JOURNAL OF APPLIED POLYMER SCIENCE VOL. V, ISSUE NO. 17, PAGES 606–611 (1961)

Improved Dyeability of Polyacrylonitrile Fibers by Radiation Grafting with Vinylpyrrolidone

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INTRODUCTION

The formation of graft polymers by high energy radiation has been intensively studied in many laboratories since the early work of Chapiro and others.[1,2] Several reviews have been written on the subject.[3,4] Grafting a monomer A on a formed polymer substrate can give the formed article many of the chemical properties of the polymer A.

Polyacrylonitrile fibers, while having many desirable physical properties, do not have optimum dyeability characteristics. If the fiber is to be used as a blend with another fiber, such as wool, it should respond to a dye treatment in the same manner as the wool. In order to get this dyeability, a substance which will take up the dye molecule is generally added. There are disadvantages to such additions. If the addition is made by making a copolymer of the acrylonitrile with a dye receptive monomer, some of the desirable physical properties of the polyacrylonitrile backbone may be lost. On the other hand, if the addition is made by impregnating the fiber with the dye receptive substance, there are two possible sources of trouble. First, the dye receptive substance—with the dye—may leach out during subsequent washings, and, second, lack of thorough penetration of the dye receptor may cause the fiber to "ring dye," giving a color gradient from the sheath to the center of the fiber.

Ideally, the dye receptor should be grafted to the polymeric backbone of the fiber and, before grafting, should be able to swell the fiber polymer sufficiently so that thorough penetration of the dye receptor into the polymer is assured. In the absence of the ability of the receptor to swell the base polymer, it should be a small enough molecule so that it can penetrate the structure of the individual fiber filament. Use of a grafting technique assures that the polyacrylonitrile backbone remains intact, giving the desirable physical properties, and the receptor will not leach out. Use of a polymerizable dye receptor permits the utilization of a small molecule capable of diffusing into the polyacrylonitrile structure before being polymerized in place to give the added desirable chemical properties.

EXPERIMENTAL

Electron irradiations were performed using a 2 m.e.v. Van de Graaff accelerator. X-irradiation was carried out with The Dow Chemical Company's 10 kcurie Co^{06} source, with a Machlett OEG-50 x-ray tube operating at 45 kv. and 45 mamp., and with the above Van de Graaff accelerator using a tungsten target. Dosimetry, in the case of x-rays, was done with the ferrous sulfate dosimeter using $G = 15.6$. In the case of electron irradiation, radiation doses were calculated from beam currents and voltages taking into account scatter and absorption. In absolute values, the electron doses may be in error as much as 15%, but the relative doses among separate experiments are probably correct to within 5%. Wherever possible, the vinylpyrrolidone monomer bath and the fiber take-up reel were shielded from the scattered radiation. Where not possible, corrections were made by running control samples. The polyacrylonitrile fiber used was obtained from the fiber division of The Dow Chemical Company. Fibers in both the "wet stretched gel" state and the "unstretched gel" state were used.

Two separate methods were used for grafting. In the first method, the fiber was saturated with a deaerated aqueous solution of vinylpyrrolidone and then exposed to radiation until the desired amount of vinylpyrrolidone had been grafted to the polyacrylonitrile. The grafted fiber was then scoured, a portion of it dyed, and a portion analyzed for polyvinylpyrrolidone graft. For the second

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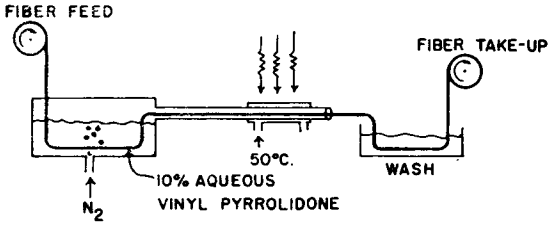


Fig. 1. Mutual method—low dose rate.

method, the fiber was saturated with deaerated vinylpyrrolidone solution as before, irradiated for a short time, and then the graft polymerization finished by heating the fiber and its adhering solution outside of the radiation field. It was then scoured and dyed or analyzed as before. Diagrammatic sketches of these methods are shown in Figures 1 and 2.

Dyeing was done with a direct dye, Calcodur Pink 2BL, manufactured by American Cyanamid Company. After dyeing and washing, a "reflectance value" was obtained. This is a measure of the amount of 520 mμ light from a standard source reflected from the dyed sample. An arbitrary scale of from 0–100 reflectance units was used with the light reflected from a white tile giving a reflectance of 100 and total absorption being zero. Lower numerical values indicate greater dye receptivity. Values of 23–25 were desirable. Analysis for vinyl pyrrolidone grafted to the fiber was made by dissolving the fiber in dimethylformamide and observing the carbonyl deformation at 7.8 μ by infrared techniques.

RESULTS AND DISCUSSION

The low dose rate one-step process is shown in Figure 1. The lower the dose rate, the less total radiation dose is needed to graft a given amount of vinylpyrrolidone to the polyacrylonitrile backbone. Figure 3 shows some data. This effect is to be expected for a radiation induced free radical reaction. In a simple radical chain reaction with

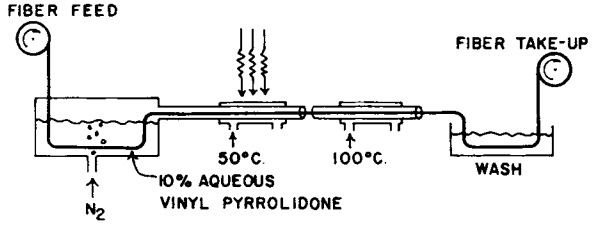


Fig. 2. Electron irradiation grafting method—high dose rate.

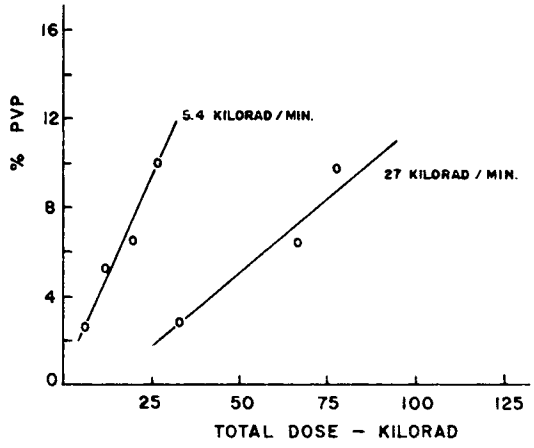


Fig. 3. Effect of dose rate and total dose on PVP pickup.

biradical termination, the dose necessary for a given yield of product is proportional to the square root of the dose rate. This is a consequence of the biradical termination and radical–molecule propagation.

The dyeability, however, is not strictly a function of the polyvinylpyrrolidone content of the fiber. It also depends on the length of the polyvinylpyrrolidone side chains and therefore on the number of side chains. Variations in the dose rate apparently cause variations in the length of the side chains so that, at a lower dose rate, less polyvinylpyrrolidone is necessary for "proper" dyeability. Figure 4 is a plot of the "reflectance" or dyeability, plotted against total dose at different dose rates. At 5400 rad/min., less than 6% grafted polyvinylpyrrolidone on the fiber gives proper dyeability while, at 27,000 rad/min., about 7% is necessary.

Rather early in the investigation it became apparent that oxygen inhibited the polymerization of vinylpyrrolidone. This was expected, since the

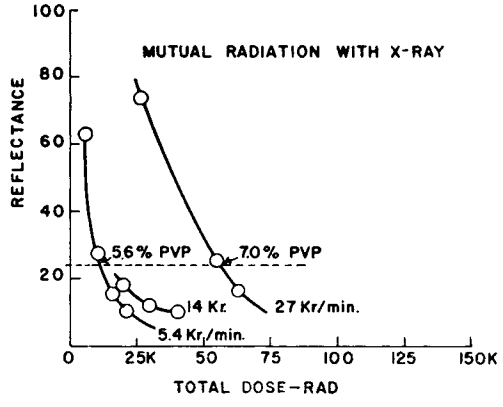


Fig. 4. Effect of dose rate on total dose required.

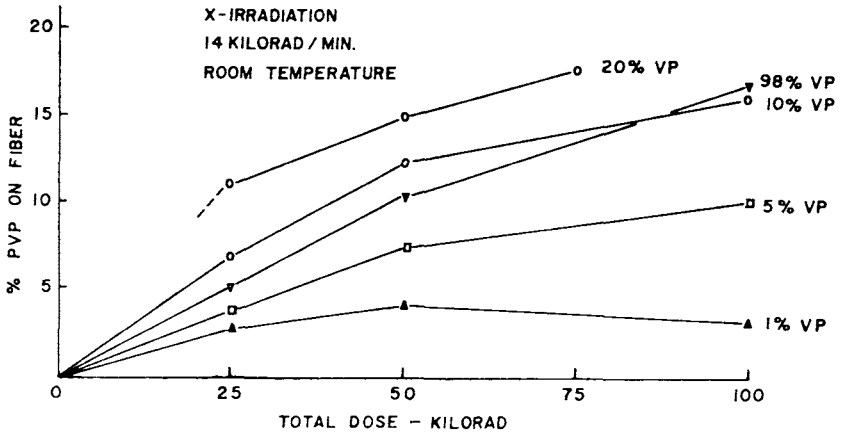


Fig. 5. Effect of vinylpyrrolidone concentration.

polymerization goes by a free radical mechanism and oxygen is known to inhibit free radical polymerization. A few per cent oxygen in the atmosphere during irradiation was sufficient to cause greatly decreased and nonuniform grafting. To remove the oxygen, nitrogen was blown through the vinylpyrrolidone impregnating bath and the bundle of fibers was agitated violently while passing through the bath. Certain inorganic salts could be added to the bath so that small amounts of oxygen were not disastrous. In fact, the nitrogen purge gas could contain as much as 0.3% oxygen when some of these salts were used. Purging only the irradiation chamber did not remove the oxygen trapped in minute air bubbles in the fiber bundle itself.

The concentration of vinylpyrrolidone in the aqueous monomer impregnating solution was varied from 1–98%. The results are shown in Figure 5. The behavior follows the results of Ballantine and Manowitz[5] on the γ-ray polymerization of vinylpyrrolidone from aqueous solution. They found a maximum conversion setting in at about 20–25% monomer in water. This maximum is probably a consequence of competition between the vinylpyrrolidone and the water for the absorption of the radiation, complicated by the transfer of energy from the solvent to the solute and the action of the H and OH radicals formed in the water on the solute. However, the higher the monomer concentration in the impregnating bath, the greater was the per cent homopolymer formed instead of graft polymer. In this process, the polyvinylpyrrolidone homopolymer is washed out in the final stage and hence would be wasted. A bath containing 10% vinylpyrrolidone was settled upon as a compromise.

At a given dose and dose rate, increasing the temperature during the irradiation resulted in a product that dyed deeper and smoother (less streaking). Figure 6 shows these results. The upper temperature limit is controlled by the fact

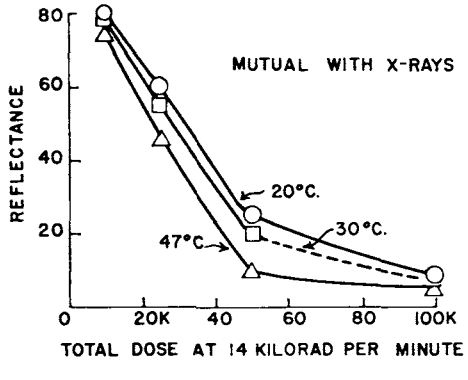


Fig. 6. Effect of temperature during radiation on dyeability.

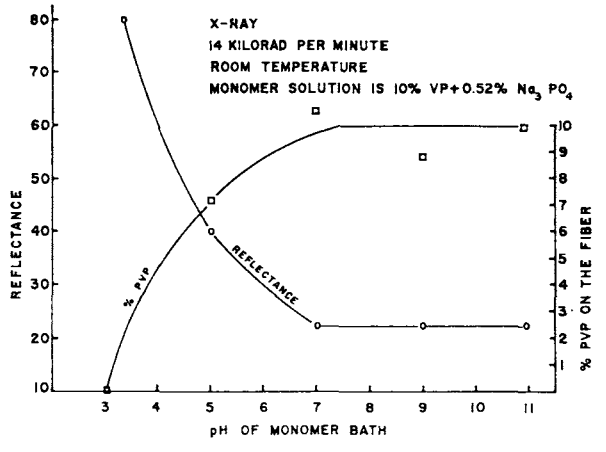


Fig. 7. Effect of pH on VP grafting and dyeability.

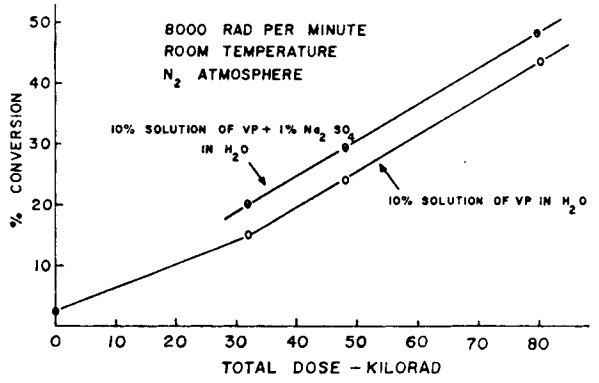


Fig. 8. Effect of Na_2SO_4 on x-ray induced polymerization of vinylpyrrolidone.

that, at temperatures above 60°C., the physical properties of the fiber are changed. Not enough polyvinylpyrrolidone analyses were made on the fiber to determine whether the increased dyeability was due to an increased amount of vinylpyrrolidone graft to the fiber at elevated temperatures or whether the elevated temperatures gave polyvinylpyrrolidone side chains that were better dye acceptors.

The inorganic salts that were added to the vinylpyrrolidone impregnating bath served several purposes. They acted as wetting agents, seemed to control the pH, and, in some cases, seemed to remove a polymerization inhibitor from the system. Figure 7 shows the effect of pH on the amount of vinylpyrrolidone grafted to the fiber and the reflectance of the dyed fiber. Typical of the agents used were mixtures of Na_3PO_4 and Na_2SO_4. Figure 8 shows the action of 1% Na_2SO_4 in enhancing the radiation polymerization of vinylpyrrolidone from a water solution.

The physical properties of the polyacrylonitrile fiber are not changed by the small amount of radiation received. Tests of yield strength, tensile strength, and Young's modulus show no change greater than the statistical variation of the unirradiated fibers. Larger amounts of radiation do give decreased values for these three tests, especially when the fibers are tested in a wet condition.

The radiation grafting is equally effective at a given dose rate whether high energy electrons, Co^{60} gamma rays, or x-rays are used. The choice of radiation depends only on the penetration desired and the economics of the irradiation source.

The two-step process shown in Figure 2 takes advantage of the long lifetime of the radicals formed during the irradiation. During a short irradiation, initial grafting of the vinylpyrrolidone on the polyacrylonitrile takes place and some homopolymer formation of the vinylpyrrolidone in solution begins. The radicals at the ends of the polyvinylpyrrolidone chains (whether graft or homopolymer) have a relatively long lifetime. By raising the temperature, the thermal polymerization reaction can now be accelerated. Thus, the grafted chains will grow and the homopolymer chains either grow or chain transfer to form new graft sites and

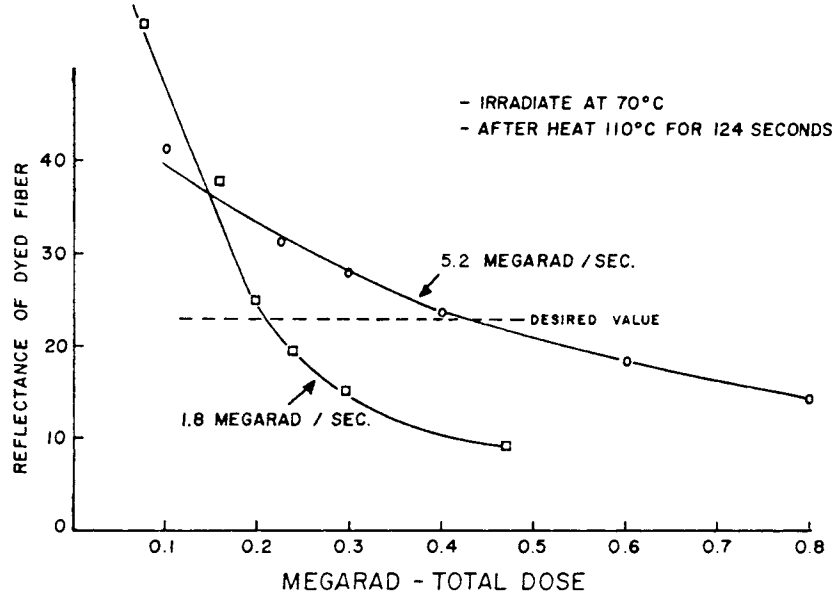


Fig. 9. Dose required in two-step process.

side chains. The total radiation dose needed in this system is thus just enough to start a sufficient number of graft side chains. Relatively high dose rates can be applied for a short time.

The actual dose required is a function of the dose rate, temperature during irradiation, temperature of the afterheat, and length of time in the afterheat section. In general, the higher the dose rate, the greater is the total dose required. Figure 9 shows the effect of total radiation dose at 1.8 Mrad/sec. and at 5.2 Mrad/sec. The radiation necessary for adequate grafting has almost doubled due to the higher dose rate. At 90 Mrad/sec., which corresponds to the highest dose rate obtainable from our electron accelerator, about 3 Mrad is required.

Because of the experience gained while developing the one-step method, the temperature during the irradiation was never lowered below 50°C. Raising the irradiation temperature did not affect the process outside of experimental variations. The temperature in the afterheater section, however, is extremely important. The higher this temperature, the shorter is the time necessary for the graft to go to completion. However, if the wet fiber dries, the desirable physical properties are lost. Putting the fiber in an oven at 150°C. for 40–45 sec. gives equivalent results to putting it in an oven at 115°C. for 120–130 sec.

The two-step process has several advantages over the one-step, low dose rate process. At the low dose rate of kilorads per minute, the fiber is in the radiation zone for several minutes. At the high dose of the two-step process, the fiber is in the radiation zone only tenths to hundredths of a second. Radiation energy at the high dose rates are available today at reasonable costs from electrostatic accelerators and resonant transformers. Finally, in the two-step process, the amount of homopolymer formed along with the graft is less than with the one-step process. This homopolymer is removed in washing and must be discarded. Unreacted monomeric vinylpyrrolidone is recycled.

The two-step process does degrade the polyacrylonitrile fiber slightly. Table I shows the physical properties of the treated and untreated wet fiber. The first part of the table shows the treatment the fiber received and the second part gives the physical properties. All irradiations were carried out at 70°C. in a nitrogen atmosphere using a 10% aqueous solution of vinylpyrrolidone as the impregnating bath.

A number of attempts were made to use the pre-

TABLE I
Effect of Process on Wet Physical Properties

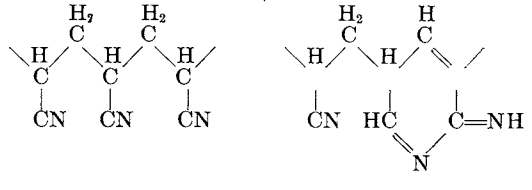
A. TREATMENT

Run No.	Dose, Mrad	Dose rate, Mrad/sec.	Afterheat Temp., °C.	Afterheat Time, sec.
A	0.2	1.8	110	124
B	0	0	112	124
C	Untreated fiber (blank)			
D	0.4	5.2	153	41
E	0	0	153	41

B. PROPERTIES

Run No.	Tensile, g./d.	Extens., %	Yield	Young's Mod.
A	2.5	34	0.85	36
B	2.7	44	0.95	36
C	2.7	44	1.03	38
D	2.4	37	0.76	32
E	2.5	43	0.85	36

irradiation technique to graft vinylpyrrolidone to the polyacrylonitrile fiber. The polyacrylonitrile was irradiated with electrons or x-rays at many different doses and dose rates, in air and in N_2 atmospheres. After irradiation, the polymers were immersed in vinylpyrrolidone solutions or pure vinylpyrrolidone. In cases in which enough vinylpyrrolidone had been grafted so that the dyeability of the resultant fiber had increased to a point that became interesting, the radiation dose had been high enough to cause appreciable degradation of the polyacrylonitrile backbone. The degradation was evidenced by yellowing of the fiber and a decrease in elongation. This preirradiation technique is generally the technique of choice when one desires to graft a radiation sensitive monomer to a less sensitive backbone. It depends on the relatively long lifetime of the radicals formed when the backbone is irradiated. With polyacrylonitrile, most of the radicals formed are probably fairly short lived. Radicals produced on the polymeric chain can discharge to form the intramolecular ring structure which is postulated for thermal degradation, thus they are not available to initiate vinylpyrrolidone grafts.



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Synopsis

X-ray, γ-ray, and electron irradiations are used to graft vinylpyrrolidone, a dye acceptor molecule, to a synthetic fiber, polyacrylonitrile. Two processes are described. In one, doses of 10–60 krad are given to the polymer–aqueous monomer system at dose rates of 3–27 krad/min. In the other process, 0.2–3.0 Mrad is given the system at 0.5–90 Mrad/sec., followed by a heat treatment to elongate the graft side chain. Oxygen inhibits the grafting and various inorganic salts such as sulfates and phosphates enhance the grafting.

Résumé

Les rayons-X, les rayons-γ et des irradiations électroniques ont été employés pour greffer la vinylpyrrolidone comme molécule acceptrice à une fibre synthétique de polyacrylonitrile. Deux processus sont décrits. Dans le premier, des doses de 10 à 60 Krads sont fournies au système polymère-solution aqueuse de monomère à des vitesses de 3 à 27 Krads par minute. Dans l'autre processus, 0,2 à 3 Mrads sont donnés au système à des vitesses de 0,5 à 90 Mrads par seconde suivi d'un traitement à chaud pour allonger le côté greffé de la chaîne. L'oxygène inhibe le greffage tandis que différents sels inorganiques comme les sulfates et les phosphates l'augmentent.

Zusammenfassung

Röntgen-, γ- und Elektronenstrahlen wurden zum Aufpfropfen von Vinylpyrrolidon, einem Farbstoffacceptor, auf eine synthetische Faser, Polyacrylnitril, verwendet. Zwei Prozesse werden beschrieben. In einem werden Dosen von 10–60 kilorad auf das System Polymeres-wässriges Monomeres in Dosisgeschwindigkeiten von 3–27 kilorad pro Minute einwirken gelassen. Im anderen Prozess wird das System mit 0,2–3,0 megarad bei 0,5–90 megarad pro Sekunde mit anschliessender Hitzeeinwirkung zur Verlängerung der aufgepfropften Seitenketten behandelt. Sauerstoff verhindert den Pfropfungsprozess, verschiedene anorganische Salze, wie Sulfate und Phosphate, beschleunigen ihn.

Received March 22, 1961