Influence of polyfunctional monomers on crosslinking of polypropylene

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Dedicated to Professor RNDr. J. Gašperík, founder of the Department of Organic Technology and of the Department of Chemical Technology of Plastics and Fibres of the Slovak Technical University on the occasion of the 40th anniversary of their foundation

The relative efficiency of crosslinking of polypropylene in the course of thermal decomposition of dicumyl peroxide in the presence of nine different polyfunctional monomers and their mixtures has been investigated. The coagents with the highest content of reactive functional groups are the most efficient, which suggests that the macroradicals originating from degrading polypropylene may be added to reactive linking bridges. Some mixtures of polyfunctional monomers exhibit synergic effect in crosslinking. It may be explained by the assumption that the alkyl radicals are transformed into allyl radicals which have considerably more favourable ratio of recombination to disproportionation. An increase in portion of recombination to the detriment of disproportionation raises the extent of formation of crosslinks between macromolecules of the polypropylene modified by the effect of polyfunctional monomer.

Была изучена относительная эффективность сшивания полипропилена при термическом разложении дикумильперекиси в присутствии 9 разных многофункциональных мономеров и их смесей. Наиболее эффективными являются соагенты с наиболее высоким содержанием реактивных функциональных групп, что показывает на возможность присоединения макрорадикалов деградирующегося полипропилена на реактивные соединительные мостики. Некоторые смеси многофункциональных мономеров оказывают синергетическое воздействие для сшивки, что объясняется переменой алкильных макрорадикалов в аллильные, которые обладают более выраженным отношением рекомбинации к диспропорционированию. Увеличение доли рекомбинации на счет диспропорционирования повышает образование поперечных связей между макромолекулами полипропилена видоизмененного многофункциональным мономером.

Polypropylene belongs among the polymers the relative molecular mass of which is rather easily reduced by the effect of free radicals und thus they undergo a crosslinking reaction only at high concentration of free radicals [1]. A possibility of supporting the crosslinking reaction is the presence of polyfunctional monomer in reaction mixture [2]. Nevertheless, the efficiency of polypropylene crosslinking is low even under these conditions and the most convenient structure of polyfunctional monomers is also not known. The particular reactions of coagents in the process of formation of crosslinks between polypropylene macromolecules are also problematic.

In this study we investigated the influence of structure of polyfunctional monomer on relative efficiency of crosslinking as well as the possibility of synergic effect of a mixture of reactive coagents and the effect of their dispersion in polypropylene.

Experimental

Chemicals

We used nonstabilized powdered polypropylene HPF (type for fibre production, Slovnaft) for crosslinking. The powdered polymer was separated in fractions by 6 h sieving through a set of screens. The fraction of polypropylene which passed through the screen with squared 0.71 mm meshes and was retained on the screen with 0.5 mm meshes was subjected to crosslinking in the presence of different monomers.

Commercial products (divinylbenzene, ethylene glycol dimethacrylate, allyl ester of methacrylic acid (Fluka, A. G.), diallyl phthalate (BDH — Chemicals Ltd.), triallyl cyanurate (Schuchhardt) as well as some compounds prepared in laboratory (difurfurylaldehyde pentaerythritylacetal, diacrylaldehyde pentaerythritylacetal, and pentaerythrityl tetraallyl ether)) were applied as polyfunctional monomers.

Dicumyl peroxide was purified by recrystallization from ethanol before use.

Method of sample preparation

Powdered polypropylene was impregnated for 24 h in a closed dark vessel at laboratory temperature with a solution of polyfunctional monomer and dicumyl peroxide in chloroform. The concentration of DCP and polyfunctional monomers was chosen on the basis of preceding studies. Then the solvent was removed from the pasty charge of reactants with a stream of air under continuous stirring of the polymer. When the polymer attained powder-like consistency, the sample was dried to constant mass in a drier at 40 °C.

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Crosslinking

Polypropylene containing reaction components was sealed in glass ampoules in nitrogen atmosphere and thermostatted for 1 h at 170 °C in an oil bath.

Extraction of noncrosslinked polymer

The content of crosslinked gel was estimated by 36 h extraction of polypropylene with boiling xylene. Before putting into solvent, the samples of polymer (2 g) were wrapped in bags consisting of glass tissue, marked, and weighed. During extraction, the solvent was always exchanged after 6 h. A small amount of hydroquinone functioning as thermooxidation stabilizer was added simultaneously with pure xylene. The extraction with xylene finished, the samples were still extracted with benzene for 4 h. Then the bags were dried to constant mass at laboratory temperature in a vacuum drier.

Results and discussion

It appears that the coagents with highest number of functional groups (Table 1) are the most effective among the examined types of polyfunctional monomers. The results suggest that the crosslinking of polypropylene is enhanced if some double

Table 1

Content of gel in polypropylene crosslinked in the presence of 4 mass % of polyfunctional monomer and 4 mass % of dicumyl peroxide after 1 h thermostatting in nitrogen atmosphere at 170 °C

Coagent	f^a	$\dfrac{c}{\text{mmol kg}^{-3}}$	$\dfrac{w^b}{\text{mass \%}}$	$\dfrac{w^c}{\text{mass \%}}$
Alkyl methacrylate	2	355	0.6 ± 0.3	0.7 ± 0.2
Ethylene glycol dimethacrylate	2	224	12.0 ± 0.8	27.9 ± 0.3
Diallyl phthalate	2	180	15.7 ± 4.4	19.0 ± 1.4
Divinylbenzene	2	341	24.9 ± 1.0	32.7 ± 0.2
Diacrylaldehyde pentaerythritylacetal	2	208	37.4 ± 3.5	54.8 ± 0.8
Diallyl maleate	3	226	22.2 ± 0.4	25.2 ± 0.5
Triallyl cyanurate	3	177	24.5 ± 1.9	27.1 ± 18.2
Difurfurylaldehyde pentaerythritylacetal	4	152	58.0 ± 1.6	56.7 ± 2.2
Pentaerythrityl tetraallyl ether	4	150	59.2 ± 2.9	70.6 ± 0.9

a) Number of functional groups of monomer coagent; *b*) mean value and deviation of the content of gel in crosslinked powdered polypropylene calculated from 5 measurements; *c*) mean values obtained from 3 measurements of polypropylene pressed in advance (170 °C, 1 min, 1.4 MPa).

bonds to which the macroradicals of partially degraded polymer may be added remain preserved after formation of crosslinks between macromolecules. Otherwise, the bifunctional monomers ought to be more effective at equal concentration of double bonds in the system because these potential crosslinks are more uniformly distributed in the polymer subjected to crosslinking. However, an unambiguous conclusion in this problem cannot be drawn because the effectivity of crosslinking is also affected by other factors such as reactivity of functional groups, solubility of monomer in polymer or even its vapour tension. By the different temperature of transition into the gaseous state may be explained the fact that the gel content is smaller in the presence of allyl methacrylate than it is in the presence of ethylene glycol methacrylate.

The importance of homogeneous distribution of coagents in polymer comes into view if we observe the content of gel by using equal polyfunctional monomer but different methods of crosslinking. It was also observed for all investigated organic polyfunctional monomers that the pressing of the powder impregnated with coagents previous to crosslinking reaction brought about an increased content of gel in polypropylene. A similar tendency of the influence of distribution of crosslinking agent on activity of the formation of crosslinks appears if polypropylene with varying granularity is used (Table 2). The distribution of crosslinking coagent gets more uniform with increasing surface of polypropylene and thus the efficiency of crosslinking increases.

Table 2

Amount of crosslinked polymer as a function of granularity of polypropylene (PP) impregnated with 4 mass % of difurfurylaldehyde pentaerythritylacetal in the presence of 4 mass % of dicumyl peroxide after 1 h thermostatting at 170 °C in nitrogen atmosphere

d (PP)/mm[a]	$1 - 0.7$	$0.7 - 0.5$	$0.5 - 0.25$	$0.25 - 0.16$	$0.16 - 0$
w (gel)/mass %[b]	55.3 ± 1.7	58.0 ± 1.6	52.7 ± 2.4	69.7 ± 6.1	70.5 ± 5.8

a) d — side of squared mesh (mm) of the sieve through which polypropylene powder passed and on which it was caught after 6 h sieving; b) w — mean value of 5 measurements with standard deviation.

Other possibilities of improving the efficiency of crosslinking of polypropylene consist in the use of mixtures of polyfunctional monomers in which their synergic effect manifests itself. Though the results given in Table 3 do not unambiguously suggest a synergic effect of polyfunctional monomers on the course of crosslinking, still, a confrontation of the gel contents presented in Table 1 and Table 3 indicates that, in some cases, a higher content of gel is reached with considerably lower total molar concentration of the mixture of polyfunctional monomers and half concen-

Table 3

Gel content in polypropylene crosslinked in the presence of 2 mass % ($c = 74$ mmol dm^{-3}) of dicumyl peroxide, 1 mass % ($c = 34$ mmol dm^{-3}) of difurfurylaldehyde pentaerythritylacetal (FP) or 1 mass % ($c = 34$ mmol dm^{-3}) of pentaerythrityl tetraallyl ether (PETA) with 1 mass % of other polyfunctional monomer

Polyfunctional monomer	c	w (gel)/mass %[a]	
	mmol dm^{-3}	FP	PETA
Allyl methacrylate	80	0.2 ± 0.1	19.1 ± 6.1
Ethylene glycol dimethacrylate	51	0.3 ± 0.1	15.7 ± 0.9
Diallyl phthalate	41	6.4 ± 1.8	25.5 ± 0.8
Divinylbenzene	77	4.0 ± 0.5	30.4 ± 1.4
Diacrylaldehyde pentaerythritylacetal	47	30.6 ± 1.8	33.2 ± 0.4
Diallyl maleate	51	17.5 ± 7.2	26.7 ± 2.9
Triallyl cyanurate	40	37.9 ± 0.7	33.8 ± 1.1
Difurfurylaldehyde pentaerythritylacetal	34	3.6 ± 2.6	41.6 ± 0.5
Pentaerythrityl tetraallyl ether	34	42.0 ± 4.6	38.5 ± 3.6

a) Mean values and deviations calculated from 3 parallel experiments.
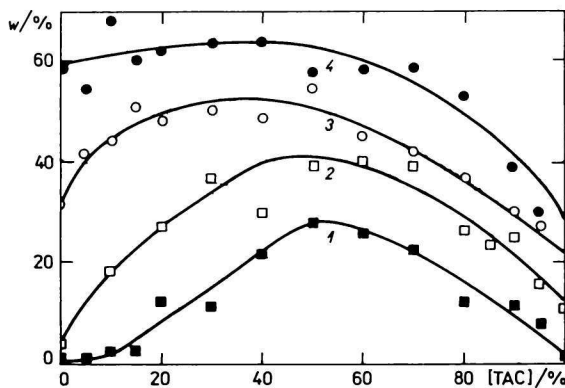

Fig. 1. Variation of mass fraction of gel with composition of the mixture containing triallyl cyanurate (TAC) and difurfurylaldehyde pentaerythritylacetal for varying total content of both components in crosslinked polypropylene: *1.* 1.5 mass % ; *2.* 2 mass % ; *3.* 3 mass % ; *4.* 4 mass %. The quantity of added dicumyl peroxide was equal to the quantity of polyfunctional monomers. Experimental points correspond to the mean of three experiments.

tration of dicumyl peroxide than it is obtained if only one polyfunctional monomer is used. The interaction and nonadditive effect of polyfunctional monomers may be also disclosed from the opposite influence, *i.e.* a decrease in efficiency of

crosslinking of a mixture of coagents when compared with the effect of a single polyfunctional monomer. A direct and more explicit evidence for the synergic effect of a mixture of polyfunctional monomers is supplied by the dependence of the content of crosslinked gel on the ratio of triallyl cyanurate to difurfurylaldehyde pentaerythritylacetal (Fig. 1). The synergic effect of a mixture of crosslinking coagents may be explained in several ways. We assume that the most probable cause of this phenomenon is different reactivity of functional groups in addition and transfer reactions of the system which, under certain conditions, may give rise to macroradicals, especially of the allyl type exhibiting the most favourable ratio of recombination to disproportionation. Owing to these facts, a selection of the optimum mixture of coagents for crosslinking of polypropylene is complicated but enables us to expect that the crosslinking shall proceed in the presence of smaller concentration of additives rather than in the presence of pure monomers.

References

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