

# A STUDY OF ELASTOMER CROSS-LINKING WITH PEROXIDES\*

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Received November 25, 1984

## Summary

The efficiency of various peroxides and coagents in the cross-linking reaction of peroxide-curable fluoroelastomers was studied by differential scanning calorimetry (DSC) and vulcametry (Monsanto Rheometer). Both methods proved satisfactory for following the cross-linking process. The differences in the efficiency of individual peroxides and coagents in the course of the cross-linking process could readily be detected. The information content of the two methods differs, and hence they successfully complement one another in both practical and theoretical problems.

## Introduction

Cross-linking with peroxides has been applied for about 70 years in the rubber industry. The role of organic peroxides has grown significantly in recent years, on the one hand by reason of the appearance of saturated elastomers (silicone rubbers, ethylene-propylene copolymer etc.) not curable by traditional methods, and on the other hand due to the increasingly severe requirements to rubber products used in particular applications. To satisfy these requirements, special formulations are requested in many cases.

Independently of the cross-linking system, the cross-linked structure and the cross-linking process can be followed by various methods:

- testing the physical properties of the cured product [1];
- determination of the density of cross-links [2]: swelling with solvents, measurement of equilibrium stress-strain characteristics;
- analytical determination of the reaction products of cross-linking agents [3, 4];
- vulcamic tests [5, 6];
- calorimetric tests [3, 4, 7, 8].

\* Based on a paper presented at the International Rubber Conference in Moscow (September 4-8, 1984)

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This paper deals with a part of our research work involving peroxide cross-linking of speciality elastomers: vulcanometric and calorimetric studies of fluoroelastomers.

Peroxide cross-linking of fluoroelastomers is a relatively recent process [9, 10]. It is of technological importance since the appearance of elastomer types developed specially for this purpose.

The manufacturing company [11] in agreement with data in the literature [9, 10] reports in detail the compound compositions to be used with peroxide-curable fluoroelastomers and the properties of the cured products that can be achieved. In the compounds with the most equilibrated properties, lead oxide is used as acid acceptor, triallyl isocyanurate as coagent and—depending on curing temperature—2,5-dimethyl-2,5-bis(*tert*-butylperoxy)hexane or 2,5-dimethyl-2,5-bis(*tert*-butylperoxy)hexyne-3 as cross-linking agent.

The major viewpoint of optimization in the cited references is maximum density of cross-links attainable, equivalent to minimum permanent deformation, this being of primary importance for seals. Other optimization principles may exist for other fields of application; for this reason it appeared of interest to compare the cross-linking process performed with various peroxides and coagents.

## Experimental

### *Materials*

The fluoroelastomer tested was Du Pont's Viton GF.

According to the literature [10] this elastomer is a terpolymer of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene containing small amounts of bromine-containing monomer units.

The peroxides studied are listed in Fig. 1, the coagents in Fig. 2. The peroxides were commercial products (rubber industry grade) with the active agent content indicated.

### *Test methods*

The compounds were made on a Banbury-type Brabender Plasticorder mixer with continuous recording of the torque and temperature.

Differential scanning calorimetry (DSC) curves were recorded on a Perkin-Elmer DSC-2 instrument at a heating rate of 5 °C/min. The areas under the curves were determined by planimetry.

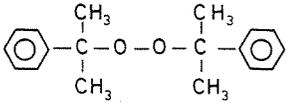
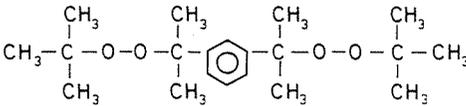
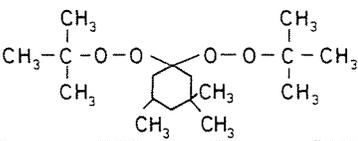
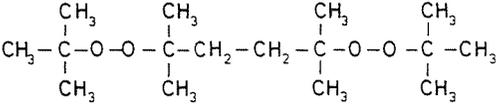
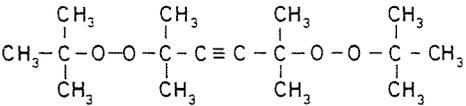
Peroxide (content of active substance)	Chemical name and structural formula
P-1 (40%)	Dicumyl peroxide 
P-2 (40%)	1,3-bis(tert-Butylperoxy)-benzene 
P-3 (40%)	1,1-bis(tert-Butylperoxy)-3,3,5 trimethylcyclohexane 
P-4 (45%)	2,5-Dimethyl-2,5-bis(tert-butylperoxy)-hexane 
P-5 (45%)	2,5-Dimethyl-2,5-bis(tert-butylperoxy)-hexyne-3 

Fig. 1. Peroxides used in the study

The symbols used are

- $T_0$  [°C] — detectable initial temperature of the process  
 $T_p$  [°C] — peak temperature where the rate of the process under the given testing conditions is maximum  
 $T_{10}$  [°C] — the temperature where the process proceeds at a rate equal to 10% of maximum rate. (The difference  $T_{10}-T_0$  characterizes, to a certain extent, temperature sensitivity of the process)  
 $T_f$  [°C] — end temperature of the process

Coagent	Chemical name and structural formula
TAIC	Triallyl isocyanurate $\begin{array}{c} \text{CH}_2-\text{CH}=\text{CH}_2 \\   \\ \text{N} \\ / \quad \backslash \\ \text{O}=\text{C} \quad \text{C}=\text{O} \\   \quad   \\ \text{CH}_2=\text{CH}-\text{CH}_2-\text{N} \quad \text{N}-\text{CH}_2-\text{CH}=\text{CH}_2 \\   \quad   \\ \text{C} \quad \text{C} \\    \quad    \\ \text{O} \quad \text{O} \end{array}$
EDMA	Ethylene glycol dimethacrylate $\begin{array}{c} \text{CH}_3 \qquad \qquad \qquad \text{CH}_3 \\   \qquad \qquad \qquad   \\ \text{CH}_2=\text{C}-\text{C}-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\text{C}-\text{C}=\text{CH}_2 \\    \qquad \qquad \qquad    \\ \text{O} \qquad \qquad \qquad \text{O} \end{array}$
TPTMA	Trimethylolpropane trimethacrylate $\begin{array}{c} \qquad \qquad \qquad \text{O} \quad \text{CH}_3 \\ \qquad \qquad \qquad    \quad   \\ \qquad \qquad \qquad \text{O}-\text{C}-\text{C}=\text{CH}_2 \\ \qquad \qquad \qquad   \\ \qquad \qquad \qquad \text{CH}_2 \\ \text{CH}_2=\text{C}-\text{C}-\text{O}-\text{CH}_2-\text{C}-\text{CH}_2-\text{CH}_3 \\   \qquad \qquad \qquad   \\ \text{CH}_3 \qquad \qquad \text{CH}_2 \\    \qquad \qquad   \\ \text{O} \qquad \qquad \text{O}-\text{C}-\text{C}=\text{CH}_2 \\ \qquad \qquad \qquad    \quad   \\ \qquad \qquad \qquad \text{O} \quad \text{CH}_3 \end{array}$
BR	1,2-Polybutadiene $\begin{array}{c} /-\text{CH}_2-\text{CH}-/n \\   \\ \text{CH} \\    \\ \text{CH}_2 \end{array}$

Fig. 2. Coagents used in the study

$\Delta H$  [J/g] — enthalpy change of the process relative to 1 g of the compound

$\Delta H_m$  [kJ/mol] — enthalpy change of the process relative to 1 mol peroxide

$\Delta H_p$  [kJ/mol] — enthalpy change of the decomposition of 1 mol peroxide

Rheometric curves were recorded at 175 °C with a Monsanto R 100 instrument.

Tensile tests were performed according to ASTM D 412-82.

## Results and discussion

The different peroxides were tested in compound compositions as recommended by the manufacturer. The compositions are listed in Table 1. In all compounds, the coagent applied was TAIC, considered the most efficient.

**Table 1**

Composition of the compounds used in the study of peroxides (mass parts)

Component	Compound				
	FP-1	FP-2	FP-3	FP-4	FP-5
Viton GF	100	100	100	100	100
Carbon black MT	30	30	30	30	30
PbO	3	3	3	3	3
TAIC	3	3	3	3	3
P-1	3				
P-2		4.8			
P-3			3.4		
P-4				3	
P-5					3

Figure 3 represents the DSC curve of the compound containing the peroxide P-4 recorded in the non-isothermal mode of operation; Fig. 4 is the Monsanto rheometric curve at 175 °C of the same compound.

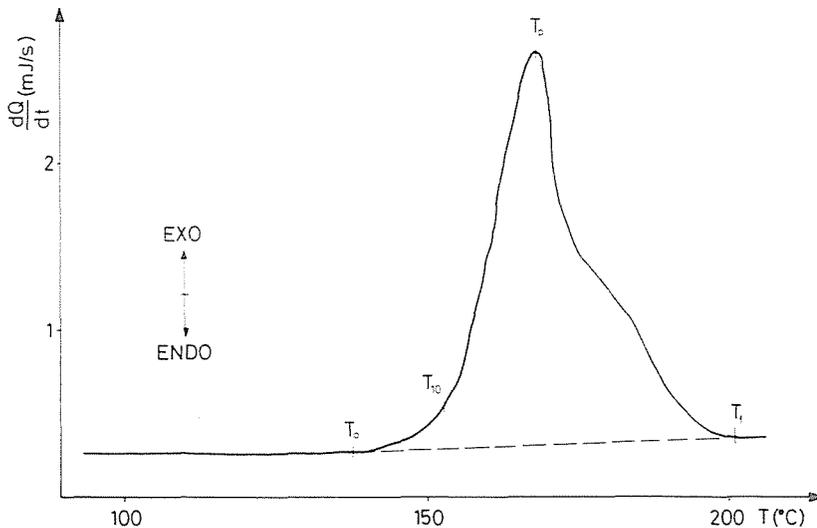


Fig. 3. DSC curve of the fluoroelastomer compound FP-4 (heating rate 5 °C/min, sample mass 10.68 mg)

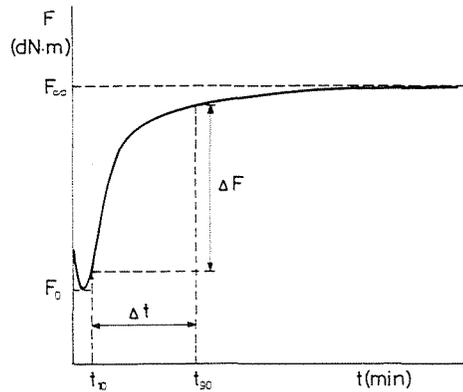


Fig. 4. Rheometric curve of the fluoroelastomer compound FP-4 recorded at 175 °C indicating the data utilized in evaluation

The rheometric curves of all tested peroxides are shown together in Fig. 5, demonstrating that the rate of cross-linking and particularly its extent varies largely for the individual peroxides: efficiency of P-4 and P-5 is outstanding as compared to the other three, and for P-3, no cross-linking could be detected by the rheometric curve.

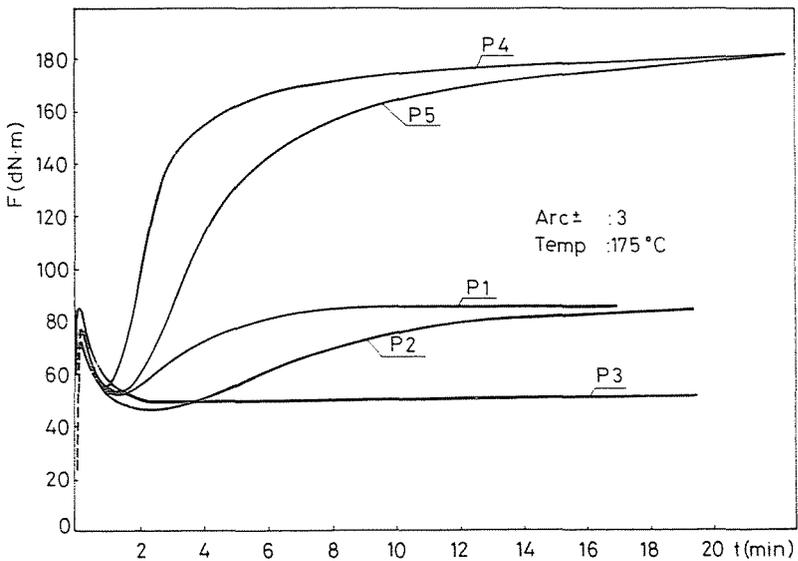


Fig. 5. Rheometric curves of the compounds containing different peroxides

The characteristics derived from the evaluation of the rheometric curves are summarized in Table 2.

Based on the shear modulus increase effectuated by unit peroxide concentration ( $F_{\infty} - F_0$ ) characterizing efficiency of cross-linking, the activity sequence of the peroxides is  $P-5 \cong P-4 \gg P-1 \cong P-2$ .

In the rheometric studies, peroxide milliequivalents in the compound were considered unit peroxide concentration, since—regarding cross-linking—both peroxide groups of  $P-2$  are active, while in the others only one peroxide group takes part in the reaction [12]. The curves produced from the primary non isothermal DSC records of the four active systems (FP-1, FP-2, FP-4

Table 2  
Rheometric data of tested peroxide compounds

Compound	$F_0$ [dN m]	$F_x$ [dN m]	$t_{10}$ [min]	$t_{90}$ [min]	$(F_x - F_0)$ [dN m]	$(F_x - F_0)_{eq}$ [dN m meq <sup>-1</sup> ]	$\Delta F/\Delta t$ [dN m min <sup>-1</sup> ]
FP-1	27	43	2.2	6.1	16	3.6	3.2
FP-2	22	43	3.6	13.6	21	1.8	1.7
FP-3	25	—	—	—	—	—	—
FP-4	28	92	1.5	8.2	64	13.7	7.8
FP-5	27	93	2.3	14.0	66	14.0	4.6

and FP-5) with a SHARP PC 1500 microcomputer are represented by Fig. 6. The experimental curves were recalculated by the computer for identical peroxide amounts expressed in mols; simultaneously the decomposition curve of the same type and amount of peroxide in the pure state was plotted.

Thus, the differences in rate, in enthalpy change, as well as in curve shapes are clearly demonstrated in the figures.

The characteristics determined from non-isothermal DSC curves are summarized in Table 3. In addition to the characteristic temperatures, the enthalpy changes measured, and for the sake of readier comparisons,  $\Delta H_m$  values relative to 1 mol of peroxide are also listed.

The rates do not agree with the decomposition rate sequence of the peroxides  $P-3 > P-1 > P-2 > P-4 > P-5$ .  $T_0$  values (and eventually  $T_p$  values) of the DSC curves should follow the same sequence, which, however, is absolutely different. Based on  $T_0$  values the rate is highest for  $P-1$ , followed by  $P-4$ ,  $P-4$ ,  $P-2$  and finally by  $P-3$ . Comparing this with the  $P-4 > P-5 > P-1 > P-2$  sequence determined from the  $\Delta F/\Delta T$  values of the rheometric curves, it becomes obvious that the rate sequences determined on the basis of enthalpy change and cross-linking, resp., differ essentially.

In the case of peroxides  $P-4$  and  $P-4$ , it could be observed that the rate of the process rapidly increased with temperature immediately after the

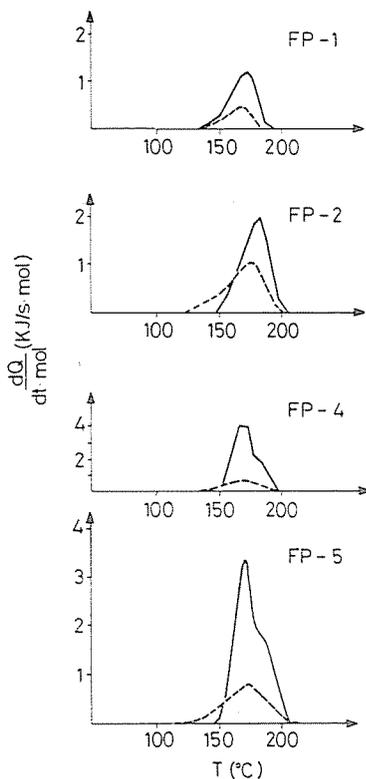


Fig. 6. DSC curves of the compounds containing different peroxides recalculated by computer for one mol peroxide. The decomposition curves of the pure peroxides are represented by dash lines

Table 3

Non-isothermal DSC data of the tested peroxide compounds (heating rate 5 °C/min)

Compound	$T_0$ [°C]	$T_{10}$ [°C]	$T_p$ [°C]	$T_f$ [°C]	$\Delta H$ [J/g]	$\Delta H_m$ [kJ/mol]	$\Delta H_m/\Delta H_p$
FP-1	133	146	174	191	-11.2	-359.7	2.76
FP-2	146	153	180	201	-9.7	-610.4	1.39
FP-3	164	169	188	204	-3.2	-100.3	0.31
FP-4	140	153	169	201	-35.4	-1082.1	4.38
FP-5	136	158	173	212	-32.8	-987.9	2.70

detectable start. Also, in both cases a well-expressed shoulder in the descending section of the curve is observed, indicating the composite character of the process.

Enthalpy changes measured in the compounds containing peroxides P-4 and P-5 are outstandingly high values, exceeding the values for P-3 peroxide by a factor of more than 10 and the values for P-1 and P-2 peroxides by a factor of three to four.

The ratios  $\Delta H_m/\Delta H_p$ , i.e. the ratios of enthalpy change in the cross-linking process and in decomposition of pure peroxide, resp., change substantially from peroxide to peroxide, indicating that the kinetic chain length in the cross-linking reaction differs.

Enthalpy change of pure peroxide decomposition is higher than measured in the cross-linking reaction only in the case of P-3 peroxide.

DSC studies also indicate large differences in the activity of individual peroxides at one given coagent. This may also appear in cases when identical-type radicals are formed from two different peroxides, but their rate of formation is different, owing to the structural differences of the initial compounds. Apparently this phenomenon can also influence the course of the overall process.

Similarly to the rheometric tests, DSC tests also demonstrated total inactivity of peroxide P-3. A very small exothermic enthalpy change could be detected on the curve at a temperature higher by 40 °C than the normal temperature of decomposition.

Presumably, this peroxide suffered partial decomposition already during compounding, without causing cross-linking, since no torque increase indicating cross-linking could be detected on the Brabender Plasticorder curve recorded during mixing.

In the followings, those experiments will be dealt with, in which the effect of the coagent on the cross-linking process, using one and the same active peroxide, was studied.

The coagents were compared in the compounds listed in Table 4; the peroxide selected was P-4. The DSC curves of the process taking place in the

Table 4

Composition of the compounds for studying the effect of coagents  
(mass parts)

Component	Compound			
	FC-1	FC-2	FC-3	FC-4
Viton GF	100	100	100	100
MT carbon black	20	20	20	20
PbO	3	3	3	3
Peroxide P-4	2	2	2	2
TAIC	8			
EDMA		8		
TPTMA			8	
BR				8

presence of TAIC and TPTMA are presented in Fig. 7, demonstrating that the process is much more rapid with TPTMA (curve 2) and consists of two partially separated processes.

In the case of TAIC (curve 1) the reaction starts at a higher temperature, and only a shoulder in the descending section of the curve is observable.

The rate maximum of the second step observed with TPTMA and the shoulder of the curve with TAIC appear in approximately the same temperature interval.

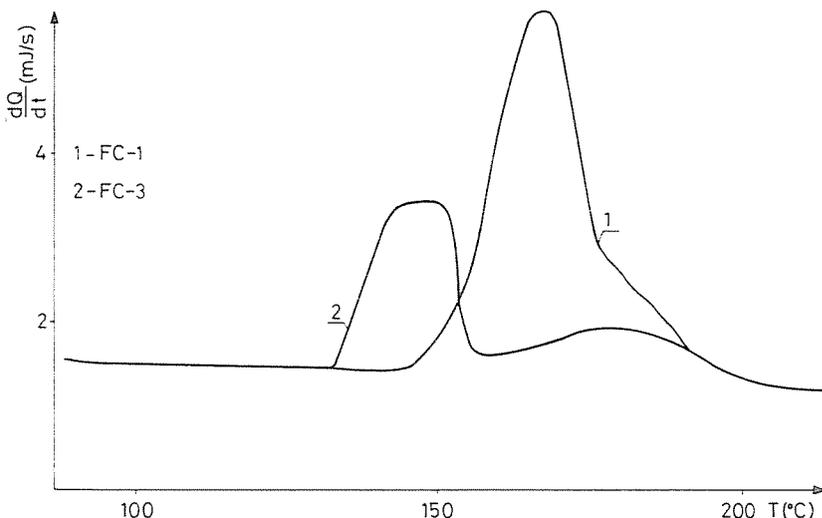


Fig. 7. DSC curves of the compounds containing TAIC (curve 1) and TPTMA (curve 2). Sample masses: 12.31 mg and 9.65 mg, resp.

A comparison of the rheometric curves in Fig. 8 allows to state a similar difference between TAIC and the other three coagents.

A regular rheometric curve is found only with TAIC. In the presence of the methacrylate derivatives and of butadiene rubber (BR) the process is separated into at least two sections. In the initial section cross-linking starts steeply at a high rate; a distinct break is then observable, followed by a lower-rate section. However, in this section too the curves tend towards a well-defined limit value.

However, even in the case of TAIC one can observe that the rheometric curve is only apparently regular, the process is composite in this case too.

This becomes evident if the curve is processed by the method proposed by Scheele *et al.* [5, 6]. This method is based on the principle that the  $(F_{\infty} - F_0)$  values read from the rheometric curve are proportional with the density of

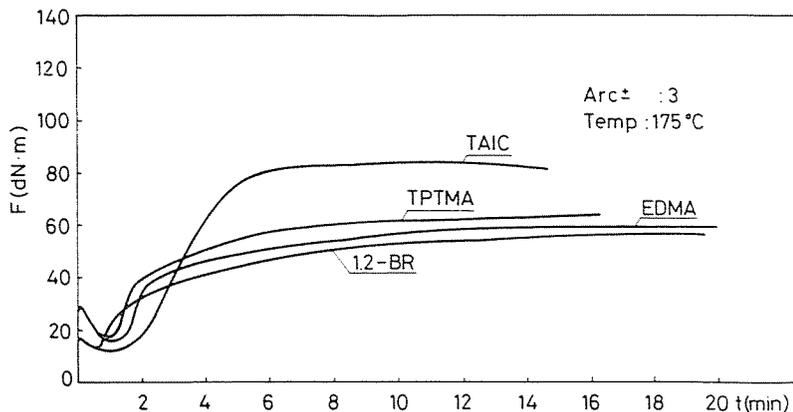


Fig. 8. Rheometric curves of the compounds containing different coagents

cross-links. Hence conversion  $x$  in the moment  $t$  can be expressed by the relationship

$$x = \frac{F_t - F_0}{F_\infty - F_0}$$

If the cross-linking reaction is of the first order, the function  $\ln(1-x)$  vs  $t$  is linear and its slope yields the rate constant of the reaction:

$$\ln(1-x) = \ln \frac{F_\infty - F}{F_\infty - F_0}$$

Figure 9 demonstrates that in the case of TAIC a break in the curve appears at a conversion of around 70–80%, indicating that the overall reaction

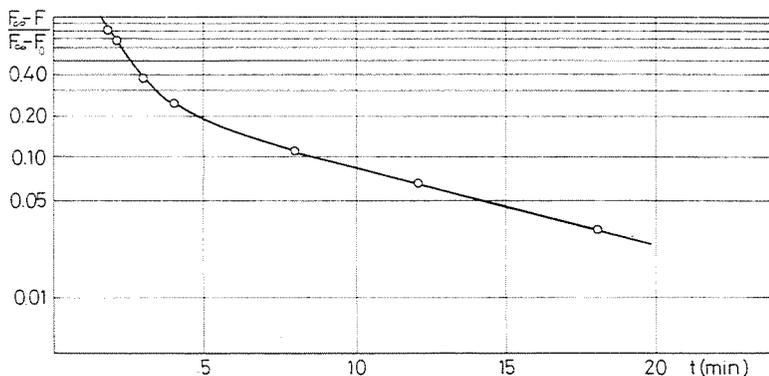


Fig. 9. Rheometric curve of TAIC-containing compound processed according to Scheele et al. [5, 6]

is either the sum of two first-order reactions differing in rate, or that the rate and order of the reaction changes during the process.

The rheometric data of the compounds containing the various coagents are summarized in Table 5. Two findings should be pointed out: TAIC provides highest  $t_{10}$  and lowest  $t_{90}$  values, and its  $(F_x - F_0)$  value exceeds the values corresponding to the other three coagents by a factor of close to 1.5.

Table 5

Rheometric data of the compounds for studying the effect of coagents

Compound	$F_0$ [dN m]	$F_x$ [dN m]	$t_{10}$ [min]	$t_{90}$ [min]	$F_x - F_0$ [dN m]
FC-1 (TAIC)	12	84	2.1	5.0	72
FC-2 (EDMA)	17	62	1.7	9.2	45
FC-3 (TPTMA)	16	66	1.4	8.6	50
FC-4 (BR)	14	60	0.9	11.8	46

The characteristics calculated from the non-isothermal DSC study of the compounds containing different coagents are listed in Table 6.

The shape of the DSC curves in these tests indicates that the processes are composite in character in all cases: simple, approximately symmetric peaks were not found.

The reactions taking place in the presence of bi- and trifunctional methacrylate derivatives appear particularly complex. In both cases, superposed and only partially separated processes could be observed. In the process corresponding to the first peak the rate of the reaction increases very rapidly.  $T_{10} - T_0$  is only one to two °C in these two cases, while in the other two it amounts to 8–13 °C.

Table 6

Non-isothermal DSC data of the compounds for studying the effect of coagents (heating rate 5 °C/min)

Compound	$T_0$ [°C]	$T_{10}$ [°C]	$T_p$ [°C]	$T_f$ [°C]	$\Delta H$ [J/g]	$\Delta H_m$ [kJ/mol]
FC-1 (TAIC)	143	150	168	210	-60.6	-2600
FC-2 (EDMA)	146	147	165 <sub>M</sub> 180	210	-46.9	-2014
FC-3 (TPTMA)	132	134	149 <sub>M</sub> 181	208	-42.0	-1802
FC-4 (BR)	136	149	153 180 <sub>M</sub>	218	-32.9	-1411.6

The course of the process was found to be close to identical in the presence of di- and trimethacrylate, but the reaction started at a significantly lower temperature in the case of TPTMA. Enthalpy change measured was highest with TAIC, and only about half that value with BR; for di- and trimethacrylate, the measured values were between these extremes.

It is of interest to compare the calorimetric characteristics of the compounds FP-4 and FC-1 listed in Tables 3 and 6, resp. The components of these compounds are identical, but their ratio is different, since in one series we studied the effect of the peroxide and in the other the effect of the coagent. This comparison, and the comparison of enthalpy changes relative to unit amount of peroxide (Table 7) allow to conclude that the larger share of

Table 7

Enthalpy changes in the cross-linking reaction of compounds with differing peroxide/coagent ratios

Compound	Peroxide content (mass parts)	Coagent content (mass parts)	$\Delta H_m$ [kJ/mol]
FP-4	3	3	-1082
FC-1	2	8	-2600

enthalpy changes measured in the cross-linking process is due to the reactions effected by the coagent.

By reason of the aspects of practice mentioned in the introduction, we also tested the physical properties of the cured products of the compounds listed in Table 4 (Table 8). The data demonstrated that the highest degree of crosslinking and the best physical properties are provided by TAIC; however, the methacrylate derivatives also yielded satisfactory results.

High elongation coupled to relatively high tensile strength, e.g. in the products made of the compounds containing TPTMA, may be of advantage in certain particular fields of application.

Table 8

Physical properties of cross-linked products prepared with different coagents

Property	TAIC	EDMA	TPTMA	BR
Tensile strength, MPa	14.7	7.5	10.5	5.1
Elongation to break, %	250	460	420	530
Stress corresponding to 100% elongation, MPa	5.0	3.2	3.7	4.0
Shore hardness	76	71	73	71
Permanent elongation, %	8.9	16.3	22.2	41.0

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