MODIFICATION OF POLYPROPYLENE WITH 2,3[EPOXYPROPYL] METHACRYLATE

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2,3[Epoxypropyl] methacrylate is in water emulsion bound on a low-oxidized isotactic polypropylene powder. Polymerization is carried out at low temperature in the presence of an activator of the initiator — chelate of Fe^{2+}–dinatrium salt of ethylenediaminetetraacetic acid; under these conditions epoxy group is preserved. The homopolymer formation is decreased with the increasing chelate concentration. From these results and those obtained when styrene was used follows, that the monomer type is one of the factors which can principally influence the formation of certain polymer type in this polymerization system.

The chelate, composed of ferrous sulphate and 3,6-diaza-1,8-octanediamine, is an excellent activator of the initiator for modification of oxidized isotactic polypropylene powder in water emulsion[1]. It cannot be used for those monomers which can react with amine group of the chelate. 2,3[Epoxypropyl] methacrylate belongs to this class of monomers. Polypropylene modified in this way becomes a carrier of polar and highly reactive epoxy groups and this was the reason why we studied this system. The principal problem was to develop an efficient redox system for initiating this modification. Such a system would also have to take in account specific monomer properties. The polymer prepared was employed for further studies.

EXPERIMENTAL

Chemicals

Isotactic polypropylene powder (Slovnaft, Bratislava) was extracted in boiling heptane. Air flow separation was used to obtain particle size distribution ranging from 0·1 to 0·3 mm. Emulsifier Mersol H (Leuna Werke, GDR) of this structure $CH_3(CH_2)_{16}$—SO_3Na and Slovasol 2430 (CHZWP, Nováky) — aliphatic alcohol modified with ethylene oxide (molar ratio 1/30), were commercial products. 2,3[Epoxypropyl] methacrylate, synthetized by ČSAV, Prague from potassium methacrylate and epichlorohydrine was then purified by multiple distillation. Ferrous sulphate ($FeSO_4.7\ H_2O$), dinatrium and tetranatrium salts of ethylenediaminetetraacetic acid

and trinatrium nitrilotriacetic acid, hydroquinone, diisopropylxanthogen disulphide, solvents and nitrogen were analytical grade reagents.

Methods and Equipment

Isotactic polypropylene powder was fluid oxidized at room temperature for 5 minutes by oxygen containing 12 mg l^{-1} of ozone. Polypropylene contained $0.7 . 10^{-3}$ mol kg^{-1} of hydroperoxide and $1.5 . 10^{-3}$ mol kg^{-1} of more stable peroxide[2,3]; the values were obtained by extrapolating the time dependence of peroxide formation. The oxidized polypropylene could be pressed at 230°C without evolution of gazeous products (no bubbles) and the thermooxidation stability, measured at 150°C in oxygen, was practically identical with the stability of the original polymer.

Polymerization was carried out in nitrogen atmosphere at 30°C in rotating ampoules[4]. The system contained 1 g of polypropylene, 0.5 g of monomer and 5 ml of water phase in which activator and emulsifier were dissolved. After 5 h polymerization the solid phase was separated by a sintered glass. The solid phase, containing both, the modified and the initial polypropylene, was purified by washing with water, acetone and benzene. The amount of polymer bonded on polypropylene was expressed in wt.% according to the weight of solid phase. Homopolymer in the filtrate was isolated from the emulsion by precipitation with methanol. Its amount was expressed as wt.% of the total amount of polymer formed (other reaction time and other ex-

TABLE I

Preliminary Experiments of Polypropylene Modifications with 2,3[Epoxypropyl] Methacrylate at 30°C

C — FeSO$_4$–disodium salt of ethylenediaminetetraacetic acid chelate (1 : 1 mol), E — emulsifier Mersol H, **B** — bonded polymer (in % of solid phase), H — homopolymer (in % from total amount of polymer formed).

Sample No	[C]	[E]	B %	H %	Sample No	[C]	[E]	B %	H %
	10^{-3} mol l^{-1}					10^{-3} mol l^{-1}			
1	0.72	5.04	9.0	77.3	8	4.32^c	5.04	15.9	16.8
2	2.52	5.04	12.5	51.1	9	4.32^d	5.04	23.5	37.0
3	4.32 ·	5.04	13.8	22.2	10^e			17.8	32.0
4	2.52	1.26	8.4	46.5	11^f			12.4	20.6
5	2.52	8.82	13.5	60.4	12^g			18.3	34.7
6	4.32	5.04^a	4.1	84.2	13^h			2.7	26.6
7	4.32^b	5.04	6.9	80.0	14^i	↓	↓	24.4	15.3

^{a} Slovasol 2430 used as emulsifer at the same concentration. ^{b,c} Chelate ^{b} FeSO$_4$–tetrasodium ethylenediaminetetraacetic acid (1 : 1 mol), ^{c} FeSO$_4$–trisodium salt of nitrilotriacetic acid were used at the same concentration, ^{d} FeSO$_4$, without chelating agent. ^{e,f} In the presence of hydroquinone (in mol l^{-1}): ^{e} 0.4, ^{f} 4 . 10^{-4}, ^{g,h} In the presence of diisopropylxanthogen disulphide (in mol l^{-1}): ^{g} 0.4, ^{h} 4 . 10^{-4}. ^{i} Polypropylene powder of the 0.05–0.15 mm particle size distribution was used.

pression of polymerization results was used only at kinetic measurements). Concentrations of components in the system are given in mol l^{-1} of liquid phase (emulsion).

I.R. spectrum of polypropylene powder with bonded poly(2,3-epoxypropyl methacrylate) was run on a UR 10 (GDR) apparatus without compensation. Nujol technique was employed. The sample before analysis was ground for 3 h on a Ardenn grinder and the sieve separated fraction having the diameter $\leqq 0.06$ mm was used.

RESULTS AND DISCUSSION

Modification was carried out with polypropylene oxidized to a very low extent in order to minimize the deleterious effect of this way of initiation center formation on its properties. Therefore, it was necessary to use such an activation system which would not only decompose peroxides to a large extent but also utilize them as much as possible for the modification reaction. Table I summarizes the results of 2,3[epoxy-propyl] methacrylate polymerization with respect to the formation of the main product, the bonded polymer and the homopolymer, under different polymerization conditions. The content of polypropylene (consequently also of peroxide), the volume of water phase with dissolved activator and emulsifier, the weight ratio of poly-propylene to monomer, the reaction temperature[5] and its duration are kept constant.

The fact that polypropylene can be modified with 2,3[epoxypropyl] methacrylate by such Fe^{2+} chelates which, in the presence of styrene, activated only homopolymerization[1] is the most important conclusion from Table I (see samples 3, 7, 8). The relatively best result was obtained when ferrous sulphate as such, i.e. without chelating agent (sample 9) was used, but the product was discoloured by residual Fe^{3+}, which is difficult to remove because of the character of bonded polymer. For this reason (and also to keep homopolymer formation low) was in further studies used ferrous sulphate in combination with a chelating agent — disodium salt of ethylene-diaminetetraacetic acid (sample 3) — which forms with ferric and ferrous salts extremely strong chelates[6] soluble in water, and therefore easily removable from the solid phase surface.

A serious disadvantage of these chelates is the simultaneous homopolymerization proceeding to a large extent. As it is seen from Table I, sample 6, the replacement of Mersol H by the nonionic type of emulsifier does not solve this problem. In comparison with styrene polymerisation[7], it is remarkable that polypropylene undergoes modification at all. The addition of certain compounds to the polymerization system which were efficient in lowering the styrene homopolymerization[8] appeared to be inefficient in this case (samples 10 – 13). The lowering of the homopolymer portion with respect to the total polymer amount formed can be achieved by using poly-propylene with special particle size distribution (sample 14). However, the principal solution may possibly consist in the effect of activator and emulsifier concentrations as it is seen from the experiments 1 – 5.

The concentration effect of selected components — the chelate of Fe^{2+} and disodium salt of ethylenediaminetetraacetic acid (factor x_1) and the emulsifier Mersol H (factor x_2) — on the formation of polymer initiated by peroxides of polypropylene has been in general evaluated by using orthogonal 2-factor design of the type 3^2:

Factor	Dimension	Level				Interval I_i
		−1	0	1	2	
x_1	10^{-3} mol l^{-1}	2·52	4·32	6·12	7·92	1·80
x_2	10^{-3} mol l^{-1}	1·26	5·04	8·82	12·60	3·78

TABLE II

Basic Data and Results of the Design

B — Bonded polymer, H — homopolymer, Y_{exp} — experimentally determined amount of polymer after 5 h (in %), Y_{th} — amount of polymer after 5 h calculated from the theory (in %).

i	$x_1{}^a$	$x_2{}^a$	B		H	
			Y_{exp}	Y_{tcor}	Y_{exp}	Y_{tcor}
1	−1	−1	8·4		46·5	
2	−1	0	12·5		51·1	
3	−1	1	13·5		60·4	
4	−1	2	12·9		66·3	
5	0	−1	9·2		15·6	
6	0 (−1)	0 (−1)	13·8	13·7	22·2	22·6
7	0 (−1)	1 (0)	15·4	15·7	27·1	27·1
8	0 (−1)	2 (1)	14·1	13·9	32·9	32·5
9	1	−1	10·0		6·9	
10	1 (0)	0 (−1)	14·7	14·4	8·1	7·2
11	1 (0)	1 (0)	16·1	16·6	9·6	9·7
12	1 (0)	2 (1)	15·2	15·1	12·2	13·1
13	2	−1	6·0		2·2	
14	2 (1)	0 (−1)	10·7	11·1	4·0	4·5
15	2 (1)	1 (0)	14·3	13·6	5·1	5·0
16	2 (1)	2 (1)	12·0	12·3	6·9	6·5

^{a} Working levels for the 4 alternative are given in brackets (see the text).

Besides usual levels for this type of design[9], the experiments were also done on the +2 level for both factors. In this way we have increased the probability that in some combination the sought optimum conditions for modification are involved. Table II gives the design: at its evaluation it is possible to take into consideration 4 alternatives of experiment triples (alternative — experiment number): $1 - 1-3, 5-7, 9-11$; $2 - 2-4, 6-8, 10-12$; $3 - 5-7, 9-11, 13-15$; $4 - 6-8, 10-12, 14-16$. From Table II, which shows experimental values of the bonded polymer and of the homo-polymer (Y_{exp}), is evident, that mainly from the point of view of homopolymerization the alternatives 1 and 2 are unfavourable. From the two remaining ones the alternative 4 seemed to be more advantageous; this was proved by evaluating it by general numerical methods and graphical representation (Fig. 1 and 2).
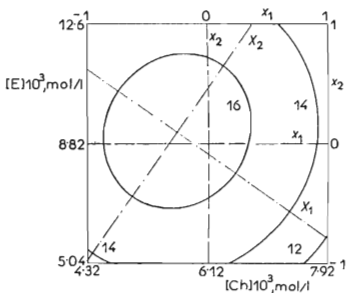

Fig. 1

Contour-Line Diagram of the Concentration Effect of Chelate Fe^{2+}–Disodium Salt of Ethylenediaminetetraacetic Acid and the Emulsifier Mersol H on % of Poly[2,3-epoxy-propyl] Methacrylate in Solid Phase Formed during 5 h

$Y = 16\cdot57 - 1\cdot05x_1 + 0\cdot35x_2 + 0\cdot25x_1x_2 - 1\cdot95x_1^2 - 1\cdot85x_2^2$, $x_{1s} = -0\cdot26$, $x_{2s} = 0\cdot07$, $Y_s = 16\cdot72$; $s(y) = \pm0\cdot30$; $F = 4\cdot60 < F_{crit.}^{0\cdot05}$ $_{3.5}$

Fig. 2

Contour-Line Diagram on the Concentration Effect of Chelate Fe^{2+}– Disodium Salt of Ethylenediaminetetraacetic Acid and Emulsi-fier Mersol H on % of Homopolymer with Respect to the Total Poly[2,3-epoxypropyl] Methacrylate Formed During 5 h

$Y = 9\cdot67 - 11\cdot03x_1 + 2\cdot95x_2 - 1\cdot95x_1x_2 + 6\cdot40x_1^2 + 0\cdot45x_2^2$; $x_{1s} = 0\cdot54$, $x_{2s} = -2\cdot11$, $Y_s = 3\cdot58$, $s(y) = \pm0\cdot42$; $F = 4\cdot57 < F_{crit.}^{0\cdot05}$ $_{3.5}$

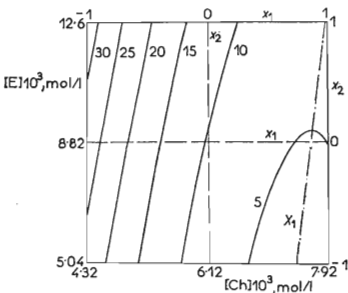Fig. 1 and 2 represent for the alternative 4 contour-line diagrams of the effect of two entering parameters — chelate and emulsifier concentrations — on two resulting parameters — bonded polymer and homopolymer formation. The values — % of polymer — stated at each controur-line are theoretical ones. Simultaneously, there is given a regresion equation which correlates the relation between variables, the data about the stationary point x_{1s}, x_{2s} and Y_s, the error in the determination of polymer percentage obtined from 6 parallel repetitions in the experiment center in the form of standard deviation $s(y)$ and the F-test result evaluating the regresion equation adequacy. From these data follows that the equations are valid and that, within the determined tolerance reliably describe phenomena under evaluation. This is also seen from the Table II where are, beside Y_{exp} values, also given the percentages of polymer formed calculated from the equations (Y_{theor}).

Fig. 1 and its mathematical description shows that the maximum percentage of bonded 2,3[epoxypropyl] methacrylate (P) in solid phase is situated within the experimental space. It is determined by the intersection point of axes of canonical form of equations X_1 and X_2 and it has the coordinates x_{1s} and x_{2s}. The maximum attainable value under these conditions is $16.7 \pm 0.3\%$; which corresponds to 1.18 mol of epoxy groups per kg of solid phase. A similar course, exhibiting a maximum, has been observed for the modification of polypropylene with styrene (S) when the Fe^{2+}–3,6-diaza-1,8-octanediamine chelate and Mersol H were used as the activator and the emulsifier, respectively[10]. As it is basically very similar system, one can accept the explanation given for styrene, i.e. to consider, besides an activation also deactivation role of the chelate, the latter becoming dominant when certain chelat concentration is reached.

In spite of the comparability of these two systems there are the differences in the type of monomer and activator used and therefore a certain differentiation has to be taken into account. This is documented by the date given in Table III, which shows the concentrations of the chelate (C) and the emulsifier (E), needed for the optimum course of polypropylene modification with both monomers. A difference becomes evident when evaluating the concentration ratio of both components [E]/[C]; this is mainly caused by a high chelate concentration when epoxidized monomer is used. This fact can be documented by further comparisons of $[C]_P/[C]_S$ and $[E]_P/[E]_S$, respectively, for the chelate being $1.9 - 4.0$ times higher in favour of 2,3[epoxypropyl] methacrylate; for the emulsifier it is approximately one half. The differences between these two chelates are due to the chemical nature of the chelating agent and its effect on the reaction ability of the central ion. While both components of the system ferrous sulphate–3,6-diaza-1,8-octanediamine are able to take part in the reaction with polypropylene peroxide or with certain part of radicals formed; in the Fe^{2+}-ethylenediaminetetraacetic acid system only central ion is capable to react in that way (similarly as in the case of ferrous sulphate alone). The chelates being compared have also very different stability constants which effect the reactivity of the metal

in all of its oxidation stages[11,12]. It should be mentioned that they differently effect pH of the emulsion which is not a negligible factor in polypropylene peroxide decomposition[13]. Moreover, an increased need of the chelate at the 2,3[epoxypropyl] methacrylate polymerization follows from its role in lowering the homopolymerization in the whole concentration range. This is documented by the data given in Tables I and II and in Fig. 2. Most probably, it again reacts with radicals that induce homopolymerization, which was not in the styrene–amine chelate system important[10]. In the relations discussed here it should also be noted an interesting fact, that for the

TABLE III

Comparison of Chelate (C) and Emulsifier Mersol H (E) Concentrations Required for Optimum Course of Polypropylene Modification with Styrene (S) and with 2,3[Epoxypropyl] Methacrylate (P)

q — Degree of polypropylene oxidation.

Monomer	$[C]^a$	$[E]$	q	H_2O ml	$[E]^b$	$[C]_P$	$[E]_P$
	10^{-3} mol l^{-1}				$[C]$	$[C]_S$	$[E]_S$
S^c	1·4 — 1·6	4·8 — 5·2	broad^d	15·0	3·3	2·5 — 4·0	1·8 — 1·9
P^e	2·7 — 3·0	6·7 — 7·6	low^f	2·5 — 7·5	2·5	1·9 — ·21	1·2 — 1·4
	5·6	9·1	low	5·0	1·6		

^{a} Fe^{2+} concentration is taken as the chelate concentration. ^{b} In case of concentration range its arithmetical mean was taken. ^{c} Chelate Fe^{2+}–3,6-diaza-1,8-octanediamine was used, concentrations were recalculated with respect to the emulsion volume. ^{d} Broad scale[10]. ^{e} Chelate Fe^{2+}–disodium salt of ethylenediaminetetraacetic acid was used. ^{f} Ref.[15].

FIG. 3

Definition of the Chelate and Emulsifier Concentration Range (hatched part) which Guarantees the Formation of $\geqq 16\%$ of Bonded Polymer and $\leqq 10\%$ of Homopolymer from 2,3-[Epoxypropyl] Methacrylate

1 Contour-Line for 16% of Bonded Polymer from Fig. 1; 2 Contour-Line for 10% of Homopolymer from Fig. 2.
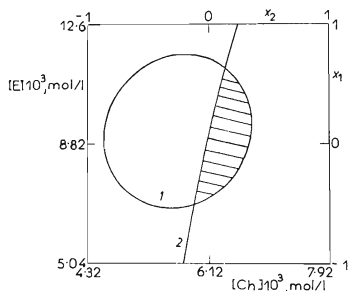
optimum reaction course the epoxy monomer requires a higher emulsifier concentration (Table III). It is somehow connected with an increased chelate concentration and with the function of these compounds in this system and mutual interactions at the polypropylene peroxide decomposition[10].

The facts stated here show that the effect of the chelate on the polymerization *via* polypropylene peroxides can not be evaluated without consideration of the
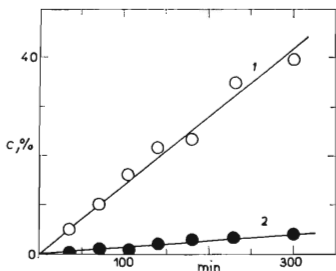

Fig. 4

Kinetics of Formation of Bonded Polymer *1* and Homopolymer *2* during Polymerization of 2,3-[Epoxypropyl] Methacrylate in Emulsion at 30°C in the Presence of Oxidized Polypropylene

Conversions are expressed in % of the reacted monomer. Composition of the polymerization system is the same as with the sample 11 in Table II.
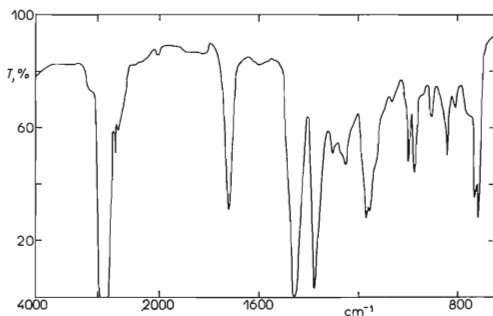

Fig. 5

IR Spectrum of Powder Isotactic Polypropylene Modified with 2,3[Epoxypropyl] Methacrylate (15% in the solid phase) Measured in Paraffin Oil

monomer used. This is evident from an example when the Fe^{2+}–dinatrium salt of ethylenediaminetetraacetic acid was used as the activator: for the styrene modification it is useless as the homopolymerization, initiated by radicals formed from polypropylene hydroperoxide, becomes a predominant reaction; but in the presence of ester-type monomers the modification reaction takes place. It is interesting that polypropylene hydroperoxides are again important for the initiation of modification reaction. This was proved by the polymerization with oxidized polypropylene from which hydroperoxides were removed[2]; negative effect on the modification reaction was noted. These facts give us the basis to affirm that the chemical nature of the monomer used belongs to the class of factors which may fundamentally influence the course of polymerisation reaction towards the formation of some type of the polymers mentioned above. This make the idea about the complex participation of polypropylene peroxides, emulsifier, activator and monomer in the initiation of polymerisation on the solid surface[10], more complete.

In Fig. 3, there is, in a common system of coordinates, given the controur-line for 16% of bonded polymer from Fig. 1 (line 1) together with the contour-line from Fig. 2 for 10% of homopolymer (line 2). The hatched part defines the chelate and the emulsifier concentrations which guarantee, within the experimental errors, the formation of 16 and more % of bonded polymer in the solid phase and 10% or less of homopolymer with respect to the total polymer amount formed. Fig. 1−3 give the evidence that this can be achieved in different ways; mainly concerning the emulsifier concentration, which effects homopolymerization less than the chelate concentration. The kinetic of polymer formation in the optimum region is given in Fig. 4.

I.R. spectrum of solid polypropylene having 15% of bonded poly(2,3-epoxypropyl methacrylate) (Fig. 5) contains a number of absorptions in the $700-1300\ cm^{-1}$ interval, which mostly belong to substituted oxirane[14] ($775-915$, $1235-1280$ cm^{-1}). They are to some extent overloped by absorptions of basic polypropylene. A sharp peak at $1725\ cm^{-1}$ belongs to a well defined ester. The hydroxyl absorption in the $3000-3550\ cm^{-1}$ range is absent. The above stated data show that epoxy groups of bonded polymeric ester are preserved during all procedures of preparation and separation.

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