

Modification of Poly(vinyl Alcohol) Fibers by Hexamethylene Diisocyanate

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Synopsis

Poly(vinyl alcohol) multifilament yarn was modified by reaction with hexamethylene diisocyanate. The effects of reaction variables such as time, temperature, concentration of reagents, solvent, and atmosphere were studied. The role of solvent appears to be very important in the reaction. Dimethylformamide, on account of its swelling power, proved better than the solvents benzene, toluene, and dioxane. Physical properties of modified fibers were compared with those of the parent. Moisture regain of the modified samples decreased with increasing add-on per cent. The elastic recovery was not improved, and there was little effect of the HMDI treatment on mechanical properties. The thermal stability of poly(vinyl alcohol) modified with diisocyanate with small add-on was slightly improved.

INTRODUCTION

Crosslinking of poly(vinyl alcohol) (PVA) fibers with a bifunctional reagent is an attractive proposition for improving the fiber properties.¹⁻⁶ Hexamethylene diisocyanate (HMDI) treatment of cotton to impart crease resistance properties is well known. PVA fibers which contain reactive hydroxyl groups as in the case of cotton and when treated with HMDI may have better elastic properties and crease resistance. Thus, in the present work PVA fibers were treated with HMDI. Samples with different crosslink densities were prepared and various physical properties (density, moisture regain, and birefringence) were investigated. Stress-strain behavior and thermal properties of these modified fibers have also been studied.

EXPERIMENTAL

The poly(vinyl alcohol) used was multifilament yarn supplied by Messrs Kurashiki Rayons under the trade name Kuralon was soxhlet extracted with petroleum ether to remove finishes and other impurities. Other BDH laboratory reagent grade chemicals were used. Hexamethylene diisocyanate was distilled under reduced pressure before use.

Crosslinking of PVA Fibers

Crosslinking reaction with HMDI was carried out in different solvents—benzene, toluene, dioxane, and dimethyl formamide (DMF)—at different temperatures, under different swelling conditions and at different HMDI

concentrations under nitrogen as well as under air. Precautions for complete exclusion of moisture were taken. Transfers of solvents and reagents were made rapidly using pipettes. After the reaction, the sample was rinsed with acetone to remove excess reagents. Unreacted crosslinking agent and homopolymer were removed by Soxhlet extraction with acetone. The samples were then dried for 24 hr at 100°C and stored in a vacuum desiccator overnight and then weighed. The difference in weights of the yarn before and after the reaction was used to calculate the percentage weight gain over the original weight.

Measurement of Physical Properties

The deniers of parent and crosslinked fibers were determined by cutting fixed lengths of the filaments and weighing them on a sensitive balance. These denier values were used in calculating the stress value. Density was determined using the density gradient column containing mixtures of benzene (0.89 g/cc) and carbon tetrachloride (1.595 g/cc) in different molar ratios. Moisture regain was determined by the vacuum desiccator method using P₂O₅ as the dehydrating agent. Birefringence of the filament was measured by the Becke line method using liquid paraffin ($n = 1.471$) and α -m-nobromonaphthalene ($n = 1.660$).

Tenacity, elongation at break, and initial modulus of the filaments were determined from the stress-strain curves obtained using an Instron. The specifications employed were: gauge length, 2.5 cm; cross-head speed, 1 cm/min; chart speed, 20 cm/min; full-scale load calibration, 100 g. All these tests were performed at 65 \pm 2% R.H. and 20 \pm 2°C.

Elastic recovery tests were conducted on the Instron. Specifications for the test were as follows: gauge length, 5 cm; cross-head speed, 1 cm/min; chart speed, 30 cm/min; full-scale load calibration, 100 g; extension given, 10% (0.5 cm); relaxation time, 30 sec; recovery time, 60 sec. Tests were performed at standard conditions.

The thermogravimetric analysis was done using a Stanton Model HT-D thermobalance in air. The samples were cut into very small lengths, and 20 \pm 2-mg fibers were taken for each run. The analysis was carried out from room temperature to 550°C at a heating rate of 6°C/min. Primary thermograms were obtained by plotting per cent residual weight against temperatures.

RESULTS AND DISCUSSION

Effect of Reaction Conditions on Extent of Reaction of HMDI with PVA

The PVA samples were treated in different liquids—benzene, toluene, dioxane, and DMF—for 1 hr, at different temperatures and then crosslinked with HMDI. No crosslinking occurred when benzene, toluene, and dioxane were used. DMF, on the other hand, proved to be an excellent solvent for PVA because it is a good swelling agent. Higher weight gains resulted when reaction was carried out in N₂ atmosphere than in air.

As shown in Figure 1, per cent add-on increases as the concentration of the reagent increases up to a certain concentration of HMDI. Further increase in the concentration of the crosslinking agent has no effect on the per cent add-on.

As seen in Figure 2, per cent add-on increases as the temperature is increased from 30° to 80°C. Further increase in temperature (to 110°C) does not cause any further increase in per cent add-on. The T_g of PVA is 85°C in the absence of swelling agents. The effect of temperature is probably attributable to increased swelling lowering the T_g increasing the mobility of chains facilitating crosslinking.

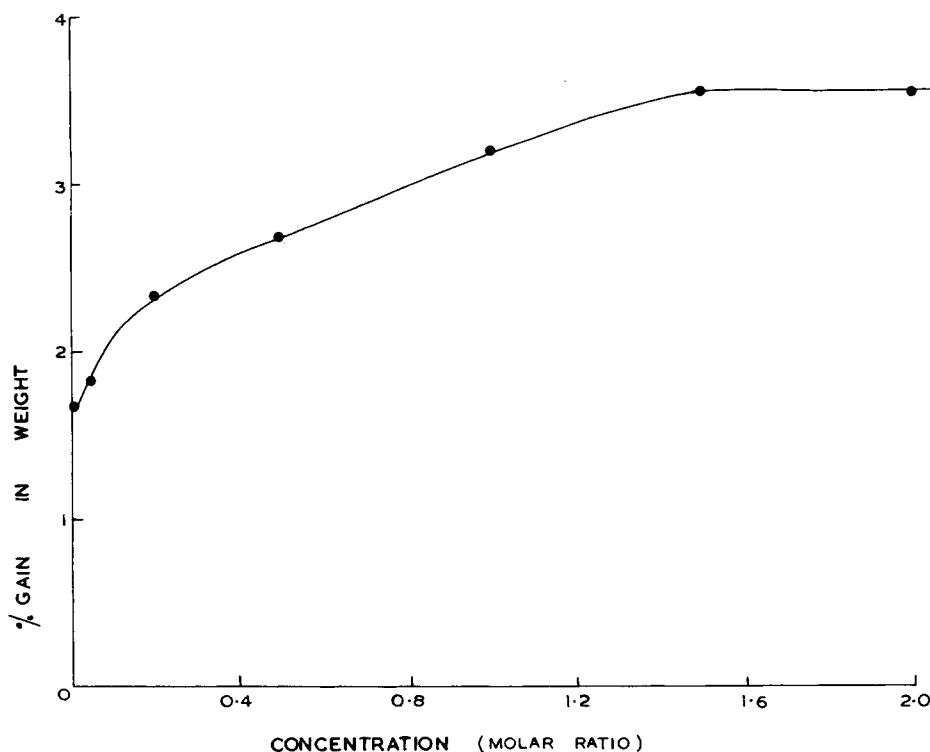


Fig. 1. Effect of HMDI concentration on per cent add-on. Swelling time = 1 hr at 110°C; reaction time = 2 hr at 110°C; solvent, DMF.

The effect of duration of reaction was studied by carrying out reaction in N_2 atmosphere for different intervals of time from 30 min to 8 hr. The reaction conditions maintained were: swelling for 1 hr at 110°C; molar ratio (fiber to HMDI), 1:0.5; and temperature of reaction, 110°C.

As the reaction time increases, an increase in per cent add-on was observed, as is evident from Figure 3. The rate of reaction is high at short duration of treatment and then shows a tendency to level off at longer times. Higher reaction rate at the initial stages may be due to the ready availability of hydroxyl groups in the amorphous region as well as on the surface of the filament. Once these hydroxyl groups have been utilized in forming crosslinks, further penetration of the reagent is considerably lowered, and also deposi-

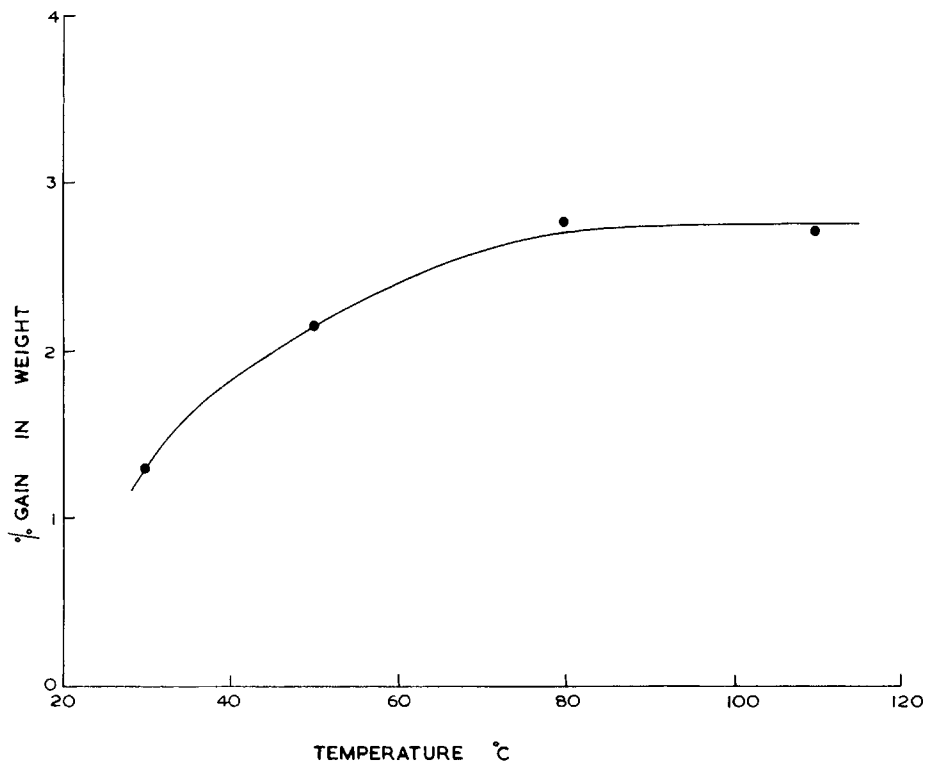


Fig. 2. Effect of temperature on per cent add-on. Swelling time = 1 hr at 110°C; reaction time = 2 hr; molar ratio of HMDI = 1:0.5; solvent, DMF.

tion of homopolymer on the surface would prevent subsequent penetration and reaction of the diisocyanate with poly(vinyl alcohol).

Physical Properties

Table I gives the values of density, birefringence, and moisture regain for control as well as samples with different amounts of crosslinks. Density

TABLE I
Effect of Hexamethylene Diisocyanate Modification of Poly(vinyl Alcohol)
on Physical Properties

Sample no.	Weight gain, %	Density, g/cc	Birefringence ($n_{11} - n_{\perp}$)	Moisture regain, %
Control	nil	1.288	0.03416	3.994
C ₁	2.139	1.284	0.03284	3.167
C ₂	2.701	1.282	0.03291	3.139
C ₃	2.698	1.280	0.03288	3.073
C ₄	2.687	1.291	0.03292	3.004
C ₅	3.821	1.273	0.03326	2.917
C ₆	4.050	1.278	0.03569	2.442
C ₇	4.897	1.275	0.03806	2.186

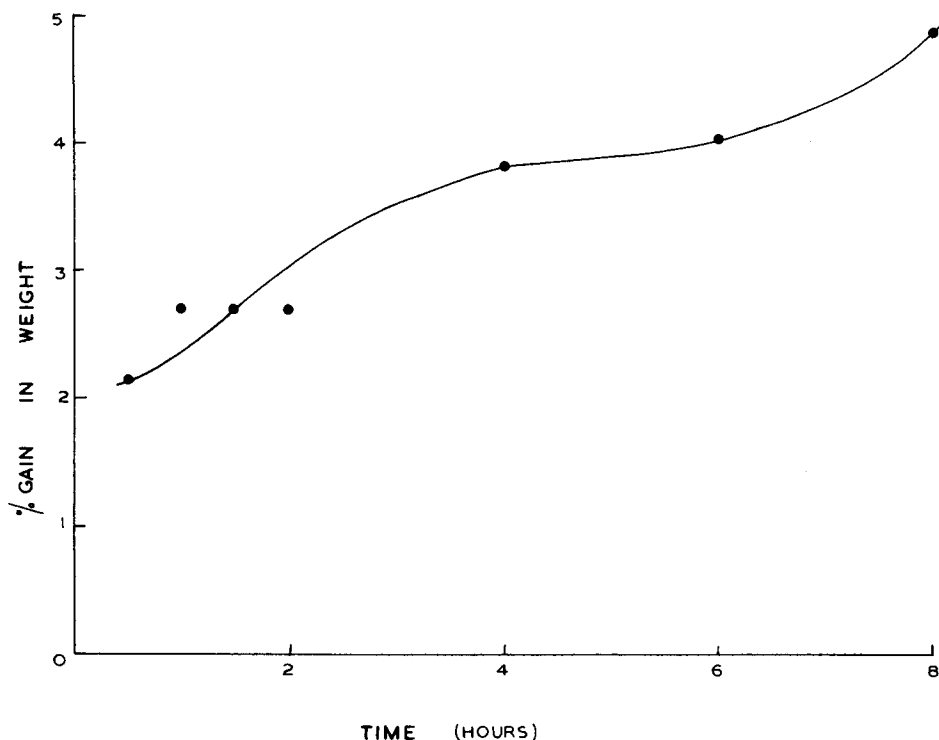


Fig. 3. Effect of time on per cent add-on. Swelling time = 1 hr at 110°C; concentration of HMDI = 1:0.5; reaction temperature = 110°C in DMF.

values show a decrease due to crosslinking with HMDI. This is expected because of the swollen nature of the fibers. Moisture regain values are also reduced in the modified fibers as compared to the control sample. This may be due to an increase in the crosslinks in the amorphous region.

The results show a decrease in birefringence at low weight gains and a subsequent steep increase at higher weight gains. The birefringence of the reacted samples is lower than that of the control up to a weight gain of about 3.9%, and then the birefringence rises sharply. The drop in birefringence at low weight gains may be due to the disorientation of chains in the noncrystal-

TABLE II
Evaluation of Relative Thermal Stability of Hexamethylene Diisocyanate-Modified Poly(vinyl Alcohol)

Sample no.	Decomposition temperature (T_D), °C							IDT, °C	
	10%	20%	30%	40%	50%	70%	90%	°C	IPDT
Control	277.5	307.5	325.0	342.5	367.5	450.0	502.5	250	383
C ₁	295.0	315.0	337.5	357.5	382.5	435.0	492.5	277	390
C ₄	277.5	307.5	330.0	347.5	372.5	435.0	485.0	255	382
C ₅	275.0	300.0	320.0	345.0	377.5	447.5	485.0	237	381
C ₆	275.0	295.0	312.5	330.0	380.0	452.5	490.0	255	385
C ₇	270.0	297.5	320.0	337.5	357.5	420.0	470.0	247	369

line regions of the fiber. At higher add-ons, the increased crosslinking density may be conducive for improved order in this region.

The stress-strain diagrams of PVA of various add-on values are shown in Figure 4. The breaking stress of all the modified samples lie below that of the control. PVA fibers are already crosslinked due to formalization. The

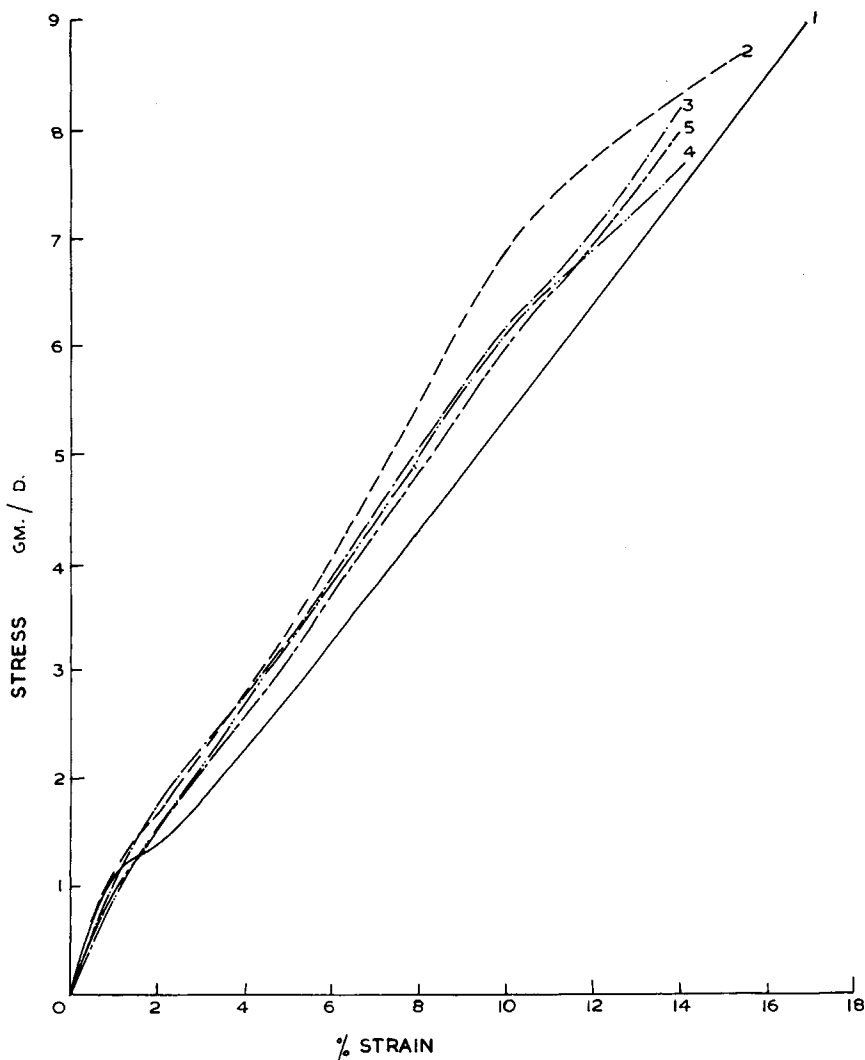


Fig. 4. Stress-strain curves for parent and crosslinked samples: (1) parent; (2) sample C₁; (3) sample C₃; (4) sample C₅; (5) sample C₇.

movement of the chains is restrained by the introduction of further crosslinks into the fiber, and there is less opportunity for chain motion to help equalize the distribution of stress on the individual chains. This will lead to a high local stress concentration, thereby increasing the probability of rupture. The breaking strain of all the reacted samples also drops below that of the control. This can be explained with reference to the stress distribution within the

fiber. Introduction of crosslinks into the amorphous regions increases the amount of strain in the chains for a given displacement. The resulting high stress causes early rupture of the chains, reducing the extensibility of the fiber. The initial modulus of the modified PVA fibers shows a sharp decrease from that of the control. This is rather peculiar, because crosslinking usually results in stiffening of the chains, thus increasing the initial modulus. The decrease in initial modulus may be due to imperfections in crystal structure.

The effect of increase in weight of modified PVA on its elastic recovery is given in Figure 5. In general, there is a decrease in elastic recovery with in-

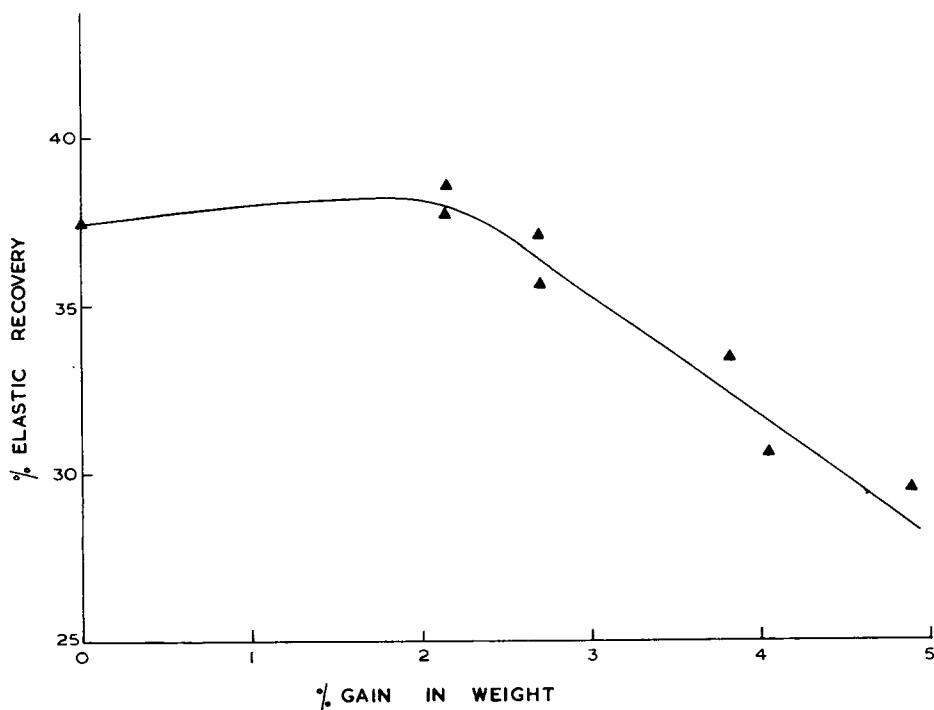


Fig. 5. Effect of increase in weight due to crosslinking of PVA on elastic recovery.

crease in add-on per cent. This may be due to the introduction of crosslinks in a swollen fiber.

From the primary thermograms of the parent and HMDI-modified PVA fibers, the values of decomposition temperature T_D at different weight losses, the initial decomposition temperature (IDT), and the integral procedural decomposition temperature (IPDT) were calculated, and these are given in Table II. In the case of the sample with an add-on per cent of 2.139, there seems to be a slight improvement in the thermal stability as seen from IDT and IPDT values. In the case of samples with higher degree of crosslinking, no improvement in thermal stability was observed. Probably, crosslinking initially reduces the rate of elimination of water by blocking "zips" but on increasing number of tertiary hydrogens would subsequently increase the rate of oxidation, reducing stability again.

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