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PRELIMINARY STUDIES ON 1-VINYL-2-PYRROLIDONE GRAFTING ONTO CELLULOSE BY PRE-IRRADIATION METHOD

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ABSTRACT

Cellulose is considered a renewable biopolymer most abundant in nature. Better functional surfaces can be obtained by modifying cellulose. On the other hand, poly vinyl pirrolidone, PVP, is a synthetic, nontoxic, water-soluble polymer frequently used in a extensive variety of applications including several pharmaceutical applications. Grafting 1-vinyl-2-pyrrolidone, NVP, onto polymeric cellulose can be obtained by ionizing radiation. Ionizing radiation grafting can be affected by several factors as environment, solvent, monomer concentration, temperature of graft reaction. Grafting by ionizing radiation can be performed by three methods, pre-irradiation, oxidation by peroxide and simultaneous irradiation. In this study, it was used pre-irradiation method of cellulose. Paper filter without ash, NVP without purification was used in this study. Paper samples were exposed to electron beam from Dynamitron Accelerator with radiation absorbed dose of 25 kGy. Influence of NVP concentration, temperature of reaction after irradiation on degree of grafting (DG) was studied. Also, cellulose radicals of grafted paper samples was studied by electron paramagnetic resonance using a Bruker X-band ESR at room temperature just after heating reaction. Small decrease of cellulose radicals was observed with increasing reaction temperature. It was observed DG small increase with increasing concentration of monomer in solution of water:ethanol 50:50 v:v and rising temperature of reaction. Further tests using simultaneous method of grafting of NVP in cellulose paper, in water:ethanol 75:25 v:v solution, induced by gamma irradiation were performed. It was observed homopolymerization forming PVP with increasing monomer concentration.

1. INTRODUCTION

The cellulose has achieved considerable attention because of potential advantages they have as, biorenewable character, worldwide availability in a variety of forms, and low cost. Cellulose fibers have been used for centuries in traditional industries, such as papermaking, textile, then, after some time, had started to be used in medicine and analytical applications. A current addition to these several areas is associated to their surface modification extending their application to new fields as reinforcing agents in macromolecular composite materials, replacing glass fibers; pollutant traps for organic molecules in a water medium; metal-coated and magnetically active products [1].

New chemical groups that functionalizes cellulose fibers occurs predominantly at the cellulose OH groups. Monomers and polymers can be attached to those sites in order to obtain functional hybrid materials [1]. Belgacem Gandini (2008) [1] has cited that surface of cellulose fibers can be modified by corona, dielectric barrier and plasma discharges, and laser, γ-ray and vacuum UV radiations. They added that γ -irradiation of cellulose in the atmosphere leads to oxidation and degradation mechanisms, as expected due to high energy involved. They have found investigation that concerning that this type of treatment favors some cellulose crosslinking, as well as a decrease in crystallinity followed by thermal degradation, whose extent increases with increasing radiation absorbed doses.

It was cited by Barsbay et al [2] that graft copolymerization introduces advantageous modified properties to the surface of a base polymer with attractive volume properties. When grafting is carried out by means of ionizing radiation, grafting techniques is uncomplicated, economically attractive, without difficulty to control and guarantee grafting of variety of monomers that are difficult to graft by conventional methods without residues of initiators and catalyst.

According to Bhattacharya (2000) [3], reactions induced by ionizing radiation can be classified into two types: (I) crosslinking and scission and (II) grafting and curing. Grafting is a method where monomers are introduced on the surface of the polymer chain whereas curing is the fast polymerization of an oligomer and monomer mixture to form a coating, which bond by physical forces to the substrate. In grafting, covalent C–C bonds are formed and proceeds in three different methods: (a) pre-irradiation; (b) peroxidation and (c) simultaneous irradiation technique. In the pre-irradiation technique, the first polymer backbone is irradiated in vacuum or in the presence of an inert gas to form free radicals [3] or even in air presence and room temperature cellulose radicals' remains for some time [4]. On the other hand, with the simultaneous irradiation technique the polymer and the monomers are irradiated simultaneously to form free radicals and further addition reaction occurs. Since the monomers are not exposed to radiation in the preirradiation technique, the evident advantage of the method is that homopolymer formation is avoided, while occurs in the simultaneous grafting technique. However, the significant disadvantage of pre-irradiation technique is that scission of the base polymer can occur due to direct radiation effect, which leads predominantly the formation of block copolymers rather than graft copolymers. One example of application of NVP is therapeutic system for local release of prostaglandin based on hydrogel devices that had been developed by irradiation of N-vinyl pyrrolidone [3].

Fahmy et al. (2009) [5] have cited that PVP polymers have wide range of application, for instance, are film formers, protective colloid and suspending agents, dye-receptive agents, binders, stabilizers, detoxicants, and complexing agents. Furthermore, the authors mentioned that PVP can be crosslinked by heating in air at 150 ^{o}C, ionizing radiation and potassium persulfate. The mechanism of crosslinking of PVP chains by heating has not been definitely explained until that time [5].

Some paramagnetic products are stable for long times at room temperature and, can be observed using Electron Paramagnetic Resonance, EPR [6]. The radiation chemical reactions induced by absorption of radiation energy can occur at any carbon atom by hydrogen and hydroxyl abstraction or C–C and C– O bond scission in the cellulose chains, leading to radical formation. The radicals produced are trapped in the crystalline and semicrystalline

region of the cellulose structure. Stable radicals would decay through recombination reactions which may lead to crosslinking or grafting, in case of monomer presence [7].

In this study cellulose paper was irradiated with EB for pre-irradiation method and also, some tests on simultaneous method by gamma irradiation were performed.

2. EXPERIMENTAL

Cellulose filter paper JP41, J Prolab, with 80 g m^{-2} grammature, ash content 0,00009 g, pore size 28 μm, were cut into 2 × 2 cm^2, average mass 0,03494 ± 0,00225 g.
Solvent was prepared using deionized water and ethanol 50:50 v:v. It was used monomer of 1-vinyl-2-pyrrolidone, NVP, 99 % supplied by Aldrich Chemical Company, without purification, concentration of 10 %, 20 % and 40 % in volume in the mixture of solvent. All solvents were PA grade. Solution with monomer was prepared just before irradiation and dispensed in individuals' vials.

2.1. EB Irradiation

Cellulose papers samples were set in partially sealed bags and fixed above a foam ice (in order to try preserve high concentration of cellulose free radicals) and placed in a Pyrex tray, as shown in Fig. 1. Irradiation was performed at Electron Beam Accelerator, Dynamitron, at IPEN. Parameters of EB accelerator: energy of 550 keV, velocity 6.72 m min^{-1}, current 16.1 mA. With radiation absorbed dose of 25 kGy, dose rate 112 kGy s^{-1}.

2.2. Gamma Irradiation

Cut cellulose paper was immersed in NVP solution of water:ethanol 75:25 v:v with 5 %, 10 % and 20 % concentration of monomer placed in glass flasks. It was also prepared 1 blank sample non-irradiated containing 20 % NVP concentration and, another without monomer, just solvent irradiated. Gamma irradiation was performed using a Gammacell with absorbed dose of 10 kGy and dose rate 0.75 kGy h^{-1}.

Figure 1: EB arrangement for paper samples irradiation, radiation absorbed dose of 25 kGy at low temperature (frozen foam ice).

2.2. Heating step

As soon as irradiation had finished, irradiated piece of paper was placed in each of the already prepared solution flasks.
It was used several temperatures for the water heated bath, at first from 40 to 70 ^{o}C and afterwards other set of test with 70 and 80 ^{o}C, as shown in Fig. 2. Temperature was measured using a thermocouple coupled to multimeter, ICEL, MD 5660C model.
After 4h of reaction, grafted paper with NVP samples were washed with solvent mixture and acetone. For drying it was used vacuum oven Marconi, MA 030/12 model. It was used temperature of oven 60 ^{o}C and -700 mmHg pressure for 120 h.

Figure 2: Heating reaction arrangement.

2.3. Degree of grafting

For weight measurements it was used Mettler, model M5SA.
Degree of grafting was calculated using Equation 1:

$$DG\ (\%) = \frac{W_f - W_i}{W_i} \times 100. \quad (1)$$

where

W_f is mass of grafted paper, W_i is mass of paper before reaction.

2.4. Electron paramagnetic resonance, EPR

Electron Paramagnetic Resonance, EPR, spectra were obtained at room temperature using Bruker EMX plus model, X band, interval from 321.9 to 361.9 mT, field modulation amplitude 0.2 mT, field modulation frequency 100 kHz, microwave power 2 mW. Samples of cellulose paper filter were cut with 2×25 mm^2 and EB irradiated above foam ice with 25 kGy radiation absorbed dose (Fig. 1). After irradiation, paper samples were immersed in the NVP already prepared solution. Few minutes (~10min) after heating reaction EPR spectra were obtained.

3. RESULTS AND DISCUSSION

It was found in the literature that ionizing radiation induces cellulose free radicals formation [4,7,8,9].

3.1. Cellulose radicals

The radiochemical reactions caused by absorption of radiation energy can occur at any carbon atom by hydrogen and hydroxyl abstraction or C-C and C-O bond inducing random chain scission in the cellulose chains, leading to two radicals' formation [7,8]. Kameya and Ukai (2013) [8] showed in their study the chemical structure of cellulose before and after irradiation, and free radical carbon position, represented in Fig. 3. Cellulose radical formed by gamma irradiation of contemporary paper and its decay was studied previously [4] and it is similar to the observed is this study, as shown in Fig. 4.

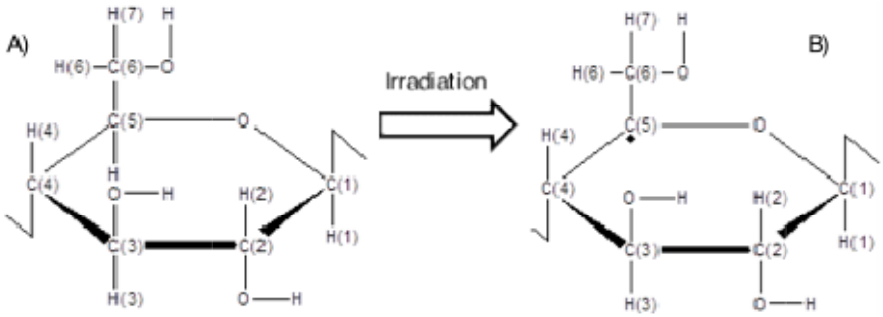

Figure 3: The chemical structure of the cellulose radical. A) before irradiation and B) after irradiation [8].

Even after heating with 40 °C and 50 °C, still high concentration of cellulose radical was observed by EPR, added to the time used for reaction (2h). It was observed in previous study [4] that at room temperature half life of cellulose radical was 55 h.

Cellulose radical concentration decreases with increasing temperature of reaction. It can be attributed to the energy from heating to the own reaction of cellulose radicals inducing crosslinking or degradation, or grafting NVP monomer into cellulose.

Also, it was observed that EPR signal of cellulose radical of sample reacted with higher temperatures shifts to higher magnetic field, indicating that some grafting should have occurred.

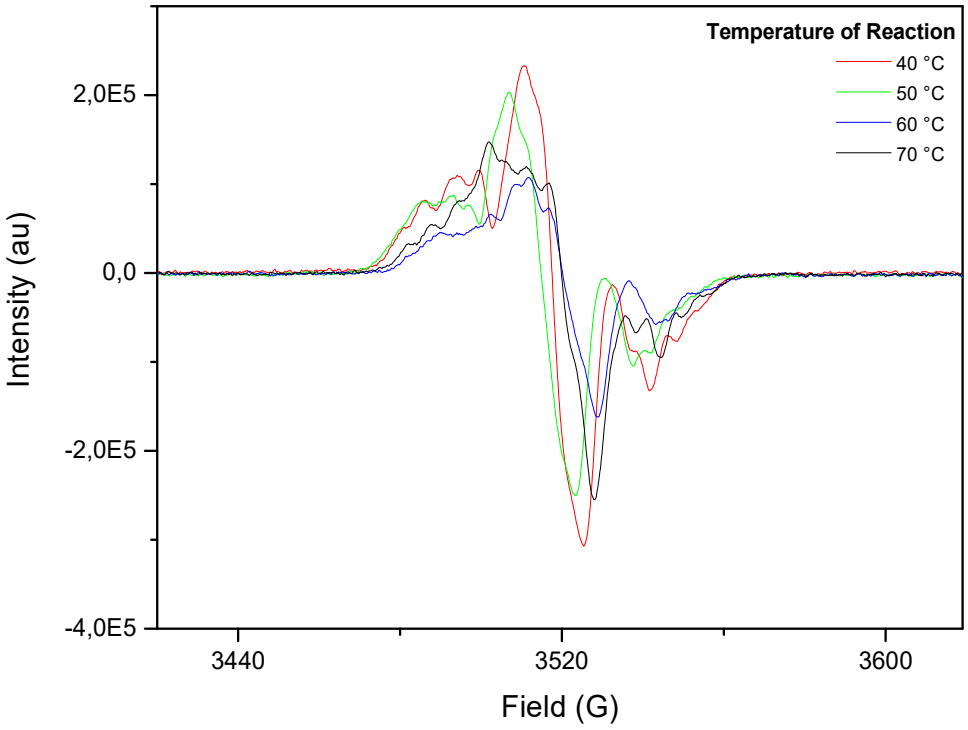

Figure 3: EPR spectra of cellulose paper EB irradiated with 25 kGy, after immersion in 20 % NVP concentration in water:ethanol, 50:50, v:v solvent mixture and reaction at several temperatures.

3.2. Degree of grafting, DG

Results of degree of grafting behavior with NVP concentration variation and two temperatures of reaction, 70 ^{o}C and 80 ^{o}C, are shown in Table 1.

DG results was not high as expected, Belgacem and Gandini (2008) [1] studied surface treatment of several kinds of cellulosic materials. They mentioned that depending on the solvent used, it is possible to induce mainly surface functionalization or reaction, preserving bulk matrix. In our study we used 50:50, v:v, water:ethanol solvent. Probably this solvent ratio was not efficient on the swelling of cellulosic fibers of paper.

Table 1: Degree of grafting, monomer concentration and temperature of reaction.

Reaction (°C)	Concentration of NVP (%)	Initial Mass (g)	Final Mass (g)	Degree of grafting (%)
70	10	0.03698	0.03697	1.41
	20	0.03394	0.03444	2.94
	40	0.03545	0.03802	8.70
	10	0.03414	0.03417	1.53
	20	0.03480	0.03505	2.15
	40	0.03644	0.03922	9.09
80	10	0.03732	0.03716	1.28
	20	0.03283	0.03364	4.19
	40	0.03517	0.03976	14.77
	10	0.03476	0.03480	1.84
	20	0.03617	0.03732	4.91
	40	0.03502	0.03793	10.04
25	40	0.03383	0.03493	

Eventhough DG was not high, it increased with increasing monomer concentration, as observable in Fig. 4. Furthermore, increasing temperature of reaction DG increases at a little higher extent. Taking into account half life of cellulose radicals [4], one alternative would be to increase time of reaction. Another option would be increase water content on the solvent ratio in order to increase swelling of cellulose paper.

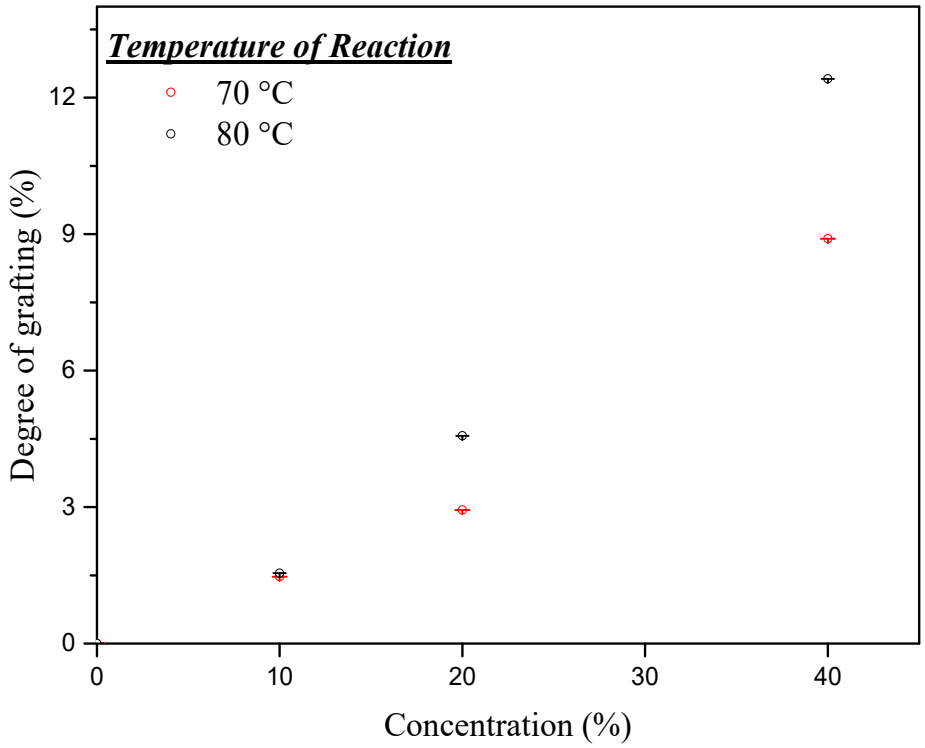

Figure 4: Effect of NVP concentration on degree of grafting, DG, reaction temperature of 70 ^{o}C and 80 ^{o}C.

3.3. Simultaneous grafting preliminary results

Increasing NVP concentration induces increase of PVP homopolymer formation with the same gamma radiation absorbed dose of 10 kGy, as shown in Fig. 5. Visually, it was observed that viscosity of remaining solution increased. With 20 % of NVP concentration it was very difficult to separate grafted paper from homopolymer formed, Fig. 5 C.

A B C

Figure 5: Simultaneous method of grafting of NVP onto cellulose in ethanol:water 25:75 v:v solution, using gamma radiation: (A) 0 %, 5 %, 10 % and 20 % NVP, left to right; (B) 10 % NVP and (C) 20 % NVP.

Further studies on the simultaneous method would be on irradiate cellulose with lower radiation absorbed doses.

4. CONCLUSIONS

It was possible to graft NVP to cellulose using pre-irradiation method, but to small degree of grafting. Concentration of 20 % of NVP lead to high homopolymerisation reaction, making difficult to remove grafted sample with 10 kGy gamma radiation absorbed dose.

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