ELECTRON BEAM APPLICATIONS IN CHEMICAL PROCESSING

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Abstract

Last results in the field of polymeric materials obtained by electron beam irradiation are presented. Two types of polymeric flocculants are described. The effects of radiation absorbed dose, radiation absorbed rate dose and chemical composition of the irradiated solutions upon the polymeric materials characteristics are also discussed. Preliminary results demonstrated that some polymeric flocculants characteristics, such as linearity and molecular weight were improved by using combined electron beam and microwave irradiation.

1 INTRODUCTION

Radiation research in the field of polymeric materials was developed over recent years at the Institute of Atomic Physics, with linacs of 6 MeV and output power in the range of 100 - 700 W. Thanks to remarkable properties of the electron beam technologies developed for our type of polymeric flocculants, it was proved that high energy linacs up to 10 MeV with modest electron beam power levels, from a few hundred to one kilowatt, such as our ALID-7 linac became economically attractive for commercial production [1-3].

2 RADIATION RESEARCH IN THE FIELD OF POLYMERIC FLOCCULANTS

During the period 1992-1996 a thorough study was made in the field of electron beam induced polymerisation of the aqueous solutions containing a mixture of appropriate monomers, initiators, complexing agents, chain transfer agents, in order to prepare polymeric flocculants for waste water treatment. First type of polymeric flocculant [1], a co-polymer of acrylamide and acrylic acid (PA type) was obtained by electron beam irradiation of an aqueous solution containing 40% total monomer concentration (90% acrylamide and 10% acrylic acid). The co-polymer of acrylamide and acrylic acid exhibits a very low toxicity, but a total conversion of acrylamide (a toxic monomer) cannot be obtained by any polymerisation method. Thus, we obtained the second type of polymeric flocculant, PV type, based on monomers without toxicity. PV is a co-polymer of acrylic acid and vinyl acetate, which was obtained into two variants, PV-10 and PV-30, by electron beam irradiation of aqueous solutions consisting of 10% TMC (8% acrylic acid and 2% acetate vinyl) and respectively, 30% TMC (24 % acrylic acid and 6 % acetate vinyl). For the PA and PV preparation our interest was focused on the basic characteristics optimisation, such as high flocculation capacity (high intrinsic viscosity or mean molecular weight) and high solubility (high linearity or low values for Haggins constant k_H) in order to obtain desired properties needed for waste water treatment. These characteristics can be improved if the chemical composition, absorbed dose (D) and absorbed dose rate (d) are controlled in certain fashion.

Preparation of the PA and PV type co-polymers depends on total monomer concentration (TMC), complexing agent concentration (CAC), chain transfer agent concentration (CTAC), initiator concentration (IC) as well as on the water presence in the system. It was proved by our research that the radicals originated from irradiated water have a predominant role on the radicals which come directly from the monomers irradiation. For an irradiated solution in which the water concentration decreases under 40% the conversion coefficient (CC) of the monomers decreases and in the case of the systems with very small water concentration, the polymerisation velocity suddenly decreases.

Fig.1 shows the graphical representation of some experimental results concerning the CC dependence versus TMC of an irradiated aqueous solution containing acrylic acid. As indicated in Fig.1, since TMC is nearly 100%, the conversion coefficient is only 10%. Irradiation over the level of the required dose leads to a crosslinking structure of the final products (become water insoluble) and an irradiation below the level of the required dose decreases CC and intrinsic viscosity (IV). High values for IV are desired because they provide a good flocculation capacity which means high flocculation velocity and small size of the sediment volume put down into a treated waste water. High values for the intrinsic viscosity or mean molecular weight are sometimes associate with a bad solubility of the PA and PV type co-polymers. The flocculation capacity (FC) was determined as the thickness of the sediment sets down, in the first 3 and 5 minutes, into a glass vessel containing 25 cm height aqueous solution of 4% diatomite concentration treated with 0.4mg/l or 1.2 mg/l polymeric flocculant concentration. Good FC means low values for the sediment thickness and high values for the sedimentation velocity.Fig.2 and Fig.3 show, respectively, the graphical representation of some experimental results concerning CC and IV dependence versus D for d = 0.8 kGy/min and for the following chemical composition of the PA type samples: 40% TMC, 0.5% CAC, 0.5% IC and 0.2% CTAC.

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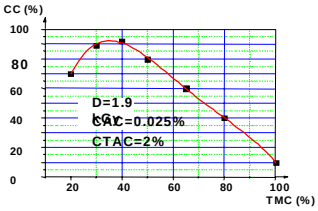

Fig.1

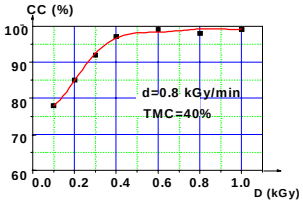

Fig.2

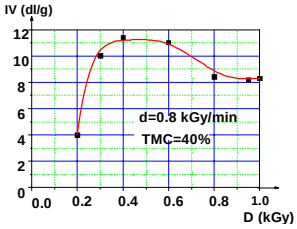

Fig.3

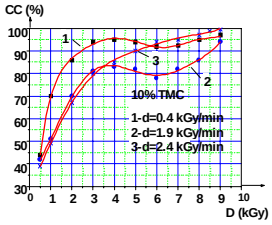

Fig.4

Fig.4 and Fig.5 show, respectively, the effect of D and d upon CC of the PV-10 and PV-30 type co-polymers. All PA samples irradiated over 1kGy, PV-10 probes over 9 kGy and PV-30 over 12 kGy have a crosslinked structure. The crosslinking effect can be controlled by CTAC. According to the above mentioned experimental results the main conclusions are:

-It is indicated to produce an over-irradiation controlled by CTAC then an irradiation below the level of the absorbed dose which makes lower values for CC;

-High values for CTAC overcome the crosslinked effect and provide for the polymeric samples a good solubility but lead to lower values for the intrinsic viscosity and sedimentation velocity. However, when level of D is nearly the proper dose (0.6-0.8 kGy) the required CTAC diminishes.

-CC, IV and FC exhibit optimal values in the ranges of 0.3 kGy to 1kGy for PA type and 3kGy to 9 kGy for PV type. These ranges as well as the size of optimum values are closely related to the chemical composition of the irradiated solution and absorbed dose rate level.

-Chemical composition of the irradiated solution and absorbed dose must be controlled and optimised in order to obtain both, high intrinsic viscosity and high linearity (Haggins constant $k_H < 0.5$) of the polymeric flocculants.

Unfortunately, neither optimised D nor optimized chemical composition are sufficient in all situations such as for high absorbed dose rate levels because of the strong dependence of the free-radical polymerisation on the radiation intensity. At high absorbed dose rates the free-radical polymerisation process is incomplete under irradiation period and continues after irradiation for an uncontrollable time period. Also, it is not possible to proceed a complete conversion of the monomers mixture. To investigate the influence of the dose rate on CC, IV and FC, special experiments have been performed in the last time.

Some of the results are already presented in Fig. 4 and Fig.5. Fig 6, Fig.7 and Fig.8 represent, respectively, the absorbed dose influence on the conversion coefficient, intrinsic viscosity and flocculation capacity for the PA type co-polymer. Fig.9 and Fig.10 show the influence of absorbed dose and absorbed dose rate on the flocculation capacity for the PV-10 type co-polymer and PV-30 type co-polymer, respectively.

The analysis of the experimental results concerning the influence of the absorbed dose rate level on the CC, IV and FC leads to the following conclusions:

-At high absorbed dose rates the conversion coefficient generally decreases, but this effect is strongly dependent on the chemical composition and absorbed dose level. For a proper chemical composition, D and should be so adjusted to provide a certain time for the polymerisation process: 0.5-1.5 minutes for the PA type and 3-4 minutes for the PV type.

-Intrinsic viscosity and flocculation capacity exhibit optimal values in the ranges of 0.3 kGy/min-1kGy/min for PA type and 0.4 kGy/min-2.4 kGy/min for PV type. These ranges as well as the size of the optimum values for IV and FC are closely related to the chemical composition of the irradiated solution (Fig.7) and absorbed dose level.

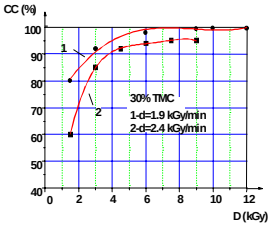

Fig.5

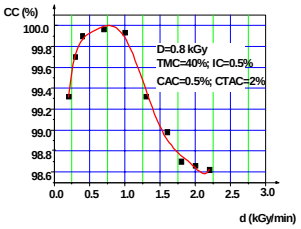

Fig.6

The PA type is used in aqueous solutions with a concentration of 0.05%-0.1% and PV type with a concentration of 0.5% - 1%. The PA type was used very efficiently for hydrometallurgy (porcelain earth) (100 g PA per 1000 kg of dry solid substance) without adding other inorganic flocculants. In other cases the PA and PV type co-polymers are used together with inorganic flocculants (aluminium sulphate or ferric chloride) but inorganic flocculants consumption may be reduced from 50% to 75%. Also, the sediment volume resulted by waste water treating with PA and PV type co-polymers was about 60% smaller than the sediment volume resulted by treating the same water with aluminium sulfate or ferric chloride only.

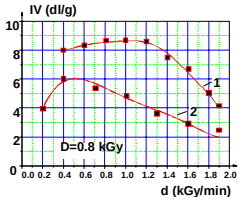

Fig.7 (1- 0.2%CTAC; 2- 2% CTAC)

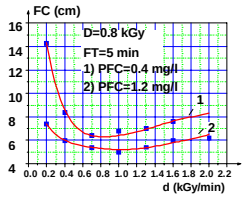

Fig.8 (FT=Flocculation Time)

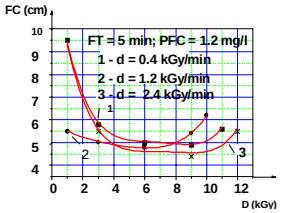

Fig.9

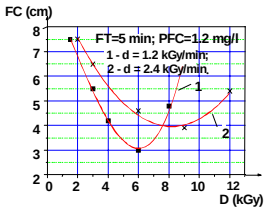

Fig.10

3 SIMULTANEOUS MICROWAVE AND ELECTRON BEAM TREATMENT APPLICATION IN THE FIELD OF POLYMERIC FLOCCULANTS

New results concerning the use of simultaneous microwave and accelerated electron beam irradiation for improving the polymeric flocculant characteristics are obtained. ALID-7 linac of 6 MeV and 0.7 kW, built in the Accelerator Laboratory from National Institute for Laser, Plasma and Radiation Physics, was completed by a specially designed reaction chamber to fulfill simultaneous electron beam and microwave irradiation. Comparative results on the preparation of acrylamide-acrylic acid co-polymer, used for wasted water treatment and obtained by classical heating, microwave heating, electron beam irradiation and simultaneous microwave and electron beam treatment, are shown in Table 1. These results are with regard to the conversion coefficient (CC), intrinsic viscosity (IV), mean molecular weight (M_w) and linearity (Haggins constant K_H) obtained by processing of the aqueous solutions containing an appropriate mixture of monomers (40% total monomer concentration: 90% acrylamide and 10% acryl acetate), initiators, complexing agents and chain transfer agents. As is shown in Table 2, IV (dl/g) and M_w (a.m.u.) are improved by simultaneous 30 seconds irradiation with electron beam of 0.4 kGy and microwave power of 430 W.

4 CONCLUSIONS

Radiation research in the field of polymeric materials (polymeric flocculants) obtained by electron beam irradiation field proved that their characteristics can be controlled and optimized by three factors: absorbed dose, absorbed dose rate and chemical composition of irradiated aqueous solution containing a mixture of two appropriate monomers, complexing agents, chain transfer agents and initiators. These factors are very strong dependent on each other. Because of the dependence of the free-radical polymerisation mechanism on the absorbed dose rate, low intensity and high energy (up to 10 MeV) electron accelerators are favoured for giving the highest yield per unit dose for our types of polymeric materials.

REFERENCES

1. Martin D. et al., Radiat.Phys.Chem.,Vol. 45, No 4, pp 615-621,1995.
2. Martin D. et al., Nucl.Instr.and Meth. in Phys.Res.B113(1996)106-109.
3. Martin D. et al., Progr.Colloid Polym.Sci.(1996)102, pp. 147-151.
4. Dragusin M.et.al., Progr.Colloid Polym.Sci.(1996)102, pp. 123-125

Table 1 : Comparative results concerning various methods of PA type preparation .

Classical				**Microwave**				**Electron Beam**				**Simultaneous E.B. & microwave**			
CC	**IV**	$\overline{M}_w$	K_H	**CC**	**IV**	$\overline{M}_w$	K_H	**CC**	**IV**	$\overline{M}_w$	K_H	**CC**	**IV**	$\overline{M}_w$	K_H
%	**dl/g**	**x10^6**	**-**	**%**	**dl/g**	**x10^6**	**-**	**%**	**dl/g**	**x10^6**	**-**	**%**	**dl/g**	**x10^6**	**-**
95	2.7	0.62	0.65	95	3.8	1.14	0.42	98	8.5	4.67	0.88	98	12	8.55	0.35

Table 2: The effects of symultaneous electron beam and microwave treatment of PA and PV flocculants (T_i=irradiation time ;MWP=microwave power ; MW in atomic mass units)

Sample	D	T_i	MWP	TMC	I	CA	CTA	CC	IV	M_W	K_H
	kGy	**sec**	**W**	**%**	**%**	**%**	**%**	**%**	**dl/g**	**x10^6**	**-**
PA	0.66	68	430	40	0.3	0.1	0.2	93	12.5	9.81	0.4
PA	0.66	63	550	40	0.1	0.1	0.2	91	12.5	9.81	0.4
PA	0.4	30	430	40	2	0.1	0.2	95	17.5	16.6	0.1
PA	0.3	30	430	40	2	0.1	0.2	94	13.5	8	0.2
PA	0.4	60	430	40	0.1	0.1	0.2	77	13	9.84	0.3
PV	9	300	430	10	0.2	0.1	0.2	65	6	-	0.1
PV	5	180	430	30	0.2	0.1	0.4	81	10	-	0.1