.80, 2.25 and 1.55g Kg^{-1} in latter anionic dyes respectively. The dye absorption is more in the case of CI Acid Red 88 than CI Acid Red 18 since the stoichiometric relations and the particle size of the dye play important role. The zeta potential developed at the interface is a measure of this barrier. The zeta potential becomes considerably negative in the case of CI Acid Red 18, thereby decreasing the rate of migration of trinegative CI Acid Red 18 ions towards the polymer surface. In other words, the dye uptake decreases as the crystallinity increases since the dye molecules do not penetrate the
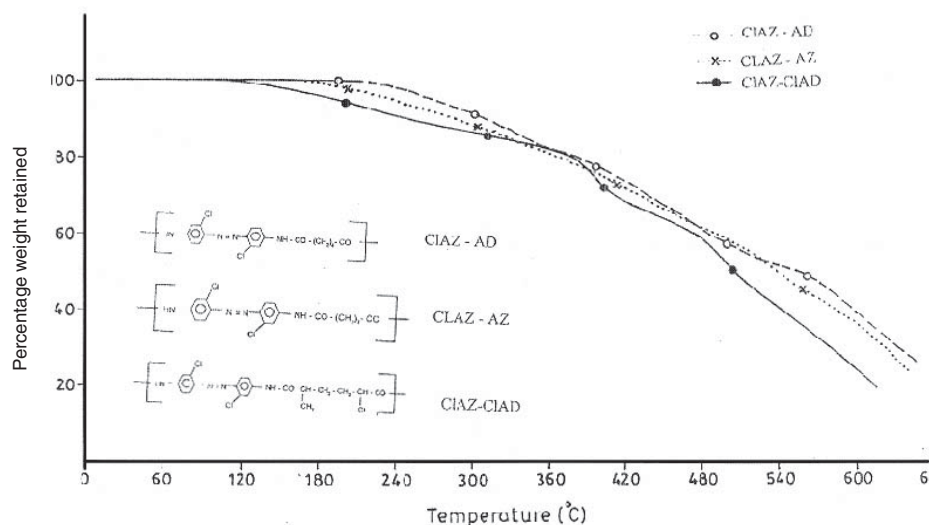

Fig. 1: TG curves of polymers in nitrogen measured at a heating rate of 2°C/mi

crystalline regions, but absorbs maximum when it is amorphous this is also evidenced by x - ray studies.

X-ray studies

Crystallinity is revealed by the sharp and high intensity peaks of the diffractograms. Comparison of the sharpness of the peaks and their intensity (Fig.2) leads to the following conclusions (i) ClAZ - PyGly has the highest crystalline order and (ii) Polyamides containing even number of carbon atoms in the aliphatic moiety is more crystalline than the corresponding odd number of carbon atoms[15].

Fibre Studies

During fibre spinning process (Table 5), it has been found that the following parameters influence the properties of fibres.

Jet stretch

The optimum stretch ratio is found to be 3. It is quite likely that fibres with higher stretch have a higher orientation of molecule along the fibre axis and such an orientation may facilitate some

interchain ring formation or strong forces which may result in orientation of fibres. Solvent penetration may also be difficult if the orientation of molecules along the fibre axis is more extensive and closely packed. This may cause on the surface only, causing greater shrinkage on the surface than in the bulk. This may lead to development of cracks and fibre embrittlement[16].

Reduction in stretch ratio results is a decrease in tenacity but an increase in denier and percent extension. At the same time, modulus is also decreasing which gives information that the fibre is weak and soft. This behaviour is quite expected because the oriented fibres will have better tensile properties.

Since glass transition either occurs in a wide temperature range or masked due to escape of impurities (typical of nematic mesophases), they are readily oriented in the extensional flow produced by passage through a spinnerette. The rate of relaxation to a disordered state is evidently slower than the rate of coagulation of the polymer dry jet - wet spinning process and so a fibre consisting of
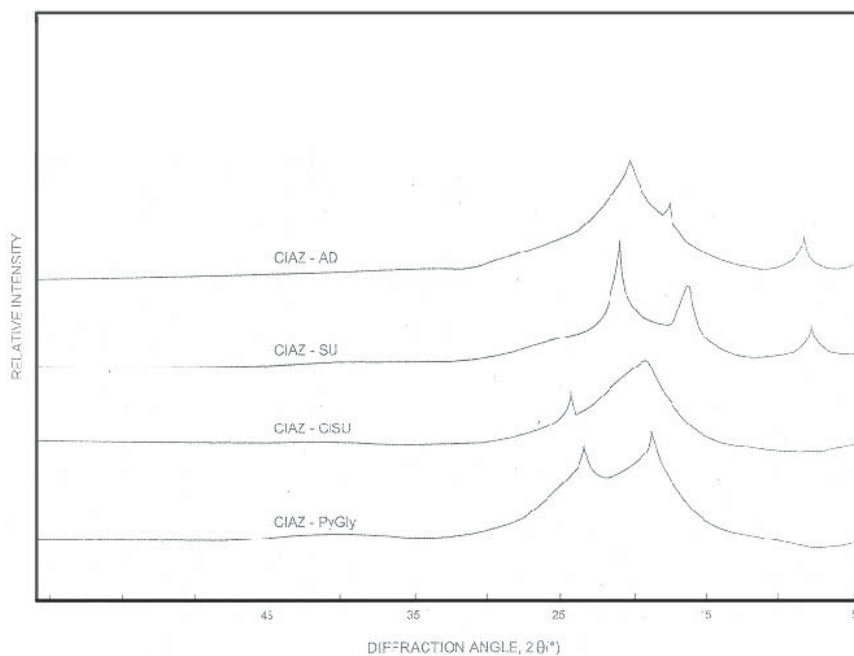
Fig. 2: X-ray diffractometer scan

highly oriented rigid chain is produced.

The fibres produced in this manner, once dry, are not capable of being drawn in the usual way. Only at the lower end of the 'as-spun' modulus range can a significant draw be applied because of the extreme thermal stability of the polyamides. However, these fibres were subjected to heat treatment upto 200°C for brief periods.

The tenacity and stiffness of these fibres (Table 5) are directly related to the degree of alignment of the molecular chains parallel to the fibre axis and hence to the degree of crystallinity as exhibited by x-ray diffractograms (Fig.2). Orientation is accomplished in amorphous polymer fibres by deforming them at a temperature above their glass transition temperature 230-232°C[17,18].

Effect of hot-drawing

The tenacity and initial modulus of all the fibres are improved at the expense of % elongation at break on hot drawing at 150°C and 200°C (Table 5). The fibre modulus is found to be increased by a factor of two or three. The increased tensile strength on hot drawing is due to the attainment of enhanced orientation through stretch at temperature sufficient to cause molecular mobility.

Effect of blend composition (Dope concentration)

Following the procedure of dry blending[9] F_{90}, F_{60}, F_{50} and F_{25} blends have been prepared by mixing 90%, 60%, 50% and 25% of polyamide (CIAZ - PyGly or CIAZ--SU) with 10%, 40%, 50% and 75% of LDPE (low density polyethylene) respectively. The blends were subjected to melt-spinning in a single holed spinnerette at a temperature of 250°C. The mechanical properties were evaluated and compared with LDPE. Fibres spun from anisotropic dopes exhibit higher moduli in the 'as-spun' state than those spun from isotopic dopes (light transmission of the solution as viewed through crossed polars).

Effect of Viscosity

It is found that polymer with high viscosity (CIAZ-PyGly) (0.80 dl g^{-1}) in the form of blend yields higher tenacity and initial modulus compared to other polyamides of our work.

Effect of coagulation bath

H_2O - H_2SO_4 mixtures in different ratios (80:20, 70:30 and 60:40) were tried as coagulants. From Table 5, it is clear that higher ratio of coagulation bath caused a very fast precipitation on the surface of the fibre. A skin was thus formed and the interior of the fibre had entrapped solvent in it. The optimum bath compositon (80 : 20) is suitable for spinning of fibres in our work. The water bath at 10°C or less is found to be adequate to real off the fibre. The fibres drawn above the room temperature were weak, thick and of high denier. This may perhaps due to high mass transfer in short times leading to large voids in the fibre during its formation.

The fibres when stressed (Fig. 3) exhibit a limited elastic region or deformation under external stress (called rheology). The material regains its original dimensions if the stress is removed. The resulting strain may be related to the extent of movement of atoms from their equilibrium conditions because atomic adjustments are localized. For long chain polymers, under the present experimental
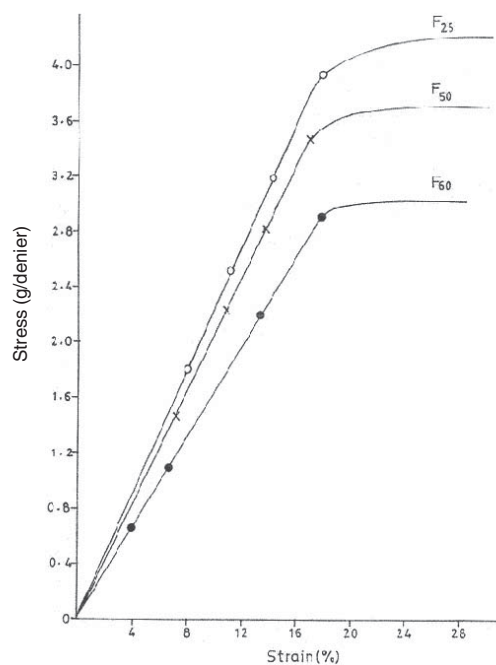

Fig. 3: Effect of jet stretch (stress- strain curve)

conditions, the situation is different. This may be due to extensive covalent bonding between the atoms to form chains, allows considerable deformation which may be accompanied by long and short range co-operative molecular rearrangement arising from the rotation about chain bonds.

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