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Qualitative analysis of aramide polymers by FT-IR spectroscopy

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ABSTRACT: *A high demand for Technical Textiles needs to develop new polymers & co-polymers. Polymers & co-polymers have special application in Technical Textiles. The identification of technical polymers is critical to forensic science, laboratories, fashion and design. There is a constant need to improve identification methodology.The actual identification, however, varies with industry and method. Various types of Aramide polymers are developed. Aramide polymers are used to make a variety of clothing, accessories, and used for safety. It's lightweight and extraordinarily strong, with five times the strength of steel on an equal-weight basis. It is best known for its use in ballistic and stab-resistant body armor. Aramide polymers are difficult to identify with conventional microscopic & chemical methods. FT-IR spectroscopy coupled with ATR technique is useful method to identify such polymers.*

KEYWORD: *Aramide, p-phenylene terphthalamide, m-phenylene terphthalamide, FT-IR spectroscopy, ATR*

I. INTRODUCTION

1.1 Aramide [1]

Aromatic polyamide described under the generic term aramide, 'a manufactured fiber in which the fiber forming substance is a long chain synthetic polyamide in which at least 85% of the amide linkages are attached directly to two aromatic rings'. Aramide fiber has unique properties that set them apart from other fibers. Aramide fiber tensile strength and modulus are significantly higher than those of earlier organic fibers, and fiber elongation is lower. Aramide fibers can be woven on fabric looms more easily than brittle fiber / polymer such as glass carbon or ceramic. They also have inherent resistant to organic solvents, fuels, lubricants and exposure to flame.

Two aramide fibers are developed one is *p*- aramide (*p*-phenylene terphthalamide) and another is m-aramide (*m*- phenylene terphthalamide) fig. 1.

Physical properties of macromolecules are determined by their structural characteristics at molecular level. Tensile modulus of fiber will be largely determined by the details of the molecular orientation about the fiber axis and the effective cross-sectional area occupied by single chains, which will of course be related to the degree of chain linearity. *p*- Aramide polymer chains are very stiff brought about by bonding of rigid phenylene rings in the *para* position. In *m*-aramide fibers the phenylene and amide units are linked in the *meta* position which results in an irregular chain confirmation and corresponding lower tensile modulus. Further *p*-aramid the presence of amide groups at regular interval along the linear macromolecular backbone facilitates extensive hydrogen bonding in a lateral direction between adjacent chains. This in turn, leads to efficient chain packing and high crystalinity.

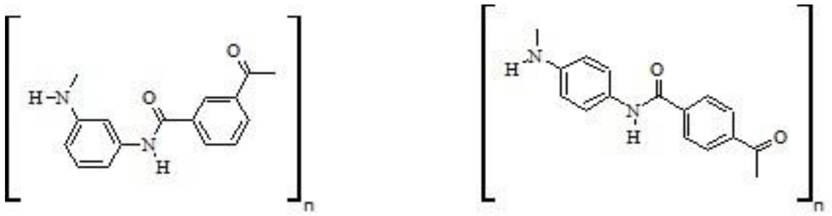

Figure 1 Structure of *m*- aramide & *p*-aramide

1.2 Identification of polymers

Burning test, microscopic examination of longitudinal & cross section, chemical solubility & physical constant such as melting point of polymers / fibers are conventionally used to identify the nature of polymer.

Burning test inferred primarily the thermo plasticity of the fiber. By microscopic examination one can differentiate between protein fiber *i.e.* silk & wool, cellulosic fiber *i.e.* cotton & viscose. Chemical solubility confirms the nature of many synthetic and natural polymers / fibers to certain extent. But there is limitation in identification of polymers such as aramide which are used in technical textiles by these conventional methods. For identification of such polymers FT-IR spectroscopy can be used. Broadly this method is matching the infra-red spectrum of unknown fiber or polymer with infra-red spectrum of known polymer. To ascertain the substitution pattern of the polymer, absorption band in infra-red spectrum is to analyzed and assigned to particular chemical group is essential.

1.3 Infra-red Spectrum of Aramide:[2][3]

Aramide polymer consists of benzene ring and amide group at either *meta* or *para* position. Hence infra-red spectrum of aramide polymer consists of major peaks or absorption band due to benzene ring and amide linkage.

1.4 Absorption band due to aromatic ring:

In polymer compounds containing aromatic group absorption band is due to out-of-plane and in-plane bending of the C-H bond. Out-of-plane bending occurs in the low frequency range between 900-675 cm^{-1} while in-plane bending absorption bands appear in the region 1300-1000 cm^{-1}.In such polymers skeletal vibrations, involving carbon to carbon stretching within the ring, absorb in the region 1600-1585 cm^{-1} & 1500-1400 cm^{-1}. This skeletal band frequently appears as doublets depending upon the nature of ring substituent. Aromatic C-H stretching bands occur between 3100 and 3000 cm^{-1}.Substituted benzene shows absorption band in the region 710-675 cm^{-1}. The pattern of absorption band in this region is different for *ortho, meta* & *para* substituted aromatic compound. Based on this pattern substitution pattern in aromatic compound can be ascertained

1.5 Absorption band due to amide group:

In general polyamide polymer -NH stretching absorption band in the region 2900-2800 cm^{-1} and also consists of Amide I, II, III, IV and V bands in the region 1500 – 600 cm^{-1} Details of these bands are as under.

1.5.1 Amide I:

Amide I is the primary band which is common to all types of polymers of polyamide. This is basically due to C=O bond stretching. It occur around 1640 -1690cm^{-1} lower than the any carbonyl compound. This lower frequency of absorption is due to the resonance in the amide functional group fig 2. The carbonyl bond of the amide carbonyl group is somewhat less than the double bond. If the amide is in conjugation with other group the carbonyl frequency is lowered still further. When carbonyl group of the amide is involved in hydrogen bonding its stretching frequency is again lowered.

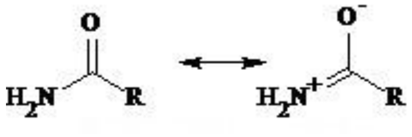

Figure 2 Resonance structure of amide

1.5.2 Amide II

Amide II bands in primary amide appears in the range of 1640-1600 cm^{-1} just to the right of amide II band and it is often enveloped by amide I band. The amide II band is due to N-H bending and therefore a tertiary amide does not show this band. Secondary amide in the solid state shows this band in the region 1570-1515cm^{-1}.

1.5.3 Amide III

This absorption band occurs in secondary amide in the region 1305-1200 cm^{-1}. It is weaker than Amide I & Amide II bands. It is due to mixed vibrations involving CN and NH modes.

1.5.4 Amide IV & Amide V

In secondary amides these bands are identify in the region 770-620 cm^{-1} and 630-530 cm^{-1}.These bands have their origins in skeletal modes and it’s have very imitated use in structural elucidation.

1.6 Attenuated Total Reflectance Technique:

Polymers such as aramide due to their high stiffness it is hard to cut & difficult to grind it in to powder to make KBr palate. Attenuated Total Reflectance Technique (ATR) is the technique in which no sample preparation is required. Acquiring infra-red spectrum using ATR technique is fast and easy. Infra-red spectrum acquired by ATR is without any interference is an advantage of ATR technique.

II. EXPERIMENTAL DETAILS:

Textiles material (yarn, non-woven & woven) made up of aramide polymer were studied. FT- IR spectrums of these aramide polymers were acquired using ABB-MB3000 spectrophotometer.ATR technique is used to acquire infra-red spectrum. Intimate contact between sample and ATR crystal was established by using a pressure clamp. Five replicates were acquired over frequency range 4000-600 cm^{-1} at a resolution of 16 cm^{-1}& detector gain of the instrument set up at 81. 25 scans for each specimen were acquired to minimize the operational error. Before each sample spectrum a reference spectrum of air was acquired. After acquisition of spectrum ATR correction was done at 1000 cm^{-1} and the normalized the spectrum by mathematical operation normalization. A database in the form of spectrum library was developed. To know any unresolved band first derivative mathematical operation was carried out. Each peak of the spectrum assigned to the corresponding chemical group.

III. RESULT AND DISCUSSION:

3.1 IR spectrum of m-aramide:

Fig. 3 is Infra-red spectrum of *m*-aramide without any mathematical operation & fig. 4 is infra-red spectrum of m- aramide after two mathematical operation *i.e.* ATR correction with respective wave-number 1000 cm^{-1} & normalization. Details of peak of *m*-aramide are given in Table I. Broad peak in the region at 3270 - 3263 cm^{-1} is corresponds to - NH stretching of secondary amide. Peak at 2924 and 2854 cm^{-1} is corresponds to =C-H stretching of benzene ring. Peak at 1643 cm^{-1} is amide I band. Peak at 1605 cm^{-1} due to C = C in-plane vibration of benzene ring. This also ruled out the *para* substitution of benzene ring. Peak at 1528 cm^{-1} is amide II band. Peak at 1474 & 1412 cm^{-1} are due to semicircle stretching of free hydrogen of aromatic ring. Peak at 1234 cm^{-1} is of amide III band; this confirms the amide is secondary amide. Amide IV & V band appears in the region 594 – 624 cm^{-1}. Peaks at 1165 cm^{-1}, 1080 cm^{-1} & 1018 cm^{-1} corresponds to the in-plane deformation of benzene ring, it infers the *meta* substitution of benzene ring. Peaks at 856, 779 & 679 cm^{-1} corresponds to *meta* substitution of benzene. Peak at 856 cm^{-1} corresponds to a single free hydrogen atom of benzene ring & peak at 779 & 669 cm^{-1} corresponds to three free hydrogen atoms of benzene ring. This confirms the substitution in benzene ring is at *meta* position

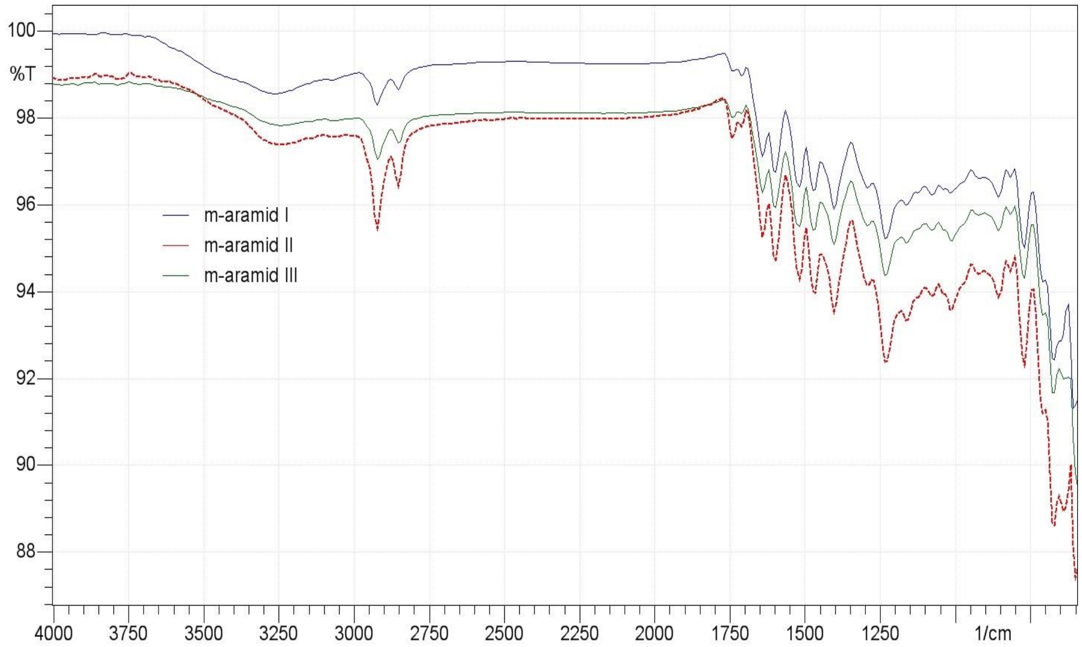

Figure 3 IR spectrum of *m*-aramide

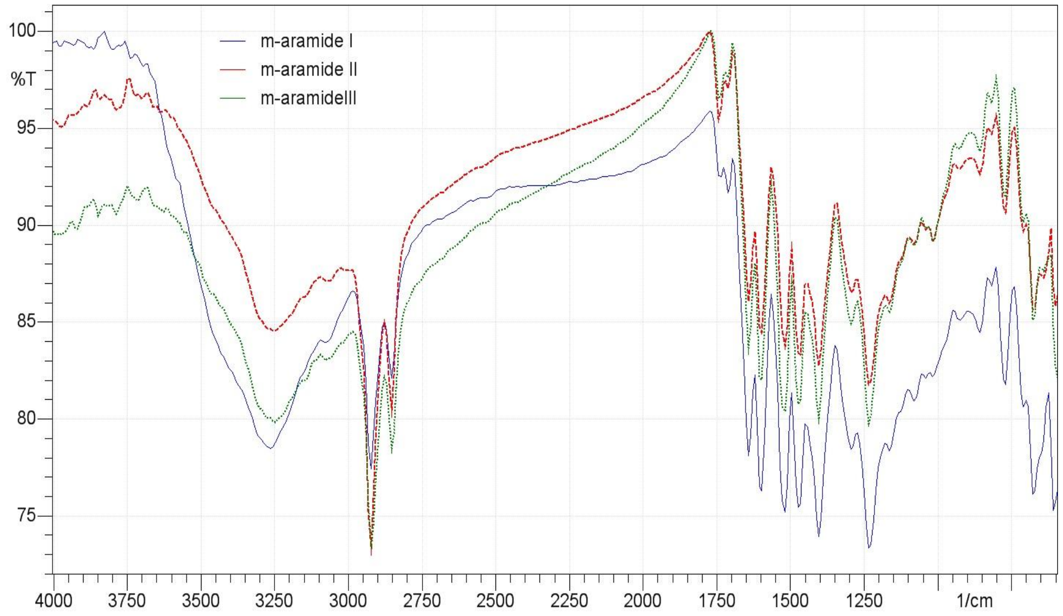

Figure 4 Normalized IR spectrum of m-aramide after ATR correction

Table 1 Peak table of *m*-aramide

Peak Number	**Begin [cm^{-1}]**	**Maximum [cm^{-1}]**	**End [cm^{-1}]**	**Width [cm^{-1}]**	**Height [%T]**	**Absolute Height [%T]**	**Peak Area (Abs. Sum)**	**Peak Area (%)**
1	594.0	609.5	624.9	30.9	-1.3	91.3	19.2	1.0
2	624.9	671.2	740.6	115.7	-2.3	92.4	142.3	7.4
3	740.6	771.5	802.3	61.7	-1.6	95.0	44.9	2.3
4	802.3	817.8	825.5	23.1	-0.2	96.6	3.9	0.2
5	833.2	856.3	902.6	69.4	-0.8	96.2	40.0	1.9
6	910.3	925.8	941.2	30.9	-0.6	96.6	19.8	0.8
7	941.2	1018.3	1049.2	108.0	-1.1	96.3	101.4	4.9
8	1049.2	1080.1	1095.5	46.3	-1.4	96.2	66.1	2.9
9	1095.5	1164.9	1180.4	84.9	-1.8	96.0	141.0	6.7
10	1188.1	1234.4	1272.9	84.9	-2.8	95.2	200.3	9.7
11	1272.9	1296.1	1342.4	69.4	-1.8	96.4	113.4	5.4
12	1342.4	1404.1	1442.7	100.3	-2.6	95.9	186.6	9.1
13	1450.4	1473.5	1496.7	46.3	-2.3	96.3	103.9	4.8
14	1504.4	1519.8	1558.4	54.0	-2.4	96.4	107.3	5.0
15	1558.4	1596.9	1620.1	61.7	-2.3	96.8	104.3	4.9
16	1627.8	1643.2	1689.5	61.7	-2.0	97.1	84.9	4.1
17	1689.5	1712.7	1728.1	38.6	-0.4	99.0	10.8	0.5
18	1728.1	1735.8	1766.7	38.6	-0.3	99.1	8.4	0.4
19	2692.4	2854.4	2877.6	185.2	-0.7	98.7	42.4	2.1
20	2885.3	2923.9	2985.6	100.3	-1.1	98.3	70.3	3.5
21	2993.3	3070.5	3093.6	100.3	-0.6	98.9	56.4	2.7
22	3101.3	3263.3	3718.5	617.2	-1.1	98.6	384.2	19.7

3.3 IR spectrum of *p*-aramide:

Fig. 5 is Infra-red spectrum of *p*-aramide without any mathematical operation & fig. 6 is infra-red spectrum of *m*- aramide after two mathematical operation i.e. ATR correction with respective wave-number 1000 cm^{-1} & normalization. Details of peak of *p* - aramide are given in Table 2. Broad peak in the region 3294 - 3047 cm^{-1} is corresponds to –NH stretching of secondary amide. Peaks at 2924 & 2854 cm $^{-1}$ corresponds to

=C-H stretching of benzene ring. Peak at 1636 cm^{-1} is of Amide I band. As there is no separate peak in the vicinity of amide I band and shape of the amide I band infers that the peak due to in-plane vibration of –C=C- is overlapped by amide I band. This infers the amide group is in highly conjugated position with benzene ring. Such conjugation is possible only in 1, 4 substitution of benzene ring *i.e. para* substitution. Peak at 1505 cm^{-1} is of amide II band. Peak at 1396 & 1303 cm^{-1} is due to due to semicircle stretching of free hydrogen of aromatic ring. Amide III band is at 1227 cm^{-1} which confirms the secondary amide. Amide IV & V band appears in the region 594 – 694 cm^{-1}.Peak at 1103, & 1108 cm^{-1} corresponds to –C-H in-plane deformation. Sharp peak at 818 cm^{-1} is corresponds to –CH out of plane deformation due to two free hydrogen atoms which confirms the *para* substitution in benzene ring.

Further derivative spectrum of m-aramide fig.7 and *p*-aramide fig.8 infers there is no unresolved beak in both the infra-red spectrum of both the aramide.

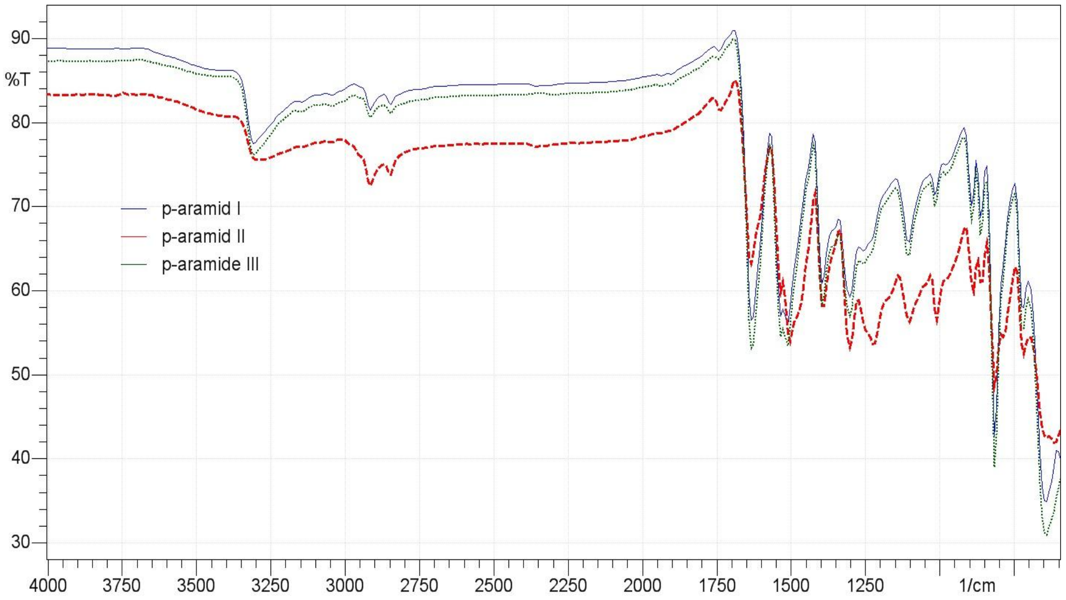

Figure 5 IR spectrum of *p*-aramide

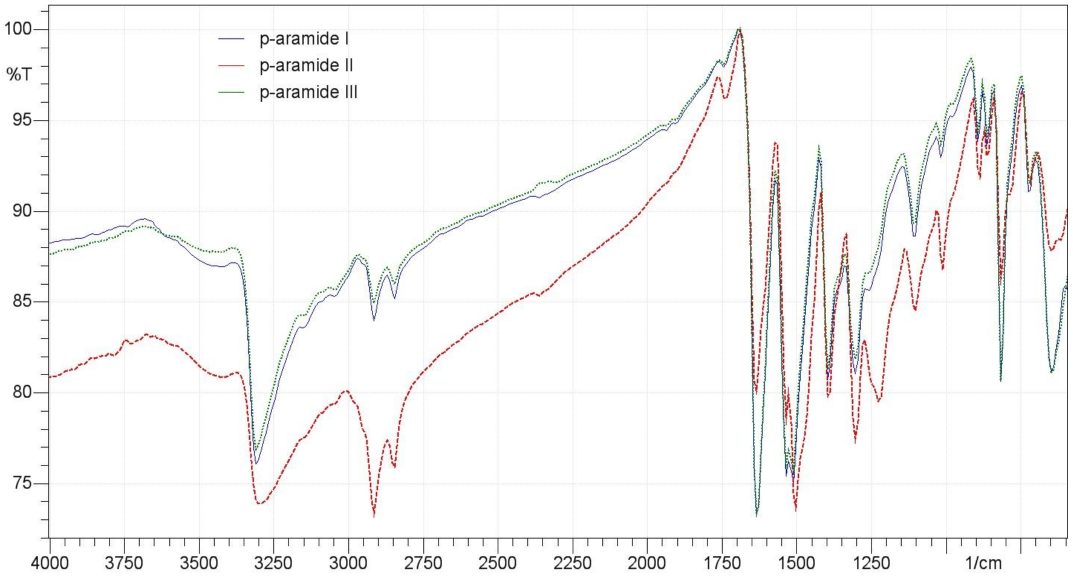

Figure 6 Normalized IR spectrum of *p*-aramide after ATR correction

Table 2 Peak table of *p*-aramide

Peak Number	Begin [cm^{-1}]	Maximum [cm^{-1}]	End [cm^{-1}]	Width [cm^{-1}]	Height [%T]	Absolute Height [%T]	Peak Area (Abs. Sum)	Peak Area (%)
1	594.0	617.2	694.3	100.3	-3.8	41.9	349.1	1.8
2	694.3	717.5	740.6	46.3	-5.7	52.6	144.9	0.7
3	748.3	817.8	840.9	92.6	-16.4	48.6	734.7	3.7
4	910.3	1010.6	1033.8	123.4	-11.9	56.5	754.5	3.7
5	1041.5	1103.2	1134.1	92.6	-12.8	56.3	987.3	4.7
6	1134.1	1226.6	1272.9	138.9	-16.4	53.7	1798.5	8.7
7	1280.6	1303.8	1334.6	54.0	-17.4	53.3	753.7	3.5
8	1334.6	1396.4	1419.5	84.9	-13.2	58.2	661.6	3.3
9	1427.2	1504.4	1566.1	138.9	-20.1	54.0	1695.4	8.5
10	1566.1	1635.5	1681.8	115.7	-18.2	63.3	1005.2	5.0
11	1689.5	1735.8	1759.0	69.4	-3.6	81.5	168.0	0.8
12	1759.0	2214.1	2237.3	478.3	-7.1	77.6	2891.6	14.3
13	2245.0	2360.7	2453.3	208.3	-7.4	77.1	1543.0	7.5
14	2461.0	2545.9	2561.3	100.3	-6.9	77.5	746.7	3.5
15	2592.1	2846.7	2869.9	277.7	-10.3	73.8	2168.3	10.6
16	2877.6	2916.2	3008.7	131.2	-11.6	72.5	1172.7	5.6
17	3008.7	3047.3	3062.7	54.0	-6.3	77.7	377.8	1.7
18	3070.5	3294.2	3679.9	609.5	-8.1	75.6	2530.8	12.6

4. Comparison between spectrum of *m*-aramide & *p*-aramide:

Fig. 9 shows the basic difference in the region 1500 - 600 cm^{-1}. Absence of band due to benzene ring in the vicinity of amide I band infers *p*-aramide, while presence of peak at 1605 cm^{-1} in the vicinity of amide I band ruled out *para* substitution. Further peak due semicircle stretching of free hydrogen of aromatic ring in *p*-aramide is at lower frequency than the *m*-aramide infers that more conjugation in *p*-aramide than the *m*-aramide. Further presence of two peaks in the region 600-800cm^{-1} confirms the *meta* substitution of benzene ring. Single sharp & intense peak at in 818 cm^{-1} confirms the *para* substitution of the polymer.

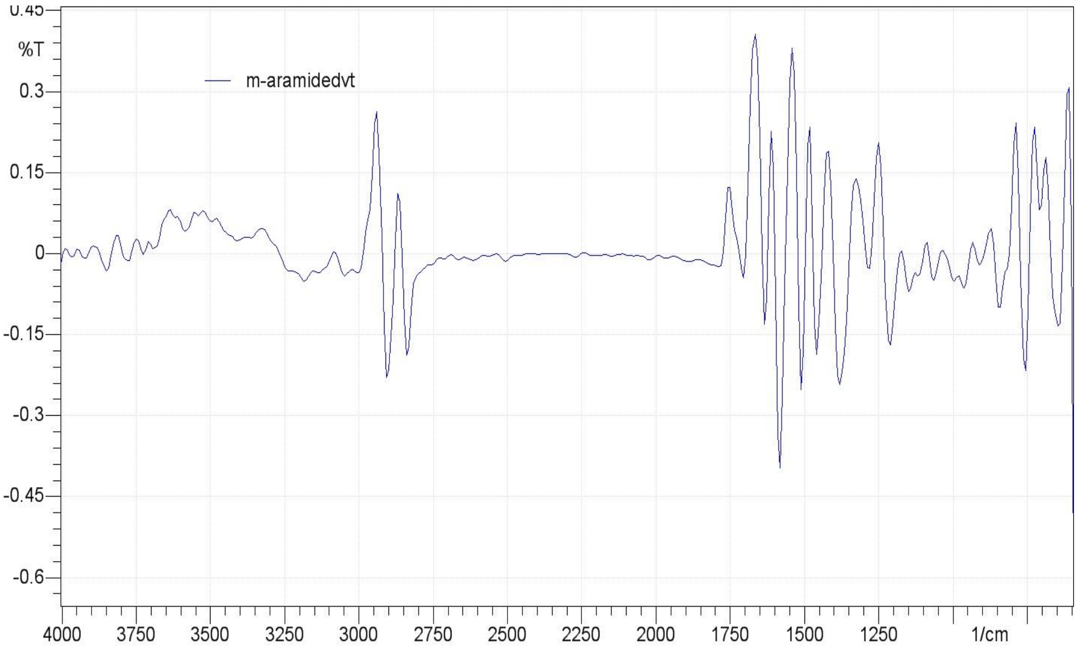

Figure 7 Derivative IR spectrum of *m*-aramide

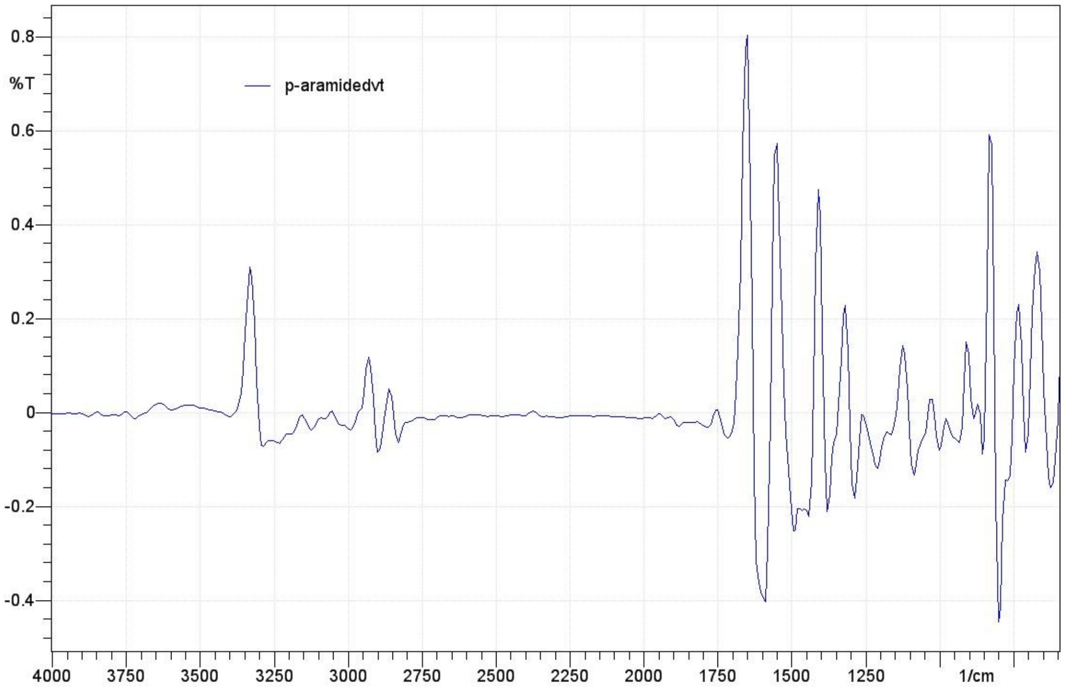

Figure 8 Derivative IR spectrum of *p*-aramide

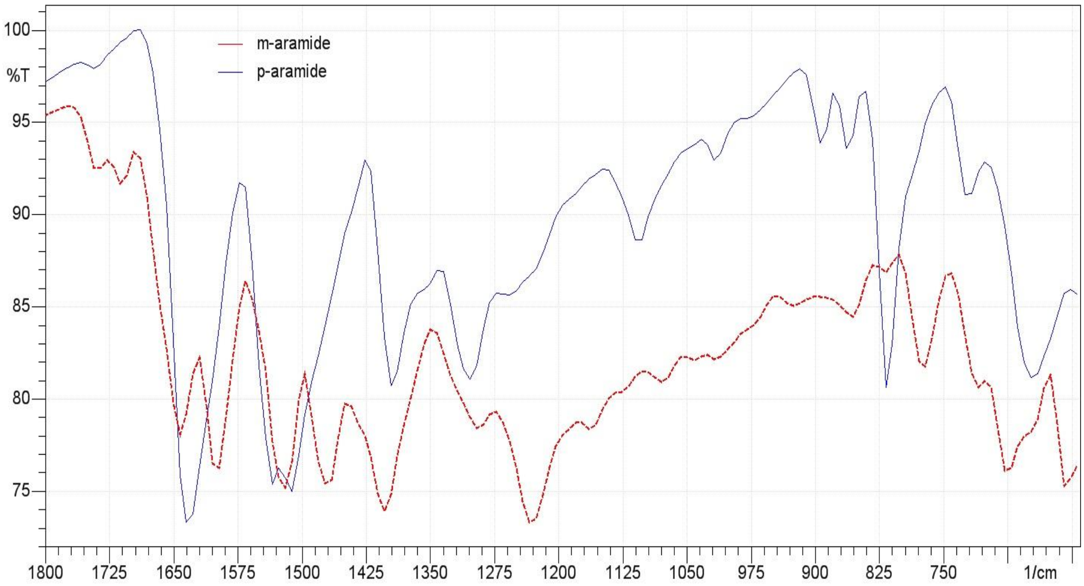

Figure 9 IR spectrum of *m* & *p*-aramide in the region 1800-600cm-1

IV. CONCLUSION

p- aramide & *m*-aramide did not have distinguished difference in their longitudinal & cross-sectional microscopic view and also not having significant difference in burning characteristics. Also these polymers are inherent to chemical action. From the experimental results the polymers of aramide i.e. *meta* & *para* aramide can be easily identified using the FT-IR spectrum coupled with ATR technique.

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