Radiation Processing for Environment-friendly Industrial Applications

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SUMMARY. Radiation processing techniques are increasingly being applied to minimize the environmental pollution associated with many industries. In the present paper, three such processes are discussed that utilize high energy electron beam (EB) radiation for minimizing environmental pollution. Emission of sulphur containing toxic gases like H_2S is an undesirable side product of viscose-rayon process. EB irradiation can significantly decrease the pollution levels associated with the process by reducing the CS_2 requirement by 40%. EB based additive-free process can be utilized for converting the polytetrafluroethylene (PTFE) scrap into industrially useful microfine powder. Development of fast-response temperature-sensitive hydrogels that swell or shrink in response to small temperature changes in the environment is being sought to reduce the energy consumption levels of many processes. EB crosslinked poly(vinyl methyl ether) gels that swell/shrink about 100 times faster than conventionally crosslinked gels have been developed.

1. INTRODUCTION

The adverse environmental impact of increasing industrialization and use of energy intensive processes have stimulated search for new industrial processes to eliminate or minimize environmental hazards and at the same time produce better materials using less energy. High energy ionizing radiation, with its unique ability to induce chemical reactions in solid, liquid or gas phase at any desired temperature without any catalyst, has many advantages. These include ability to process products in their final form, production of additive-free polymeric materials and energy savings. Thus, radiation technology, by producing better quality products, imparting unique properties to materials and increasing energy efficiency has always been *indirectly* an environment friendly process. However, in recent years this technology is being addressed to *directly* provide answers to many environmental challenges viz. flue-gas treatment, Sato et al. (1), waste water treatment, Chmielewski et al. (2) and plastic waste disposal, Ait et al. (3). Our efforts have been aimed at utilizing the benefits of radiation technology for specific processes of importance to Indian industry. The results of some of these studies are presented.

2. PROCESS STUDIES AND RESULTS

2.1 Viscose-rayon Process

Due to a very tight hydrogen-bonded structure, cellulose can neither be easily dissolved, nor melted and hence this technology depends upon a very convoluted process where cellulose chains are forced apart by reaction of carbon disulphide (CS_2) with soda cellulose, which subsequently decomposes in acid bath to yield rayon fibre; the process generates sulphur containing decomposition products of xanthates which pollute the atmosphere. Rayon manufacture around the world has diminished over the last few years for this reason. The industry is therefore examining appropriate ways to reduce the levels of these emissions in atmosphere. It has been observed that the radiation treatment of paper pulp, increases its sensitivity to enzymatic hydrolysis and its solubility in CS_2; this markedly reduces the quantity of CS_2 required in the viscose process, Charlsbey (4). We have studied the effect of EB treatment on indigenous paper pulp on a laboratory scale to standardise the conditions to obtain the desired degree of polymerization. The effect of radiation dose on the various chemical properties of the paper pulp is presented in Table 1. The results clearly indicate that a dose of 5 to 10 kGy can reduce the degree of polymerization (DP) of pulp from 625 to about 400-450. In the conventional process, this is achieved by steeping the pulp with alkali for long durations. For the EB treated paper pulp, the quantity of CS_2 required is reduced by about 40% ; a plant consuming about 300 tons of pulp per day can reduce the CS_2 consumption by 40 tons a day.

2.2 Radiation Degradation of Polytetrafluoroethylene (PTFE)

The microfine PTFE powder, due to its outstanding anti-friction properties and non-toxic nature, is extensively used as a non-stick coating material for kitchenware and electric appliances. The polymer, however, is extremely resistant to pulverization and when pulverized by cooling it to -180°C, the high molecular weight powder thus produced has a tendency to progressively agglomerate. It is well known that PTFE predominantly undergoes chain scission on exposure to radiation, therefore its molecular weight can be significantly reduced by irradiation. It was observed that an EB dose of 1-2 MGy was adequate for producing a low molecular weight (1×10^4 - 1×10^5) product amenable to conventional high speed grinding.

Figure 1 shows the particle size distribution of PTFE powder produced by this process using conventional high speed grinding techniques.

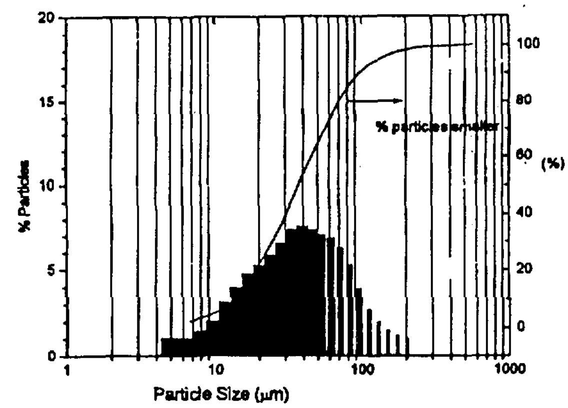

Figure 1: Particle size distribution of EB radiation degraded PTFE.

2.3 EB Crosslinked Fast Response Temperature Sensitive Hydrogels

Generally, aqueous solutions are concentrated by evaporating the water at high temperatures. This is an energy consuming process. Environmentally sensitive polymer gels are an alternative for concentrating many biological slurries near room temperature. These gels display phase transitions in response to small environmental changes, viz. pH, temperature, solvent composition and electric field.

Table 1. Effect of EB radiation dose on the properties of paper pulp for rayon.

Property	EB Irradiation Dose (kGy)				
	0	5	10	15	20
Viscosity, cp	10.84	7.26	6.30	5.13	4.33
Degree of Polymerisation	635.0	461.0	399.0	310.0	236.0
Alpha Cellulose, %	95.13	94.18	92.69	91.63	87.61
Beta Cellulose, %	3.61	4.44	5.70	6.67	10.63
Gamma Cellulose, %	1.26	1.38	1.60	1.70	1.76
Rayon Yield, %	97.52	97.07	97.06	96.79	96.02

Temperature sensitive gels are produced by crosslinking linear polymers that display lower critical solution temperatures (LCST), e.g. poly (vinyl methyl ether) (PVME) and poly (N-isopropyl acrylamide) (PNIPAm). However, the conventional method of crosslinking these polymers by thermochemical route, leads to the formation of homogeneously crosslinked material with an extremely slow response, rendering them unsuitable for industrial applications. For instance, a conventionally crosslinked 1 mm thick sheet of temperature sensitive PNIPAm hydrogel takes more than 24 hours to swell or shrink to equilibrium, Hoffman et al (5). This slow response is due to the fact that the conventionally crosslinked gels are homogeneous to atleast a submicron level. Our recent pulse radiolysis results have shown that by irradiating the aqueous solutions of these polymers at high dose rates with EB accelerators, inhomogeneous crosslinking can be induced, resulting in the formation of fast-response hydrogels, Sabharwal et al, (6,7). We have used irradiation to create inhomogeneous crosslinking of a temperature sensitive polymer- PVME, so as to produce a fast response hydrogel which undergoes a phase transition at 37°C. Figure 2 shows the swelling behaviour of a few hydrogels at various temperatures. The curve clearly indicates a

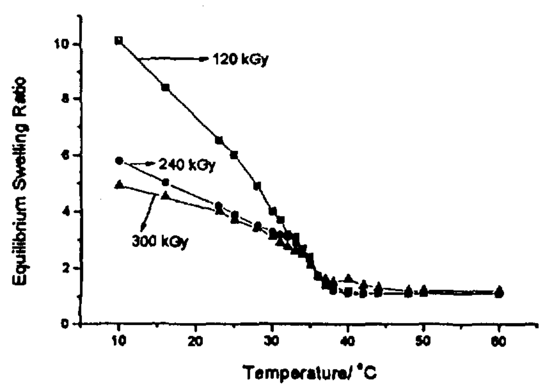

Figure 2: Equilibrium swelling behaviour of EB crosslinked PVME hydrogels at different temperatures.

transition point at 37°C. The hydrogel is produced by irradiating linear PVME to a dose of 300 kGy. The coefficient of diffusion of polymer(D) into water matrix has a value of about 10^{-5} cm^2s^{-1} as compared to conventional hydrogels which generally have (D) value of about 10^{-7} to 10^{-8} cm^2s^{-1}. EB processed gels therefore exhibit faster response time.

The swelling and deswelling response of these hydrogels, shown in Figure 3, clearly indicates that these hydrogels require just a few seconds to reach equilibrium swelling.

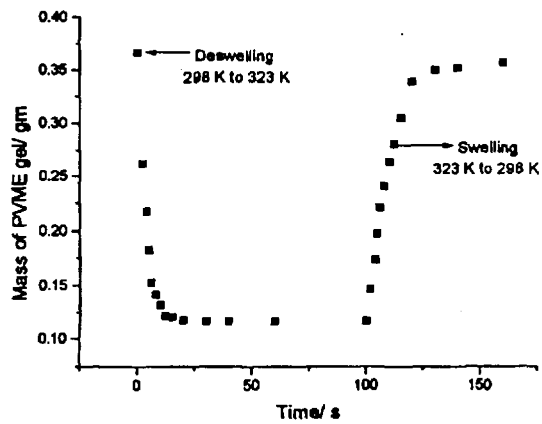

Figure 3: Swelling and shrinking kinetics of EB crosslinked PVME hydrogel.

These materials could be beneficial in reducing the energy requirements for a variety of applications, such as concentrating biological or coal slurries. We have studied the use of those hydrogels for concentrating dilute sewage sludge. In this study, the sludge (2% solids) from input line of Sludge Hyginisation Research Irradiator (SHRI) was used. The PVME gel equilibrated at the temperature of 323K was added to the sludge at 298K and allowed to swell to equilibrium for varying lengths of time (15s to 120s). The gel samples were then taken out, equilibrated at 323K for the same length of time as for swelling, so that they shrink and desorb water. The process was repeated for 10 cycles; the amount of water desorbed by the gel was estimated gravimetrically. The results of this study, shown in Figure 4, indicate that 1 g of gel could remove 9 to 12 g of water from 25 g of sludge, in ten cycles.

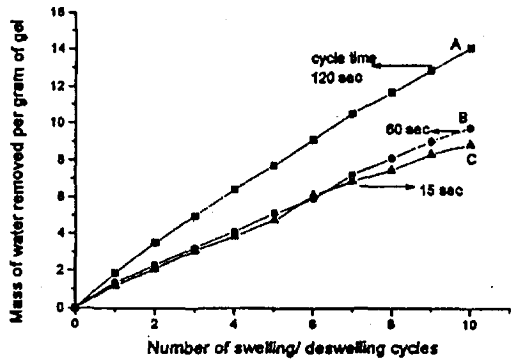

Figure 4: Dewatering behaviour of sewage sludge with PVME gels.

3. CONCLUSIONS

Radiation processing has great potential to reduce environmental pollution from chemical processing industries. EB treatment of pulp for viscose rayon industry, for recycling polymeric wastes and production of fast response temperature-sensitive polymers are promising areas wherein radiation technology can play a major role, provided reliable, high power and cost effective EB machines are available.

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