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DEVELOPMENT OF RADIATION PROCESSES FOR BETTER ENVIRONMENT

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Abstract

The increasing population and industrialization, worldover, is placing escalating demands for the development of newer technologies that are environment friendly and minimize the pollution associated with the development. Radiation technology can be of benefit in reducing the pollution levels associated with many processes. The sulphur vulcanization method for natural rubber latex vulcanization results in the formation of considerable amounts of nitrosoamines, both in the product as well as in the factory environment. Radiation vulcanization of natural rubber latex has emerged as a commercially viable alternative to produce sulphur and nitrosoamine free rubber. A Co-60 γ-radiation based pilot plant has been functioning since April 1993 to produce vulcanized natural rubber latex (RVNRL) using acrylate monomers as sensitizer. The role of sensitizer, viz. n-butyl acrylate in the vulcanization process has been elucidated using the pulse radiolysis technique. Emission of toxic sulphur containing gases form an inevitable part of viscose-rayon process and this industry is in search of ways to reduce the associated pollution levels. The irradiation of cellulose results in cellulose activation and reduction in the degree of polymerization (DP). These effects can reduce the solvents required to dissolve the paper pulp. There is a keen interest in utilizing radiation technology in viscose rayon production. We have utilized the electron beam (EB) accelerator for reducing the degree of polymerization (DP) of paper pulp. Laboratory scale tests have been carried out to standardize the conditions for production of pulp having the desired DP by EB irradiation. The use of irradiated paper pulp can result in ~40% reduction in the consumption of CS_2 in the process that can be beneficial in reducing the pollution associated with the process. PTFE waste can be recycled into a low molecular weight microfine powder by irradiation. An EB based process has been standardized to produce this powder for different industrial applications. "Responsive polymers", are being studied as energy saving materials for a number of novel applications. EB irradiation has been utilized to create inhomogeneous crosslinking in polyvinyl methyl ether to produce fast response hydrogels, that exhibit different swelling behaviour and faster response in comparison to hydrogels obtained by conventional methods.

1. INTRODUCTION

The radiation processing technology has been commercialized for last 30 years and has brought considerable economic benefits to a number of industries, specially the polymer industry by providing energy efficient processes for applications such as crosslinking, curing and degradation. In recent years, however, the focus of radiation processing has shifted to developing such technologies, that besides being economically beneficial, are environment friendly also. These include, flue-gas treatment, sewage sludge treatment, waste water treatment and polymer recycling. Our current studies have also

been directed towards developing the radiation based processes that are currently of relevance to Indian industries *viz.* radiation vulcanization of natural rubber latex, viscose-rayon industry, recycling poly tetrafluoroethylene (PTFE) waste into industrially useful product and synthesis of fast-response temperature sensitive hydrogels. The current status of these programmes as well results of our recent studies are presented in this paper.

2. ENVIRONMENT FRIENDLY APPLICATIONS OF RADIATION

2.1 Radiation Vulcanization of Natural Rubber Latex (RVNRL)

Natural rubber latex is an important raw material for many south -east Asian countries. India is also one of the major producers of natural rubber latex with an annual production of over 300,000 tons. A significant part of this is used for producing dipped goods such as rubber gloves, teats and soothers. It is now well established that the necessity of using chemical accelerators in conventional sulphur vulcanization of natural rubber latex results in the formation carcinogenic nitrosoamines in the environment as well as in the final product. As the society is realizing the harmful effects of formation and presence of such toxic chemicals, severe limits are being put on the concentration of nitrosoamines produced. The joint efforts put in by the RCA member countries during last 10 years have culminated in the development of a promising new technology- Radiation vulcanization of natural rubber latex (RVNRL) using nBA as sensitizer. This technology has now emerged as a commercially viable alternative to the conventionally sulphur vulcanized latex [1]. The radiation dose required for vulcanization has been brought down from the level of 200 kGy to about 15 kGy [2]. The product formed, besides having all the characteristics of conventionally crosslinked rubber, offers additional advantages such as absence of nitrosamines, low cytotoxicity and better transparency [3]. Realizing the benefits this technology can offer to the Indian rubber industry, a pilot scale rubber latex irradiator was commissioned at Kottayam, Kerala in April 1993. The plant has been designed to irradiate 1000 t of latex per year. In the initial stages, the plant was operated to produce 50 t/y of irradiated latex but after the successfully demonstrating advantages of this technology to Indian rubber industries, it is being scaled up to process 300 t of latex per year. The process of radiation vulcanization does not lead to formation of any nitosoamines during the process as well as in the product. Since, the process also does not require any sulpur and ZnO, the final product on incineration does not release any SO_2 and leaves much lesser ash content as compared to a conventionally vulcanized product. Thus, both the radiation vulcanization process as well as the product are environment friendly.

Latex being a natural product, the physico-mechanical properties of the radiation vulcanized products are dependent on the origin as well as micro nutrients present in the rubber. Presently, details regarding the understanding of the radiation chemistry of the natural rubber latex (NRL), crosslinking mechanism and the factors affecting it are not available in the literature because of the extremely complex nature of the rubber latex. It has been reported that about 50% of the sensitizer nBA added remains unutilized in the vulcanization process and has to be removed. Therefore, there is still a need for better understanding of the role of nBA in the vulcanization process. Our recent studies have been directed towards this objective. Monofunctional and polyfunctional acrylates are also widely used in radiation processing industry and their polymerization kinetics have been recently studied employing the pulse radiolysis technique [4-6]. We have also undertaken a study with the following two objectives in mind (i) to utilize the pulse radiolysis technique to study separately the reactions of RVNRL sensitizer n-butylacrylate (nBA) with the primary (and some selected secondary) radicals produced in the radiolysis of water

viz.·OH, H·, e^-_{aq}. (and $Cl_2^{\cdot -}$ in presence of dissolved Cl^- *etc.*) and subsequently study the decay behaviour of the transient radicals formed in these reactions in order to establish the primary mode of polymerization reaction and (ii) to apply the results obtained by pulse radiolysis studies to understand the vulcanization mechanism by studying the effect of specific radical and electron scavengers, having preferential solubility either in serum phase or in rubber phase, on the radiation crosslinking behaviour of natural rubber latex in presence of nBA. The time resolved pulse radiolysis results have shown that the transients produced by the reaction of nBA with both the primary radicals *i.e.* ·OH/H· approach the diffusion controlled limit with their respective bimolecular rate constant, k values being $5x10^9$ and $2x10^9$ dm^3 mol^{-1} s^{-1}. These transients subsequently tend to undergo dimerization reaction with their second-order decay rate parameters ($2k$) being $1x10^9$ dm^3 mol^{-1} s^{-1}. This clearly suggests that these transients preferentially undergoes a radical-radical recombination reaction (as in equation 1 and 2) and does not propagate the polymerization process.

$$nBA + \cdot OH \longrightarrow nBA\cdot \ (or\ nBAOH\cdot) + H_2O \quad (1)$$

$$2\ nBA\cdot \ (or\ nBAOH\cdot) \longrightarrow \text{permanent product} \quad (2)$$

In the presence of secondary oxidizing radicals, the formation of the radical cation transient (nBA^+) is resisted and has been observed only in the presence of a strongly oxidizing secondary radical $Cl_2^{\cdot -}$, the bimolecular formation rate constant being $2.4x10^6$ dm^3 mol^{-1} s^{-1} at pH 2, which shows that the cationic polymerization is also not a favorable route for nBA polymerization. On the other hand, the radical anion transient, nBA^- produced in the reaction of nBA with e^-_{aq} (formation rate constant value being $6.5x10^9$ dm^3 mol^{-1} s^{-1}) decays following first-order kinetics in presence of excess nBA in the solution. The high bimolecular rate constant k = $1.4x10^8$ dm^3 mol^{-1} s^{-1}, for the reaction indicates that the anion alone is capable of propagating the polymerization reaction and can enhance the vulcanization process .

$$nBA + e^-_{aq} \rightarrow nBA^- \quad (3)$$

$$nBA^- + nBA \rightarrow (nBA)_2^- \quad (4)$$

These results have been further confirmed from the effect of electron scavengers on the radiation vulcanization behavior of natural rubber latex in presence of nBA as sensitizer, wherein the electron scavengers having preferential solubility in the rubber phase exhibited a pronounced decrease in crosslinking [7].

2.2 Viscose-Rayon Process

The growth of petrochemical industry, energy and environmental problems have dealt a disastrous blow to the man made fiber industry. Of the two industrial processes used for regenerating cellulose in the fiber from pulp, the "cuprammonium" process has already become obsolete and the "viscose-rayon" process also is facing stiff regulations from environmental control agencies because of the emission of sulphur containing gases, such as H_2S, to the atmosphere. Therefore, suitable modifications in the process, that can result in lowering the associated pollution levels, are being sought. The effect of ionizing radiation on cellulose has been extensively studied during last 40 years. These studies have shown that irradiation of cellulose with high energy radiation results in two major effects *viz.* (i) it reduces the degree of polymerization (DP) and (ii) it results in the activation of

cellulose by altering its crystallites thereby increasing its sensitivity to process such as enzyme hydrolysis and solvation characteristics. Both these effects can be immensely beneficial to the viscose-rayon industry as reducing the DP by irradiation can eliminate the "aging" process necessary in the conventional technology, and enhancement of solvating characteristics of irradiated pulp can considerably reduce the requirement of CS_2 in the process. The viscose-rayon industry, worldover, has shown keen interest in adapting EB based technology in the manufacturing process. We have studied in collaboration with Indian industries, the effect of irradiation on the chemical-properties of the paper pulp. The results of these studies, shown in Table I, indicate that a dose of 5-10 kGy is sufficient to reduce the DP of paper pulp from 650-800 to about 400-450 that is generally achieved by the conventional aging process. The concentration of CS_2 required to dissolve the irradiated paper pulp was 18% as compared to the 34% for the conventional process. This can substantially reduce the consumption of CS_2 and hence reduce pollution levels associated with the process.

2.3 Recycling of Waste Poly tetrafluoroethylene (PTFE)

The high temperature stability coupled with chemical inertness and low coefficient of friction has made PTFE an industrially important polymer. However, its these very characteristics are also responsible for generation of PTFE waste during its processing, that is difficult to recycle. It is well known that PTFE on exposure to high energy radiation predominantly undergoes chain-scission and becomes very brittle and can be easily powdered. The low molecular weight PTFE has been found useful for many industrial applications such as dry lubricant, additive to paints for coating electric appliances and kitchenware. We have studied the effect of irradiating PTFE waste, with and without containing fillers, with the 2-MeV electron beam accelerator to various radiation doses. The PTFE after irradiation is milled and the micro-fine powder so produced is analyzed for its molecular weight and particle size distribution. From the Differential Scanning Calorimetry results, the molecular weight of the irradiated PTFE powder was determined to be $5x10^4$. Figure 1 and 2 show the particle size distribution of unfilled and 30% carbon filled PTFE powder respectively, produced upon exposure to 1MGy of EB radiation. These results indicate that the carbon-filled PTFE scrap results in a smaller size distribution as compared to unfilled PTFE scrap. Both these products have found useful for industrial applications.

2.4 Development of EB irradiated fast response hydrogels

A variety of crosslinked polymer gels display phase transitions resulting in an abrupt change in their swollen volume in response to specific environmental stimuli viz. temperature, pH, electric field, solvent composition, light intensity and specific chemical triggers like glucose. In recent years, interest in such gels, also termed as *responsive gels*, has increased as these gels are fast emerging as energy saving materials for many applications such as recyclable absorbents for concentrating solutions near room temperature. Gels which undergo volume transition due to change in temperature of environment are termed 'thermo responsive" gels. These type of gels shrink abruptly with an increase in temperature above a critical temperature which is near the lower critical solution temperature (LCST) of the linear polymer. Temperature sensitive gels are generally prepared by crosslinking polymers that display LCST, such as poly(N-isopropylacrylamide)(PNIPAAm), poly(vinyl acetate-co-vinyl alcohol) and poly(vinyl methyl ether)(PVME). The conventional techniques-chemical/physical crosslinking of

TABLE I : EFFECT OF EB IRRADIATION ON VARIOUS PROPERTIES OF PAPER PULP

Sr. No.	Particulars	Control	Set1	Set 2	Set 3	Set 4
	Electron Dose (Mrad)	------	0.5	1.0	1.5	2.0
1	Viscosity cp	10.84	7.26	6.30	5.13	4.33
2	Cellulose DP	635	461	399	310	236
3	Alpha Cellulose %	95.13	94.18	92.69	91.63	87.61
4	Beta Cellulose %	3.61	4.44	5.70	6,67	10.63
5	Gamma Cellulose %	1.26	1.38	1.60	1.70	1.76
6	S_{10} %	5.80	7.26	8.58	10.67	14.43
7	S_{18} %	2.92	3,44	3,58	4.12	4.93
8	$S_{10} - S_{18}$ %	3.88	4,82	5.00	6.55	9.50
9	$S_{21.5}$ %	2.48	2.93	2.94	3.21	3.98
10	Rayon Yield%	97.52	97.07	97.06	96.79	96.02
11	$S_{7.14}$ %	9.31	12.94	16.14	21.05	24.15
12	Copper No.	0.60	0.83	1.21	1.77	1.95
13	Pentosans %	3.04	2.88	2.85	3.09	3.20
14	Resin %	0.50	0.48	0.47	0.48	under test

linear polymers or by chemical conversion of one gel type into another, result in the formation of gels that are homogeneous to atleast a submicron level. Since the volume kinetics change of gel is controlled by the mutual diffusion of the polymer chains and the solvent, the rate of volume transition of these gels is very slow, typical diffusion coefficients being 0.8 - $8x10^{-7}$ cm^2 s^{-1} . For example, a 1 mm gel slab having a diffusion coefficient of 10^{-7} $cm^2 s^{-1}$ will need about an hour to reach equilibrium and over 6 hours to reach 90% of equilibrium in response to an external stimuli. These systems are therefore far too slow for many practical applications such as mechano-chemical actuators or switches. Our recent pulse radiolysis results have shown that by irradiating the linear polymer at extremely high dose rates as available from high energy EB machines, *inhomogeneous* crosslinking can be induced as the number of radicals per polymer chain increases instantaneously [8]. Under high dose rate conditions, the large number of

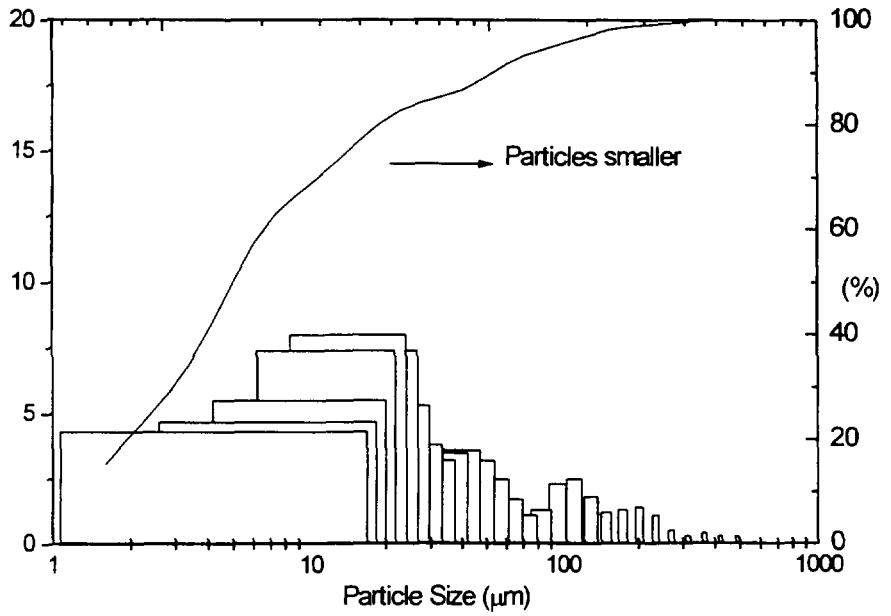

FIG. 1. Particle size distribution of unfilled PTFE scrap irradiated to 1 MGy.

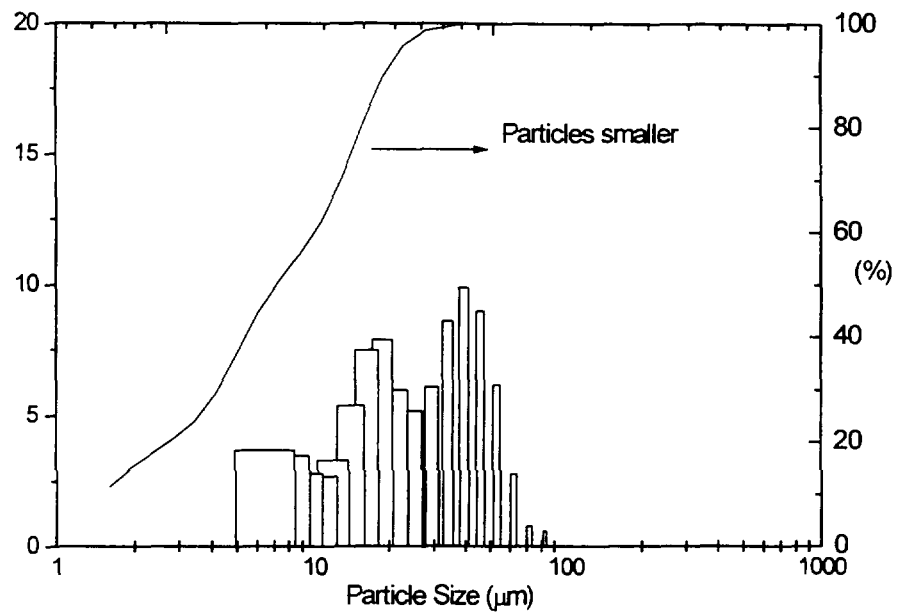

FIG. 2. Particle size distribution of 30% carbon filled PTFE irradiated to 1 MGy.

radicals produce tend predominantly undergo *intramolecular* crosslinking instead of intermolecular crosslinks and this results in the formation of fast-response hydrogels. We have irradiated 30 wt% aqueous solution of poly (vinyl methyl ether) (PVME) to 300 kGy of EB radiation to produce fast-response hydrogels that swell/shrink about 100 times faster than the conventionally crosslinked hydrogels. These hydrogels are being studied to concentrate biological slurries such as sewage-sludge which are otherwise difficult to concentrate. Our preliminary results have shown that such systems can be very effectively used to concentrate such solutions near room temperature thereby offering substantial energy savings.

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