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The application of thermoanalytical methods on the reactive processing of polyolefin compounds[1]

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Abstract

The influence of different peroxide concentrations and processing conditions on crosslinking of polyolefin compounds has been investigated. The radical reactions and changes in melting and crystallization behaviour were studied by differential scanning calorimetry. With thermogravimetry the thermal degradation of the crosslinked products was determined. The thermoanalytical data were correlated with gel content.

INTRODUCTION

In these investigations thermal analysis was used to better understand reactive polymer processes. Special problems of initialization of radical reactions and the characterization of the structural changes in the polymeric material after crosslinking were the objects of this research.

The aim of reactive polymer processing is to combine conventional polymer processing with simultaneous chemical reactions [1].

Well known key words are RIM (reaction injection molding) and REX (reaction extrusion). Crosslinked polyolefins are used in the packaging industry, in cable insulations, pipes etc. [2, 3]. The crosslinking process generally starts after the extrusion by heating the material.

EXPERIMENTAL

The components of the polyolefin compound were HDPE (high density polyethylene) 80 percent by weight and a batch of EVA (ethylene vinylacetate copolymer) including carbon black and stabilizer. Various amounts of peroxides (dicumyl-peroxide (DCP) and 3,3,6,6,9,9-hexamethyl-1,2,4,5-tetra-oxacyclononan (HMCN) as a solution of 30 percent by weight in white oil) and the coreagent triallylisocyanurat (TAIC) were used for crosslinking the polymeric material.

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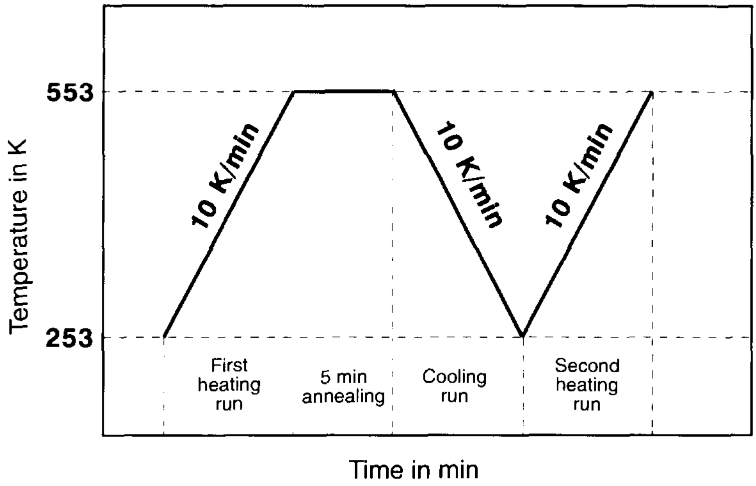

Fig. 1. Temperature programmed DSC measurements.

The experiments were carried out in a Brabender Plasticorder by changing temperatures step by step in the range 433–553 K at an evolution per minute of 60 rpm. After processing, the products were investigated by thermoanalytical methods. The temperature programme for DSC measurements (DSC-2C, Perkin-Elmer) is shown in Fig. 1.

Figure 2 is a scheme of a DSC curve. Only the second run was analysed

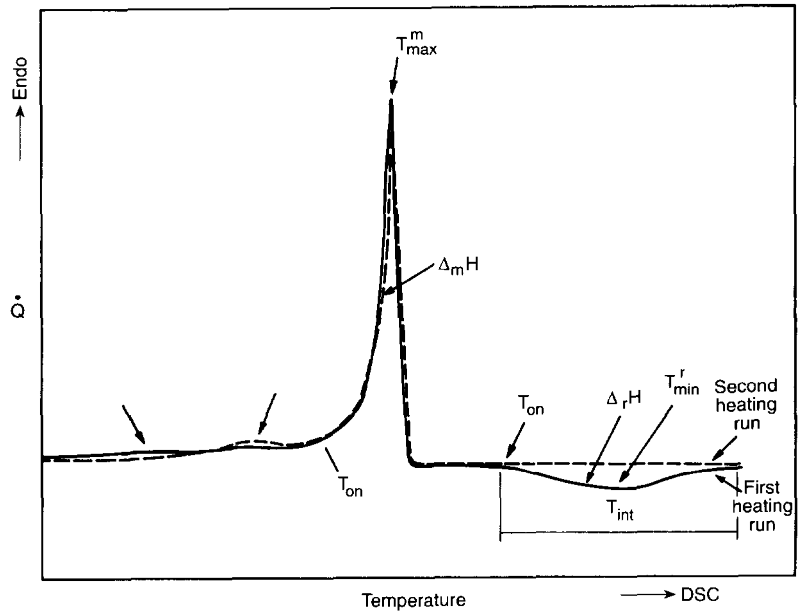

Fig. 2. Schematic DSC plot.

for characterization of the melting and crystallization behaviour: the first run may be strongly influenced by the thermal history of the sample. This problem has already been discussed, especially for compounds containing EVA [4].

Thermal stabilities were measured using a TGS-2 (Perkin-Elmer) in dynamic experiments (continued rising of temperature) within the range 573–773 K.

Solvent extraction studies were made with xylol at a temperature of 417 K over a period of 8 h. The gel content was calculated from this test.

RESULTS

Differential scanning calorimetry

Table 1 shows the decomposition of DCP in the polymeric matrix. The DCP decomposition takes place in the range 410–450 K, but the range is increased to 480 K when decomposition occurs in a polymeric matrix. It is evident that the value of the exotherm energy in the region of DCP decomposition is much higher when polymer is present. This is a result of crosslinking reactions.

Table 2 describes the decomposition of HMCN. It was not possible to determine the decomposition of the pure peroxide by DSC because of problems in using liquid sample pans for the oily solution of HMCN. The analysis of the decomposition peaks was very difficult and the reproducibility was very bad. The reason could be the irregular distribution of the peroxid dispersion in the PE compound.

The melting and the crystallization temperature of the DCP crosslinked samples are illustrated in Fig. 3. The crystallization temperature shifts to lower values with higher perioxide concentrations. This indicates that molecular structures were created which need stronger undercooling for crystallization than the non-crosslinked samples. The crystallinity is constrained. The shape of the heating curve also changes. The melting process starts at lower temperatures and the heat of fusion is significantly

TABLE 1

Heat of reaction $\Delta_r H$ of DCP and related reactions

Sample	$\Delta_r H$ in J/g	Temperature range in K
DCP	−320	410–450
DCP (1 mass%) in EVA	−1100	400–480
DCP (1 mass%) in PE	−700	400–480
DCP (1 mass%) in PE/EVA	−800	400–480

TABLE 2

Peroxidic reactions of thermally initiated crosslinking ("cool" premixed, 403 K)

Sample	Temperature in K	First heating run		
		T_{on}/K	T_{min}/K	$\Delta_r H$/J/g
Compound + 3 mol pure white oil	No peroxidic reactions			
Compound + 1 ml HMCN	455–505	Insufficient signal		
Compound + 3 ml HMCN	445–505[a]	456	481	−244
	445–520[a]	455	481	−302
		464	480	−232
	455–520[b]	472	479	−191
Compound + 6 ml HMCN	435–520[a]	438	487	−140
		442	483	−137
	440–518[b]	446	479	−133

[a] First heat run. [b] First heat run, repetition.

reduced (see Fig. 4). The crystallization of crosslinked semi-crystalline polymers is prevented by the network [5].

In contrast to these results the HMCN-crosslinked samples show no changes in melting and crystallization behaviour. Although the gel content grows with increasing concentration of crosslinking agent, the DSC plots of heating and cooling runs show, surprisingly, no significant differences. It seems that drastic changes in the melting as well as in the cooling behaviour happens only beyond an upper critical limit of degree of crosslinking. In our investigations the highest gel content of the HMCN-crosslinked samples is about 60%.

Figures 5 and 6 are illustrating the effect of the co-reagent TAIC on DSC data. No influences on melting and crystallization temperatures of the HMCN-crosslinked samples were detectable by DSC. This is also time for the heat of fusion and the crystallization enthalpy. The DSC data were therefore plotted against gel content (Figs. 7 and 8). These diagrams show that the melting and crystallization of the crosslinked compounds only significant changes beyond an upper gel content of about 60%. If this critical limit is not reached, no changes in melting and crystallization are found.

Figure 9 shows the influence of the processing temperature on the enthalpy values of melting and crystallization. With rising temperature the half-life times of peroxides decrease, and the shorter the half-lifetime the higher the resulting crosslinking density. A result of the prevention of crystallization is that the heat of fusion and the crystallization enthalpy decrease. If the processing temperature is further increased, thermally

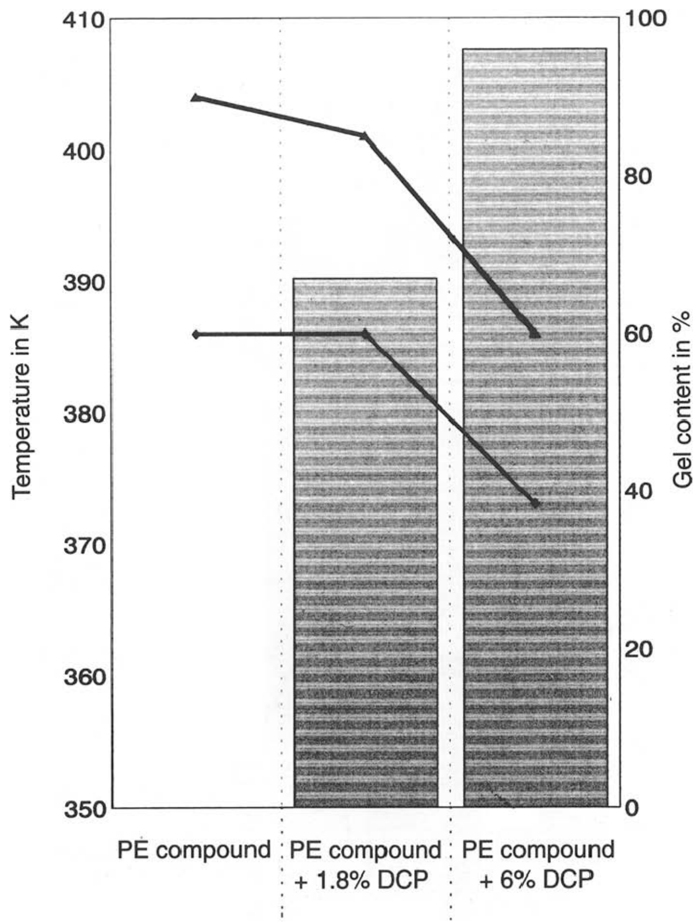

Fig. 3. Melting temperature and crystallization temperature for various amounts of DCP. ▲, T_{max}; ◆, T_{min}.

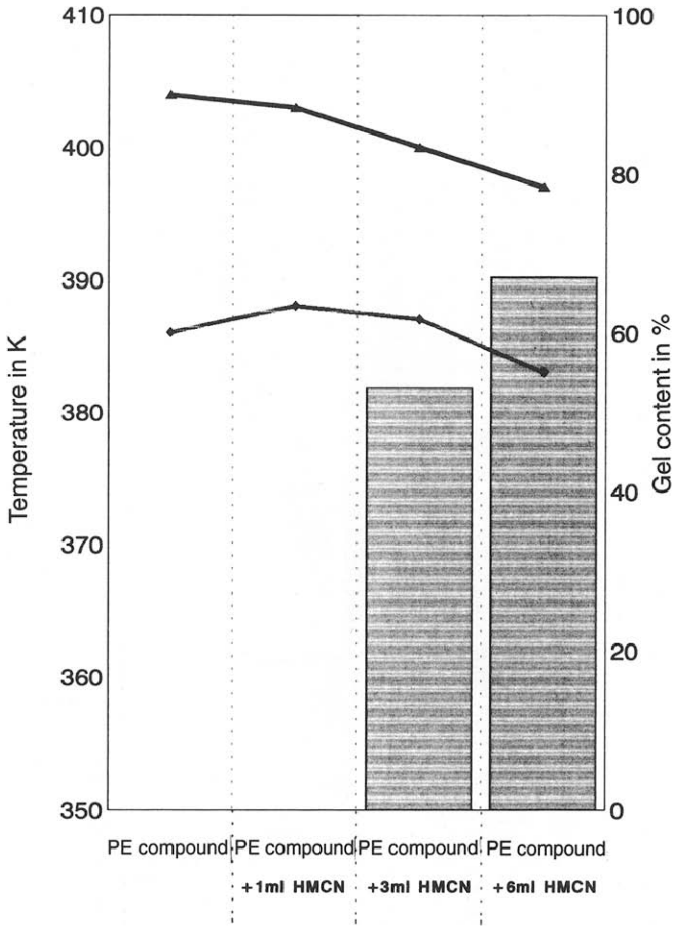

Fig. 4. Melting temperature and crystallization temperature for various amounts of HMCN. ▲, T_{max}; ◆, T_{min}.

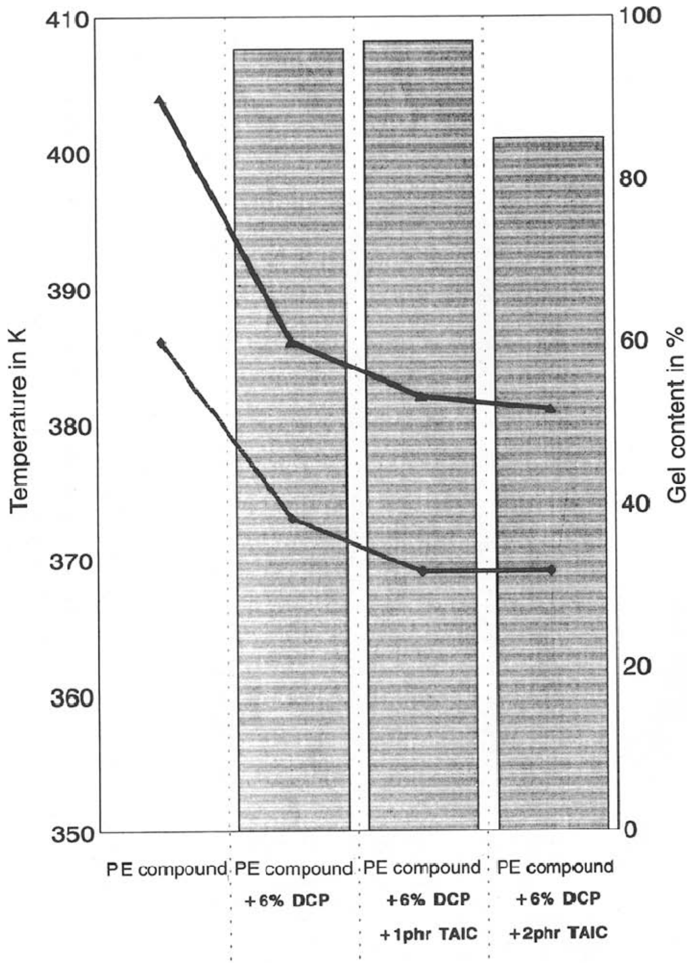

Fig. 5. Effect of TAIC on melting temperature and crystallization temperature (DCP-cured samples). ▲, T_{max}; ◆, T_{min}.

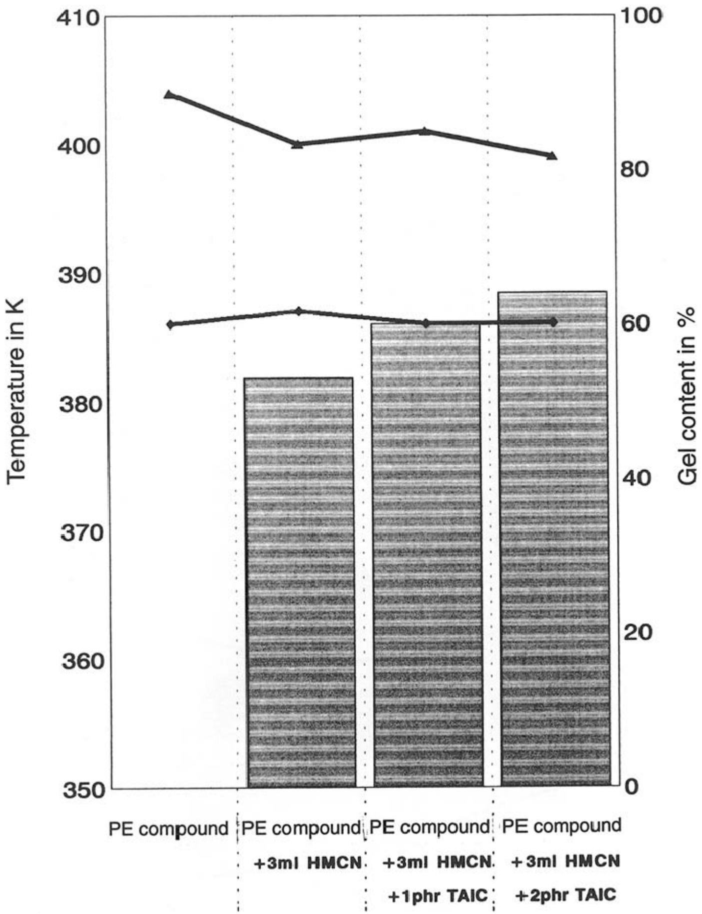

Fig. 6. Effect of TAIC on melting temperature and crystallization temperature (HMCN-cured samples). ▲, T_{max}; ◆, T_{min}.

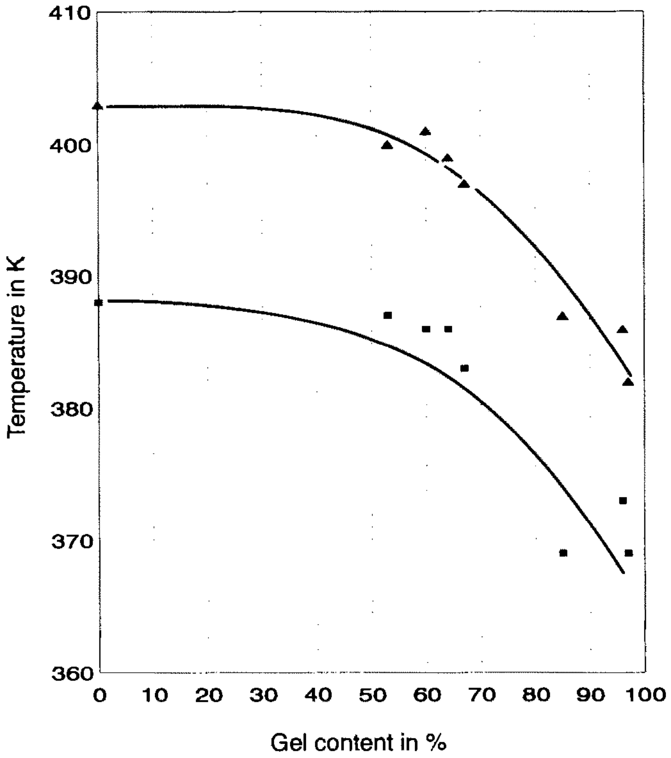

Fig. 7. Melting and crystallization temperature versus gel content. ▲, T_{max}; ■, T_{min}.

initiated and peroxide promoted degradation occurs. Because of the resulting smaller molecular weight the ability to crystallize improves. The values of ΔH_c and ΔH_m are increased.

Thermogravimetry

The thermal degradation of the polyethlene compound indicated by TGA occurs in two steps (Fig. 10). The onset temperatures were higher with higher gel content, but the conversion at the first degradation step was also increased. The degree of conversion at the end of the TGA measurements was nearly constant (Fig. 11).

DISCUSSION

The decomposition of the peroxide leads to a wide exothermic peak in the first heating run of the DSC experiment. The temperature range gives information about favourable processing conditions. It is also possible to come to conclusions about reaction energy of the peroxide decomposition and the crosslinking reaction. Commonly, first-reported data about peroxide decomposition temperatures give the half-life. But this value given

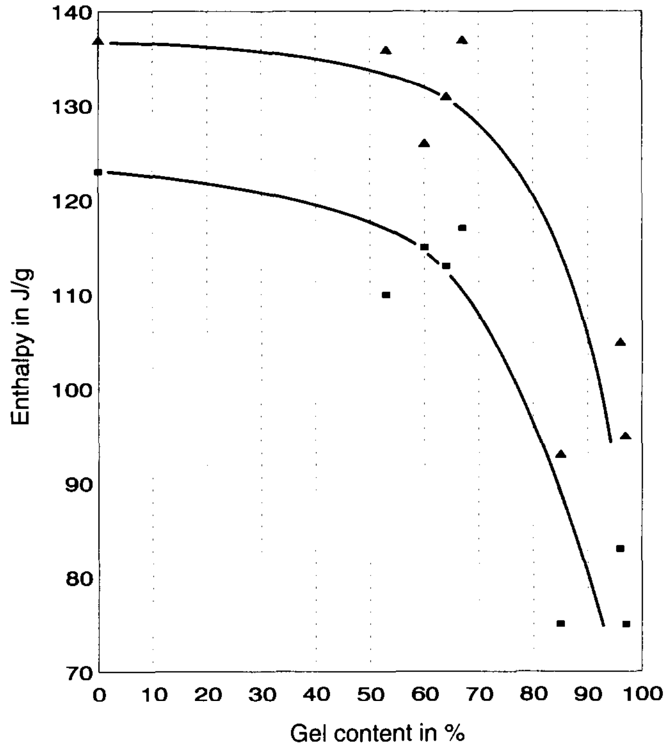

Fig. 8. Melting and crystallization enthalpy versus gel content. ▲, $\Delta_m H$; ■, $\Delta_c H$.

in the literature is generally determined in solution with low concentration of peroxide, and these conditions never correspond to real reactive processing conditions. The well established method of differential scanning calorimetry is useful to analyse the peroxidic reaction in a polymer matrix.

The sample volumes required for DSC measurements are very small (about 10 mm^3), though heterogenities in crosslinking structure in such small volumes of the HMCN cured samples are probably. The necessary sample volumes for the determination of gel content are greater (50 mm^3),

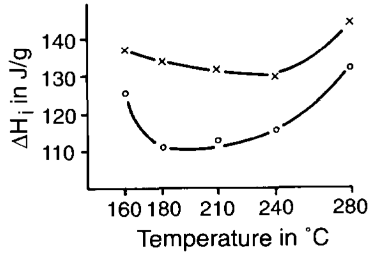

Fig. 9. Influence of crosslinking temperature on melting and crystallization enthalpy. ×, $\Delta_m H$; ○, $\Delta_c H$.

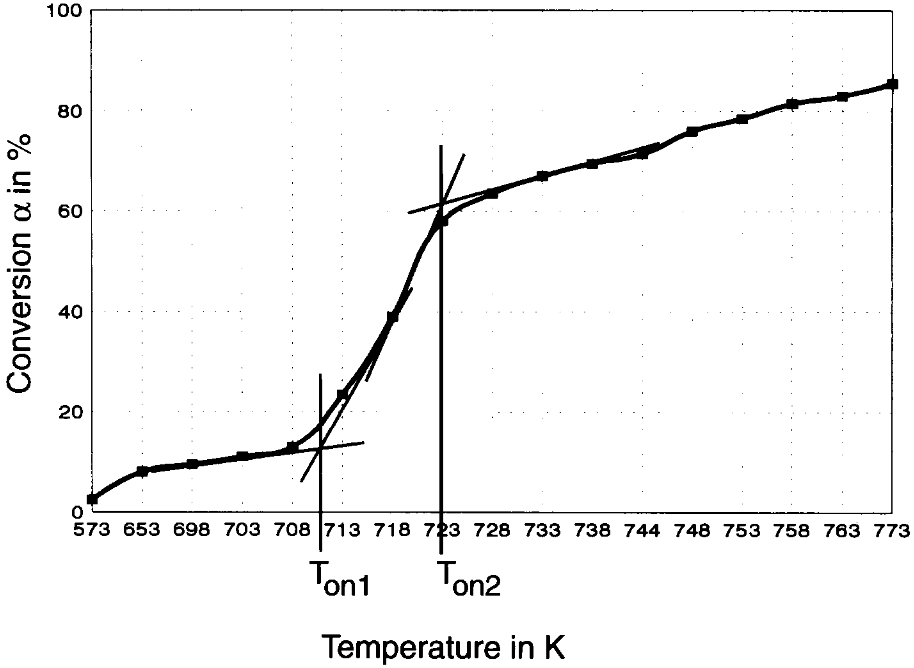

Fig. 10. Thermal degradation of the polyethylene compound determined by TGA.

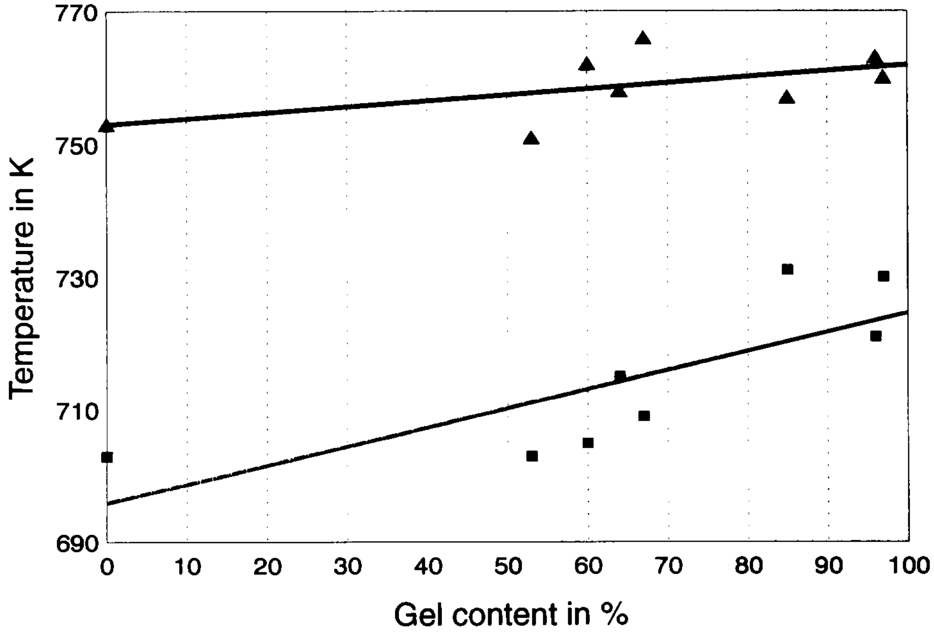

Fig. 11. Onset temperatures of thermal degradation versus gel content. ▲, T_{on1}; ■, T_{on2}.

and in these larger volumes no heterogeneities were detectable. The application of different independent methods is desirable to obtain conclusions about crosslinking homogenity.

The gel content increases with increasing amount of the crosslinking agent, but the melting and crystallization behaviour of the HMCN-crosslinked samples are not changed. The DSC data in dependence on gel content show that there exists a critical limit of crosslinking degree. Only above 60% gel are changes in melting and crystallization detectable with DSC.

The conclusions that slightly increased thermal stability could be shown in our investigations is not confirmed. On the contrary the onset temperature of the first degradation step is raised as is the amount of mass loss in this area. The first indicates higher thermal stability; the second supports lower thermal stability.

CONCLUSIONS

Thermoanalytical methods are useful for investigations of objects connected with reactive processing of polymers. One can obtain information about initializing steps, about influencing crystallization and about the resulting state of the process, for example the thermal stability. But one also has to take into account that the results depend on the polymeric and peroxidic substances used.

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