

SHORT COMMUNICATION

Radiochemical Graft Copolymerisation of 2-Hydroxy Ethylmethacrylate onto Polyamide-6, 6-Nylon

Inderjeet Kaur, Raghuvir Barsola, B.N. Misra and Ghanshyam S. Chauhan

Himachal Pradesh University, Shimla - 71 005

ABSTRACT

Polyamide-6,6-nylon has been modified by radiation-induced graft copolymerisation of 2-hydroxy ethylmethacrylate (2-HEMA) in nonaqueous medium (ethanol). No homopolymer formation was observed during grafting. Optimum conditions for affording maximum percentage of grafting have been evaluated. Maximum percentage of grafting (170 per cent) was obtained at a total dose of 0.74×10^4 Gy using 2-HEMA (8×10^{-3} moles) in ethanol (10 ml). The grafted samples were characterised by thermogravimetric analysis and it was observed that grafting slightly decreased the thermal stability of the polyamide-6,6 fibre. Dyeing properties of polyamide-6,6 fibre and grafted fibre have also been investigated.

1 INTRODUCTION

The dominant role of polyamide in the field of industrial fibres is related to their high toughness, strength, ability to absorb high velocity impact and the specific tailoring of polyamide towards the intended industrial end-use. Polyamide is specifically used in seat belts in automobiles, in parachute cloth and in diverse industrial applications because of its excellent abrasion resistance. Polyamides are high modulus polymers that have applications where high molecular weight and lightweight are required. Nylon shows distinct advantage over metals and ceramics on property-weight basis. Currently available commercial polyamides fulfil considerable number of end-use requirements. They have certain deficiencies in selected applications. Their high cost, relatively poor heat resistance, light fastness, only fair pilling resistance¹, etc., have directed research efforts towards

product improvement and search of even better polyamide-type.

Improvement in stain resistance, static and soil resistance, increased ironing temperatures, increased dyeability, etc., may be achieved by reacting the fibres with a suitable material. Adipoyl chloride-treated with polyamide-6,6 fibres have increased the melting temperature (T_m) and the dyeability properties²⁻⁴. Increase in crystalline T_m has also been observed when the polyamide fibre is treated with cyanuric chloride⁵, $ZnCl_2$ ⁶, $HCHO$ ⁷ and $SnCl_2$ ⁸. However, modification of polyamide fibre by grafting appropriate vinyl monomers has been extensively studied but only limited commercialisation has been obtained. Grafted nylons have generally improved the physical properties over the conventional nylons. Properties improved by grafting a polymer, such as polyacrylic acid in the form of its sodium salt onto

polyamide fibre increases in wet crease recovery and moisture absorption⁹. Preparation of a fire-resistant nonmelting polycaprolactam fibre with improved *O*-index by grafting 2-methyl 5-vinyl pyridine with addition of chloride, bromide or antimony compounds has been reported¹⁰. The colour strength of prints on acrylonitrile (AN)-grafted nylon-6,6 fibres has increased with increasing grafting, temperature and transfer printing time. The prints showed excellent washing and rubbing fastness and good perspiration fastness¹¹.

Graft copolymer prepared by reacting nylon¹² with polypropylene¹² in the presence of di-tert. butylperoxide, is used as a coating material. Photochemical grafting of acrylamide onto polyamide has been studied by Mukherjee^{13,14}, *et al.* Radiation-induced grafting of acrylic acid onto nylon-6 fabric in the presence of ferrous ammonium sulphate (FAS) has been carried out by Zaharan¹⁵, *et al.* Nylon-6-knitted fabric grafted with acrylic acid by means of electron beam bombardment produced a fabric with decreased melting point and decomposition temperature¹⁶. Radiation-induced grafting of 4-vinyl pyridine and its binary mixture with AN, (4-VP + AN) onto polyamide-6 has been reported¹⁷. Nylon fabric were grafted with AN at different graft levels and their dyeing properties with acid dyes were determined and compared with unmodified fibres¹⁸.

Lokhande and Teli¹⁹ studied grafting of various vinyl monomers onto synthetic fibres, such as polyester, nylon and polypropylene, and the dyeability of the resulting fibres. The effect of pH of the dyeing bath, temperature and concentration of KIO_4 -a-D- glucose redox system on dyeing of nylon-6 fibre using Telon red BLL and Telon blue ANL dyes has been studied by Chinese²⁰. This work reports the grafting of 2-hydroxy ethylmethacrylate (2-HEMA) onto polyamide-6,6 fibres in nonaqueous medium in air using γ -radiation as means of initiation. The work aimed at modifying properties of nylon-6,6 fibre, specially dyeing property. For this reason, 2-HEMA, a polar monomer has been chosen for grafting. Only a few works have been reported on grafting of vinyl monomers onto nylon-6,6 by radiation method. This modest objective has been investigated in the present work.

2. EXPERIMENTAL SETUP

2.1 Materials & Method

Polyamide-6,6 fibre was received from Prof P. Bajaj, Indian Institute of Technology, New Delhi. 2-HEMA (Fluka) was distilled before use. ⁶⁰Co isotope (2100 Ci) housed in a γ -chamber-900 was used as a source of γ -rays.

2.1.1 Graft Copolymerisation

Polyamide-6,6 (100 mg) fibre was suspended in a definite amount of ethanol in a flask. To it was added a definite amount of monomer (2-HEMA). The reaction flask was irradiated from a ⁶⁰Co source at a constant dose rate of 0.14×10^4 Gyh⁻¹ for different time periods. After the stipulated time, the reaction flask was removed from the chamber and the reaction mixture was filtered. No homopolymer formation was observed during grafting. The grafted fibre was thoroughly washed with methanol to completely remove the unreacted monomer. Solvent extracts from the grafts were dried and no homopolymer was isolated. In the mutual method, usually homopolymer along with graft copolymer is expected but this happens when excess of monomer is used. It was observed that at or below optimum $[M]$, no homopolymer formation occurs. The grafted film was dried to a constant weight in a vacuum oven. Percentage of grafting has been calculated from the increase in the weight of original fibre as follows:

$$\text{Percentage grafting} = \frac{W_2 - W_1}{W_1} \times 100$$

where W_1 and W_2 are the weights of original fibre and grafted fibre, respectively.

2.2 Dyeing Procedure

An aqueous solution of crystal violet (50 ml of 0.1 per cent) was taken in a round-bottomed flask and was placed in an oil bath constantly maintained at 70 °C. To it was added the sample (100 mg) to be dyed and the temperature of the bath was increased to 115-120 °C within 45 min. Dyeing was continued at this temperature for 1 hr after which the samples were filtered,

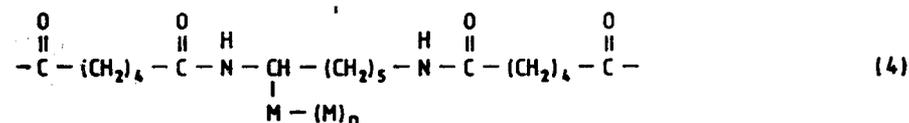
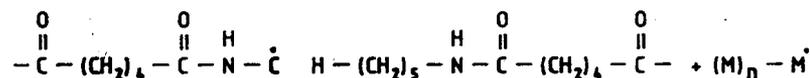
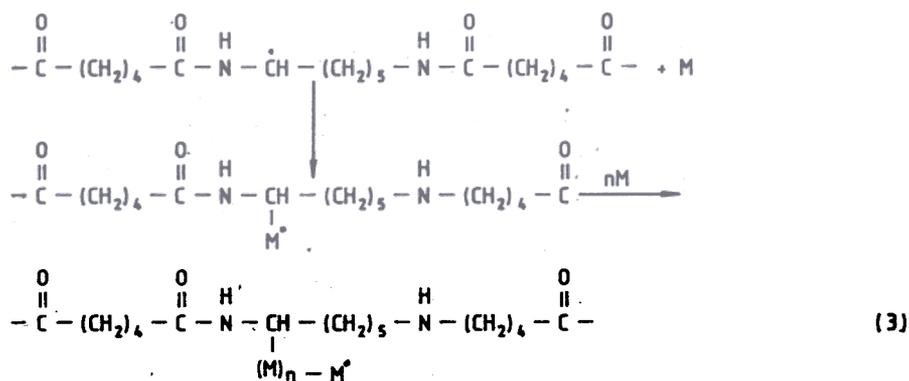
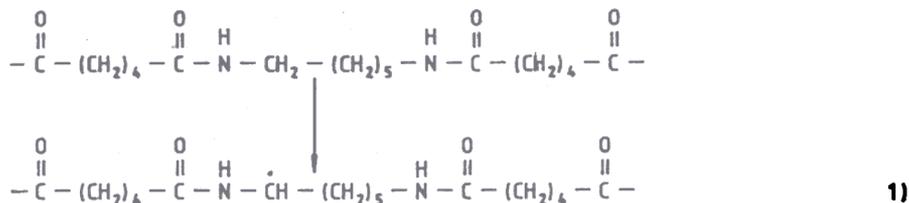
washed with water and dried at 50 °C in hot air oven.

2.3 Extraction of Dye

To measure quantitatively the total dye-uptake by the fibres, washing of the dyed samples was carried out with different solvent systems used in the order: Water, acetone and DMF- H_2O - $HCOOH$ (60:19:1) system. The dyed fibre was first refluxed in water for 30 min and then filtered. The process was repeated till the filtrate was colourless. This sample was then treated with acetone and DMF solvent system in the same manner and the filtrates collected. Optical densities of each washed out solvent were measured at 540 nm and 590 nm on spectronic-20.

2.1.4 Standard Curves of the Dye in Different Solvent Systems

Solution of the dye (0.1 per cent) made in water, acetone and DMF- H_2O - $HCOOH$ solvent system separately is used for extracting the dye from the dyed samples. The concentration of each of the dye solution was varied and the optical density of each dilute solution was measured at 540 nm and 590 nm. A plot of optical density versus concentration of the dye in respective solvent is a straight line which is the standard curve for the dye in that solvent. From the optical density of the washed out solvents, the concentration of the dye can be determined using the standard curves which gives the quantity of the dye being



Structure I

washed out in that particular solvent. The sum of the concentration of the dye washed out in different solvents gives the total dye-uptake by the sample.

3. RESULTS & DISCUSSION

When polyamides are subjected to high energy irradiation, the most obvious change is the production of transient colour which is the manifestation of a free radical formation generally on the carbon atom adjacent to the amide nitrogen by the removal of hydrogen atom. The high degree of specificity of free radical formation can be attributed to the concentration of energy in the vicinity of the amide group prior to the elimination of α -proton, regardless of where the initial ionisation or excitation occurs which is presumably, randomly along the chain.

Chain scission and cross-linking of nylon-6 fibre upon irradiation has been observed by Chaudhari, *et al.*, during the studies on kinetics of swelling of nylon-6 films in benzyl alcohol and relative viscosity of formic acid solution of γ -irradiated nylon-6 sample. These processes have been observed to occur at higher total doses. However, these reactions are not significant in the present study, since all the experiments are carried out at a total dose of <1 Mrad. A plausible mechanism has been proposed to explain the graft copolymerisation 2-HEMA onto polyamide-6,6 by mutual irradiation method and is depicted here as structure I.

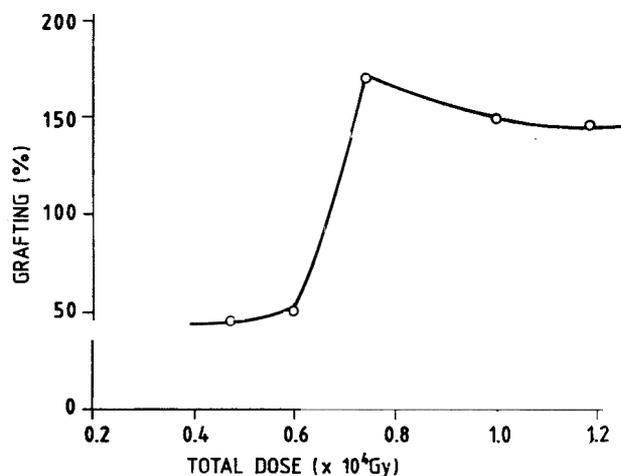


Figure 1. Effect of total dose on percentage of grafting of 2-HEMA.

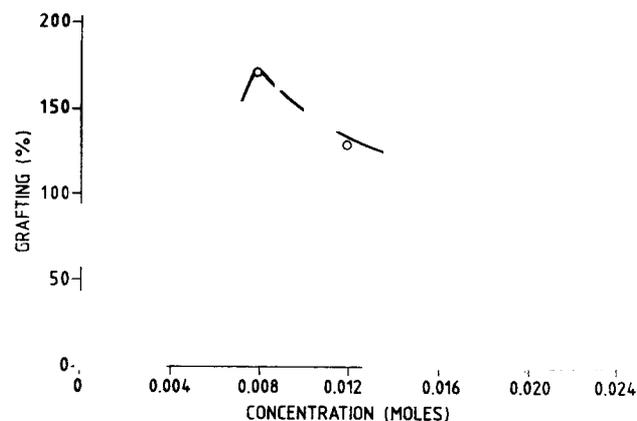


Figure 2. Effect of 2-HEMA on percentage of grafting

In this structure, it can be seen that the formation of the graft can take place either by direct attack (grafting from) of the monomer on the active site [Eqn (3)] or by the attack of the growing polymeric chains (grafting onto) *via* [Eqn (4)]. However, the formation of the graft copolymer involving direct attack of the monomer on the active site seems to be less probable since the initiation of the monomer [Eqn (2)] is a rapid process with lower energy of activation as compared to the generation of active sites on the polymeric backbone by hydrogen abstraction [Eqn (1)]. Various reaction parameters that affect the formation of graft copolymer have been investigated and the results are explained in the light of proposed mechanism.

3.1 Effect of Total Dose

Percentage of grafting of 2-HEMA has been

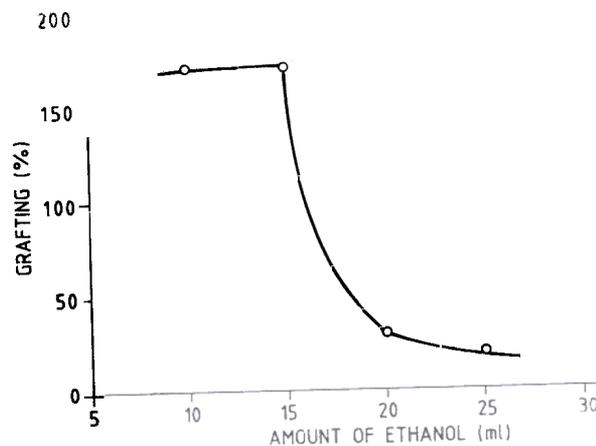
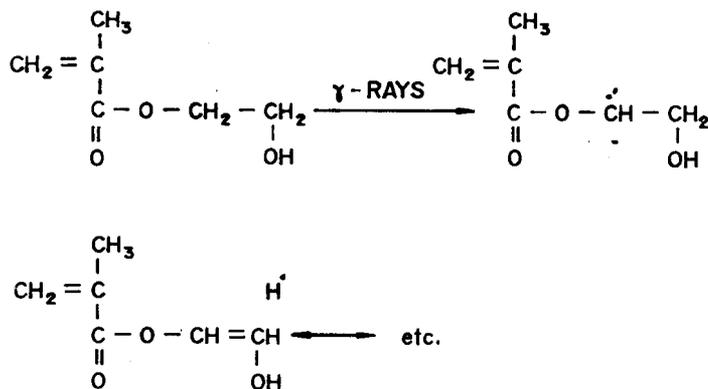


Figure 3. Effect of amount of ethanol on percentage of grafting of 2-HEMA.



Structure II

studied as a function of total dose and the results are presented in Fig. 1. The figure reveals that the percentage of grafting shows a sharp rise in grafting giving maximum (170 per cent) at a total dose of 0.74×10^4 Gy beyond which it decreases and becomes almost constant.

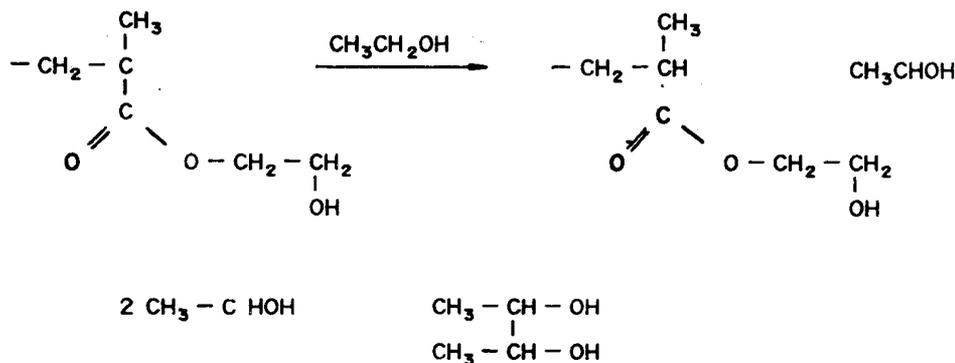
With increasing total dose generation of active sites as well as initiation of monomer forming growing polymeric chains are promoted and hence, a sharp increase in the percentage of grafting is observed. A slight decrease in the grafting beyond optimum total dose may be due to the fact that at higher doses, side reactions, such as cross-linking, chain transfer reactions, etc., are accelerated, leading to decrease in percentage of grafting. Wastage of the monomer at higher doses by hydrogen transfer reactions can also lead to decrease in percentage of grafting, which is depicted in structure II.

3.2 Effect of Monomer Concentration

presented in Fig. 2. It is observed from the figure that the percentage of grafting increases with increasing monomer concentration producing maximum grafting (170 per cent) at $[2\text{-HEMA}] = 8 \times 10^{-3}$ moles and then decreases gradually. Since very little or no homopolymer formation is observed during grafting, the monomer seems to be wasted in various chain transfer reactions.

3.3 Effect of Solvent

Sample	Percentage grafting	IDT (°C)	FDT (°C)	DT (°C) at every 10 per cent weight loss								
				10	20	30	40	50	60	70	80	90
Polyamide-6, 6		320	572.5	380.0	480	562.5	657.5	695	725.5			
Polyamide-g-poly (2-HEMA)	45	280	490.0	67.5	250	307.5	335.0	375	427.5	450	467.5	482.5



Structure III

3.4 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) of polyamide-6,6 fibre⁹ and 2-HEMA has been studied and the results are presented in Fig. 4. The initial decomposition temperature (IDT), final decomposition temperature (FDT) and decomposition temperature (DT) at every 10 per cent weight loss are presented in Table 1. From the table, it is observed that the values of DTs of the grafted samples are lower than those of the original fibre suggesting that the thermal stability of polyamide fibre decreases upon grafting. This may be due to the fact that in addition to the disturbances occurring in the crystallinity of the fibre upon grafting, intramolecular hydrogen bonding present in the fibre is also lost, thus causing decrease in the thermal stability of the fibre. Polyamide-6,6 fibre as such degrades upon heating

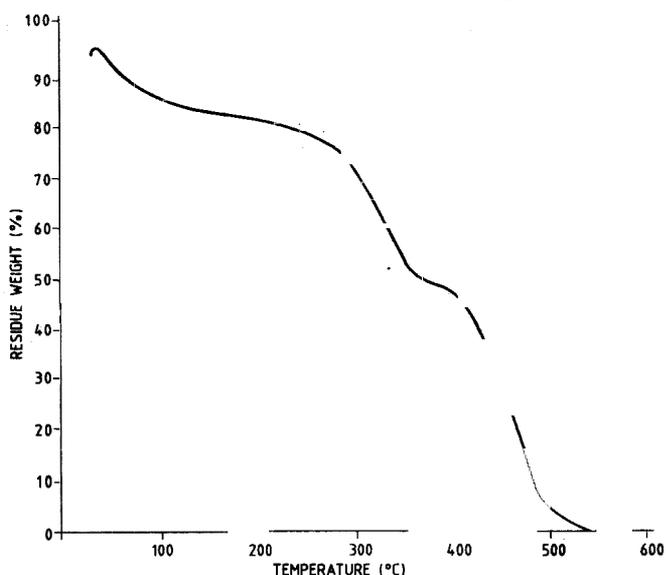


Figure 4. Primary thermogram of polyamide-g-poly (2-HEMA) (percentage G = 45).

with the formation of volatile products, such as CO_2 , H_2O , NH_3 , etc.

3.5 Dyeing behaviour of Polyamide-6,6 and Polyamide-g-Poly(2-HEMA)

Dyeing behaviour of polyamide-6,6 fibre and 2-HEMA has been studied by dyeing the fibres with crystal violet. The percentage of total dye-uptake for each of the samples is presented in Table 2. and the plots of percentage of total dye-uptake as a function of percentage of grafting are presented in Fig. 5.

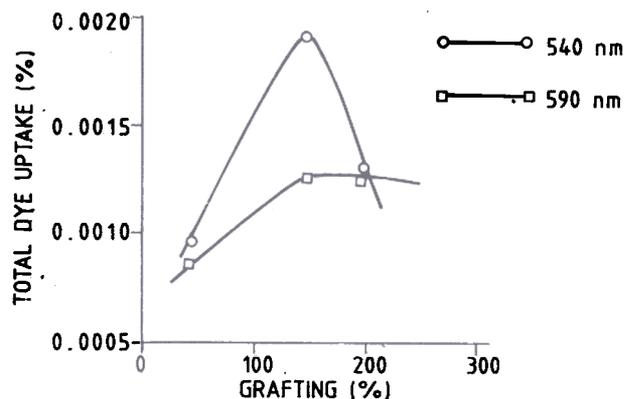


Figure 5. Total dye-uptake (per cent) for polyamide-g-poly (2-HEMA) as a function of percentage of grafting.

It is observed from the table that the total dye-uptake of the grafted sample is higher than that of the ungrafted fibres. However, when the grafting percentage is low (45 per cent) the total dye-uptake is almost the same as that of ungrafted fibre but with increase in percentage of grafting to 150 per cent, the total dye-uptake of the grafted fibre increases and then decreases at 540 nm and becomes constant at 590 nm. Thus, grafting of

Table 2. Total dye up-take by polyamide-6, 6 and polyamide-g-poly (2-HEMA)

Sample	Water system					Acetone system				DMF-H ₂ O-HCOOH[69 : 3 : 1]				Total	
	540 nm		590 nm			540 nm		590 nm		540 nm		590 nm		540 nm	590 nm
	Grafting	O.D.	Conc. [%]	O.D.	Conc. [%]	O.D.	Conc. [%]	O.D.	Conc. [%]	O.D.	Conc. [%]	O.D.	Conc. [%]	Conc. [%]	
Polyamide-6,6		0.95	0.000660	-	-	0.13	0.000125	0.35	0.000130	0.14	0.000240	0.33	0.000650	0.001025	0.000780
Polyamide-g-poly [HEMA]	15	0.34	0.000245	0.70	0.00025	0.41	0.000565	1.2	0.000480	0.09	0.000150	0.28	0.000140	0.000960	0.000870
-	150	1.10	0.00076	2.00	0.0070	0.44	0.000615	1.3	0.000535	0.32	0.000545	1.0	0.000035	0.001920	0.001270
-	200	0.62	0.00435	1.30	0.00046	0.38	0.000520	1.1	0.000450	0.21	0.000355	0.64	0.000310	0.001310	0.001250

Weight of sample used = 100 mg; initial dye concentration = 0.1 per cent

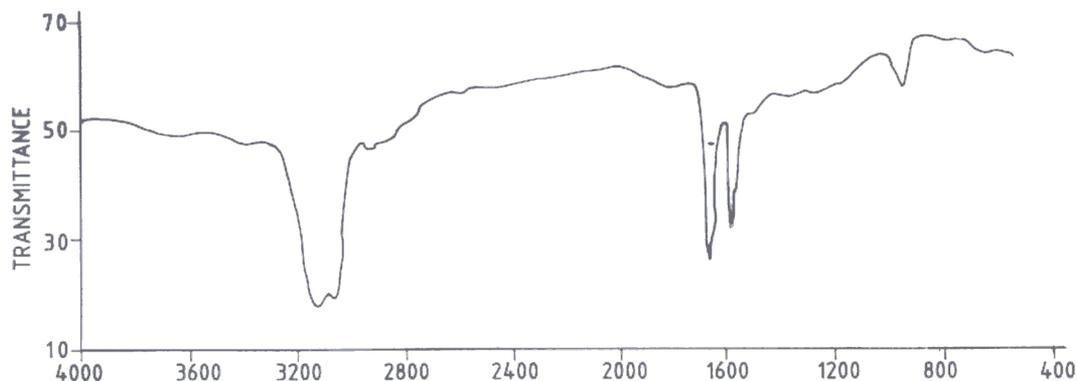


Figure 6. IR spectrum of polyamide-g-poly (2-HEMA)

2-HEMA onto polyamide fibre improves the dyeing property of polyamide-6,6 fibre.

3.6 IR Spectroscopy

IR spectrum of polyamide-g-poly (2-HEMA) showed peaks at 3150 cm^{-1} due to associated hydroxyl group of $-\text{CH}_2\text{CH}_2\text{OH}$ and a peak at 1650 cm^{-1} due to ester group of grafted polyhydroxyethyl methacrylate (Fig. 6).

ACKNOWLEDGEMENTS

Shri R. Barsola, Senior Research Fellow, is thankful to the Council of Scientific & Industrial Research (CSIR), New Delhi, for providing financial assistance to carry out this work.

REFERENCES

- Textile World*, January 1968, **118**, 50.
- Perry, E. & Sarory, J. *J. Appl. Polym. Sci.*, 1967, **11**, 2473.
- Smolnikova, L.G. & Konkin, A. A. *Khimicheskaya Volokna*, 1965, **5**(1), 41.
 - Hornuff, G. Von & Jansch, M. *Melliend Textile Ber.*, 1964, **45**, 768.
 - Moncrieff, R.W. *Textile Manufacturing*, 1996, **92**, 586.
 - Hershier, R.J. USA Patent 3, 023, 074. 22 February 1962.
 - Tanner, D. USA Patent 3, 294, 755. 27 December 1966.
 - Strashnova, T.T.; Mikailov, N.Y. & Maiboroda, V.I. *Khimicheskaya Volokna*, 1966, **1**, 22.
 - Magat, E.E.; Miller, I.K.; Tanner, D. & Zimmerman. *J. Polym. Sci. (C)*, 1964, **4**, 615.
 - Efros, A.V.; Tyinganova, M.A. & Gal'braikh, L.S. *Khimicheskaya Volokna*, 1983, **6**, 31
 - El-Shahed, M.F.; Shalaby, S.E. & El-Kashouti, M.A. *Amer. Dyest. Rep.*, 1985, **74**(12), 40-2,50.
 - Saotome, Kazuo. Jpn.Kokai Tokkyo Koho, 8000, 741. 7 January 1980, Appl. 78/74, 555, 20 January 1978, 4p.
 - Mukherjee, A.K.; Sachdev, H.S. & Gupta, A. *J. Appl. Polym. Sci.*, 1983, **28**(6), 2125.
 - Mukherjee, A.K.; Sachdev, H.S. & Gupta, A. *J. Appl. Polym. Sci.*, 1983, **28**(7), 2217.
 - Zahran, A.H.; El-Hasaby, M.B. & El-Gendyl E. *Amer. Dyest. Rep.*, 1985, **74**(5), 34.
 - Vesely, P. & Provaznikova, D. *Morphol. Polym. Proceedings of the European Physics Conference on Macromolecular Physics*, 1986, 645.
 - Kaur, Inderjeet; Misra, B.N. & Barsola, Raghuvir. *Morphol. Polym. Die Angewandte Makromol. Chemie.*, 1996, **234** (Nr.3786), 1.
 - El-Shahed, M.F.; Shalaby, S.E. & Kamal, M. *Amer. Dyest. Rep.*, 1983, **72** (11), 42.
 - Lokhande, H.T. & Teli, M.D. *Chem. Engg. World*, 1985, **20**(3), 63.
 - Wang, H.S.; Lin, C.H. & Teay, C.W. Fang Chih. *Kunng-Cheng Husehan*, 1983, **10**, 132.