Macromol. Symp. ***129,*** *151–161 (1998)*

THE EFFECT OF CROSSLINKING ON MECHANICAL PROPERTIES OF LDPE FILLED WITH ORGANIC FILLERS

Ivan Chodak[1], **Zuzana Nogellova**[1], **Bohuslav V. Kokta**[2]

1. **Polymer Institute, Slovak Acad. Sci. 842 36 Bratislava, Slovakia**
2. **Univ. Quebec Trois Rivieres, Trois Rivieres, Canada**

Dedicated to the founder of the Polymer Institute Prof. Milan Lazár in honour of his 70th birthday

ABSTRACT : Mechanical properties of low density polyethylene filled with various organic fillers were investigated. Different effect of different fillers on the properties was observed and the effect of crosslinking of these materials is also different. Fine anisotropic fillers behave similarly as inorganic fillers. The effect of crosslinking is the highest for composites containing large particulate fillers like beech wood flour. The effects are discussed in terms of mechanical behaviour and crosslinking degree determined from extraction or equilibrium swelling data. A formation of covalent bonds between the filler surface and polymeric matrix is proposed as a result of crosslinking.

INTRODUCTION

Organic fillers are attracting attention as fillers for various plastics mainly due to their low price, low density and renewable nature. However, their direct application as a filler for thermoplastics generally and particularly for polyolefins is hindered by a serious drawback, namely insufficient wetting of the hydrophilic filler by hydrophobic polymeric matrix resulting usually in inferior mechanical properties. Various procedures were suggested for improving the

CCC 1022-1360/98/$ 10.00

polymer - filler interactions in the polypropylene or polyethylene filled with carbohydrate polymers such as cellulose, starch, sawdust, or aspen fibres. Usual attitude consists in a modification of the filler surface to make it less hydrophilic. The application of various coupling agents such as silanes [Ref. 1-3], isocyanates [Ref. 4], or derivatives of triazine or melamine [Ref. 5-7] was reported leading to an improvement of the properties of polyethylene or polypropylene filled with particles or fibres of various organic nature. Better mechanical properties of polypropylene filled with wood fiber were reported if silanes and maleated polypropylene was added to the mixture [Ref. 8]. Maleated polypropylene was also examined as a compatibilizing agent for polypropylene filled with reclaimed paper; dicumyl peroxide was added as the radical initiator [Ref. 9]. The same reactants were also used for improvement of the properties of LLDPE filled with chemithermomechanical aspen pulp [Ref. 10]. An alternative procedure consists in a modification of the filler by grafting with styrene, acrylamide or their mixtures while the process was initiated by ozonation of the filler surface [Ref.11].

A substantial improvement of mechanical properties was also observed for polyethylene filled with cellulose fiber if the composite was modified via radical reaction initiated by organic peroxide [Ref. 12, 13]. No other agent was added in this case and crosslinking to a low degree occurred.

Peroxide initiated crosslinking to rather high level was shown to be a powerful tool to compatibilization of blends of polypropylene / polyethylene [Ref. 14, 15], and proved also to be beneficial for improvement of mechanical properties of polyethylene filled with inorganic fillers, e.g. silica [Ref. 16]. Obviously, similar effect of crosslinking should be expected for polyolefins filled with organic fillers. Therefore in this paper we investigated the effect of crosslinking on the properties of polyethylene filled with various organic fillers. No surface pretreatment of the filler was made, neither any additional modifier, besides peroxide, was added.

EXPERIMENTAL

Low density polyethylene (Bralen RA-2-19, Slovnaft, Slovakia MFI = 2.0 g/10 minutes, ASTM D 12138) containing a common thermal antioxidizing system (BHT based) was used as the polymeric matrix. Several organic fillers were used differing in the shape and size of particles: wood flour (birch wood, large particles), milled dried canadian switch grass (particles

+ fibres), potato starch (particles), modified starch (O-propyl starch, aggregates), aspen fibres (fibres + particles), and reclaimed newspaper (fibres). Some characteristics of the fillers obtained from optical microscopy observation are given in Table 1. (2,5-dimethyl-2,5-ditertbutyl peroxy)hexyne (Luperox 130, Luperox GmbH, Germany, 90 mol % of active component) was used as the peroxidic initiator of the crosslinking.

Table 1 : Characteristics of the organic fillers used

Filler		Size, μ		aspect.	Note
	average	largest	smallest	ratio	
Recl.paper	220 x 15	1800	55	10	1
Aspen fibres	200 x 40	500x100	50x5	7	2
Beech flour	460 x 100	650 x 325	150x40	3.5	
Grass	135 x 30	410 x 55	45x15	3.5	3
Starch	20	67	8	1	
Mod. starch	10	15	7	1	

1. About 20 % small fibres, 20 x 2 μ, only length is given in column largest and smallest size
2. About 50 % small isotropic particles, diameter 5 - 15 μ
3. About 30 % small isotropic particles, diameter 5 - 25 μ

The blends were prepared in the Brabender PLE 331 mixing chamber at 140 °C for 10 minutes. Under these conditions conditions less than 5 % of the initiator added was decomposed during mixing. Crosslinking occured in a laboratory press Fontijne 50 at 180 °C for 20 minutes. More than 97 % of the peroxide was decomposed under these conditions.

Mechanical properties were measured using an Instron 4301 universal testing machine at deformation rate 10 mm/minute. Thermal dependences of Young's modulus were measured using a DMTA instrument Rheometric Scientific MK III in a bending mode at heating rate 3 °C/minute and frequency 10 Hz in bending mode.

Gel content of the samples after crosslinking was determined according to weight of the sample after 14 hour extraction in boiling xylene. The equilibrium swelling of pre-extracted samples was determined from the solvent uptake in xylene at 110 °C after 4 hours.

RESULTS AND DISCUSSION

A formation of insoluble portion, gel, of crosslinked samples is the first indication of the crosslinking degree. The results of gel content for all crosslinked samples are given in Table 2.

Table 2 : The content of insoluble gel formed in samples crosslinked by 1 wt % of peroxide in samples filled with various fillers.

filler	gel content, wt %					
wt %	aspen	paper	beech	grass	starch	mod.starch
0	85	85	85	85	85	85
10	89	88	86	93*	93	89
50	98	95	91	96	100	99

* 20 % of the filler added

The mechanical properties in dependence on the concentration of the filler are shown in Fig. 1 - 3. Although the composites with only two concentrations of filler were prepared, the tendency of properties change is obvious. Apparently, the fillers used can be divided into three groups, considering the effect of the filler itself and the effect of crosslinking on the mechanical properties. Aspen fibres and reclaimed paper (first group of fillers) resemble in the composites the effect of inorganic filler, e.g. silica (Ref. 16), at least qualitatively. Tensile strength values, after initial drop, slightly rise with increasing the filler content. Steady and rather extensive increase of the Young's modulus was observed while quite substantial decrease of elongation at break was found. The crosslinking results in an increase of tensile strength and elongation, while a drop of Young's modulus occured. Similar to the composites filled with silica (Ref. 16), the drop in modulus values can be ascribed to a decrease in crystallinity which always occurs in polyethylene due to crosslinking (Ref. 17).

Both starch - based fillers behave similarly. A presence of the filler leads to a substantial decrease in both tensile strength and elongation at break while certain increase in Young's modulus data was observed. Crosslinking resulted in a marginal increase in tensile strength and modulus but, rather surprisingly, no significant change in elongation at break was found.

The most interesting features were observed with the last group of fillers, namely beech wood flour and milled switch grass. A steady decrease in the tensile strength and elongation data were found with the increase of the filler content and modest increase in Young's modulus was

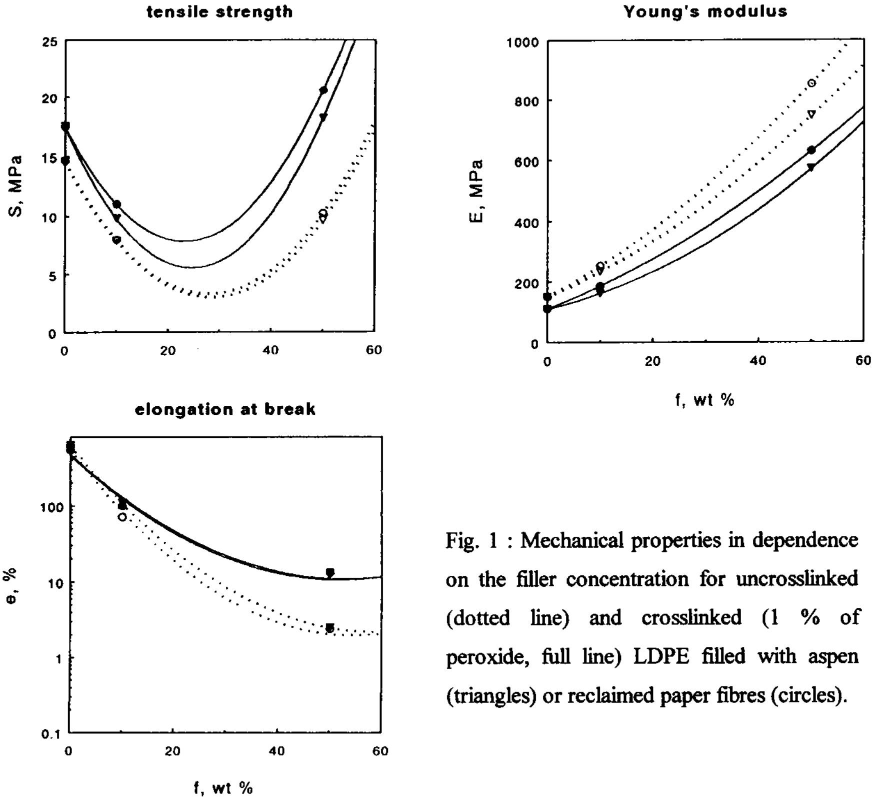


Fig. 1 : Mechanical properties in dependence on the filler concentration for uncrosslinked (dotted line) and crosslinked (1 % of peroxide, full line) LDPE filled with aspen (triangles) or reclaimed paper fibres (circles).

registered. Crosslinking leads to a small increase in elongation at break, two - fold increase in Young's modulus data, and a substantial increase in tensile strength. Moreover, the shape of the tensile strength dependence is quite different, compared to uncrosslinked composites. A steady decrease was found in the latter case while an increase after initial decrease was observed for the crosslinked samples.

Temperature dependence of the modulus data was measured as well. In this case we are only reporting on the data for one sample of the first and third group and for the unfilled polyethylene. From Fig. 4 a, b it is seen that the modulus of both filled composites is higher than the modulus of polyethylene. Compared to uncrosslinked materials, crosslinking leads to an increase in Young's modulus for the samples containing grass but a decrease was observed for both unfilled LDPE and for sample filled with reclaimed paper. Considering crosslinked samples, the interesting region is above melting temperature. In both filled samples the

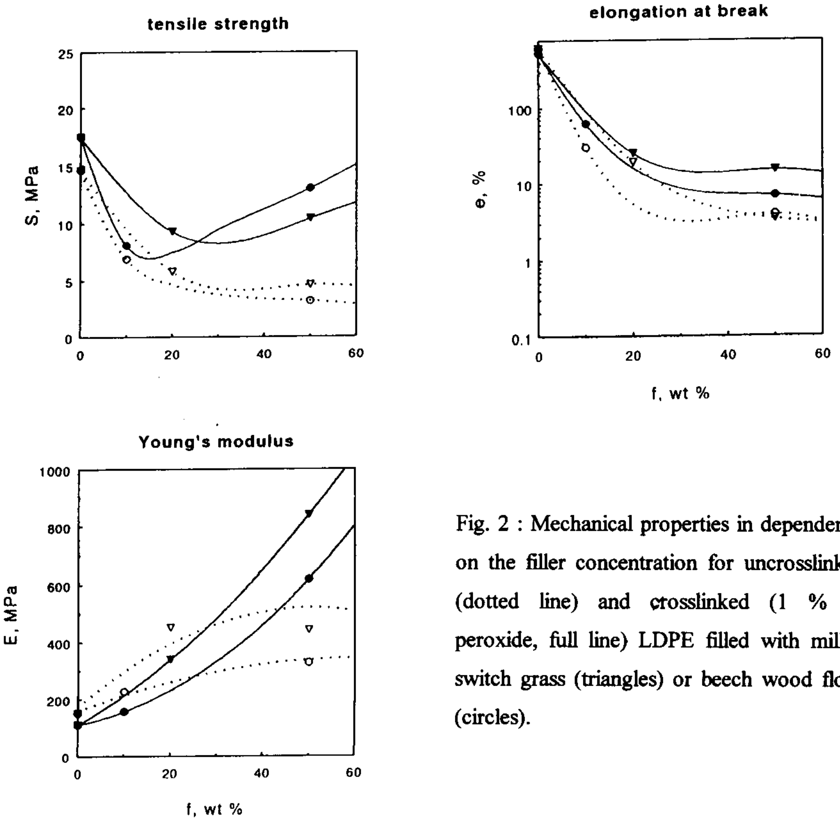
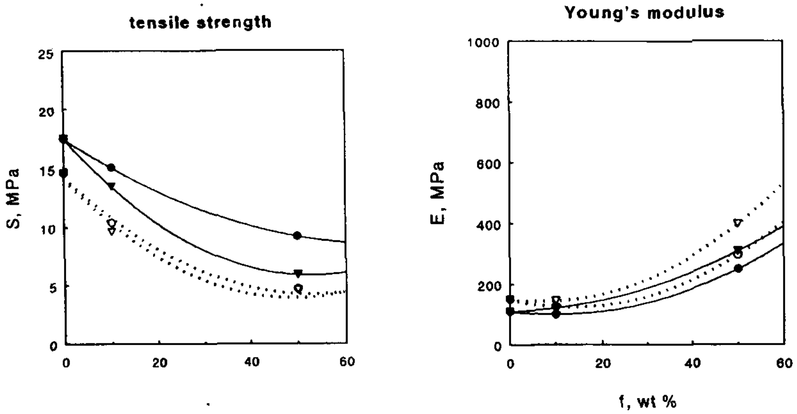


Fig. 2 : Mechanical properties in dependence on the filler concentration for uncrosslinked (dotted line) and crosslinked (1 % of peroxide, full line) LDPE filled with milled switch grass (triangles) or beech wood flour (circles).

modulus above Tm is higher after crosslinking compared to uncrosslinked material. It is of interest that the difference in moduli for crosslinked and uncrosslinked material is substantially higher for the sample filled with grass than for the one filled with paper. Another point worth to mention is that there is a measurable modulus for the filled samples above Tm, although for LDPE, both uncrosslinked and crosslinked, the modulus values were found to be undetectably low. It means that the reinforcing effect of the filler is higher than the effect of crosslinking, regarding mechanical properties above Tm.

The observed results can be explained, if considering a concerted effect of both the reinforcing activity of the filler and the crosslinking. The reinforcing and stiffening effect of the filler presence depends on the contact area between the filler and polymeric matrix. Crosslinking results in a decrease of the matrix crystallinity but, at the same time, an increase in polymer -



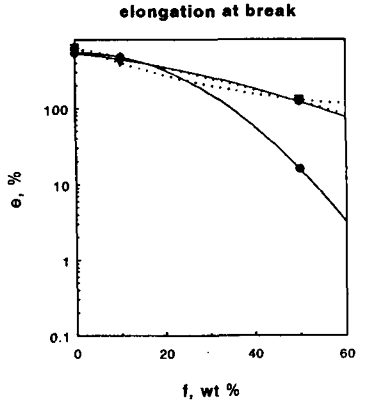


Fig. 3 : Mechanical properties in dependence on the filler concentration for uncrosslinked (dotted line) and crosslinked (1 % of peroxide, full line) LDPE filled with O-propyl starch (triangles) or native potato starch (circles).

filler interaction on the filler interface is suggested due to, presumably, a formation of direct covalent bonds as a result of peroxide - initiated radical reactions. If these effects are considered, following preliminary conclusions can be made :

1. Aspen and paper fibres : In spite of difference in hydrophilicity between filler and matrix, the interaction is rather high due to high surface area (high aspect ratio) of the filler. A contribution of crosslinking to the reinforcing effect is low and is overlapped by a decrease in crystallinity. Therefore the summation of the effects results in a decrease of the modulus in crosslinked material.

2. For composites filled with more or less anisotropic fillers (beech wood flour and milled switch grass, aspect ratio less than 4) the reinforcing effect of the filler is overcompensated by

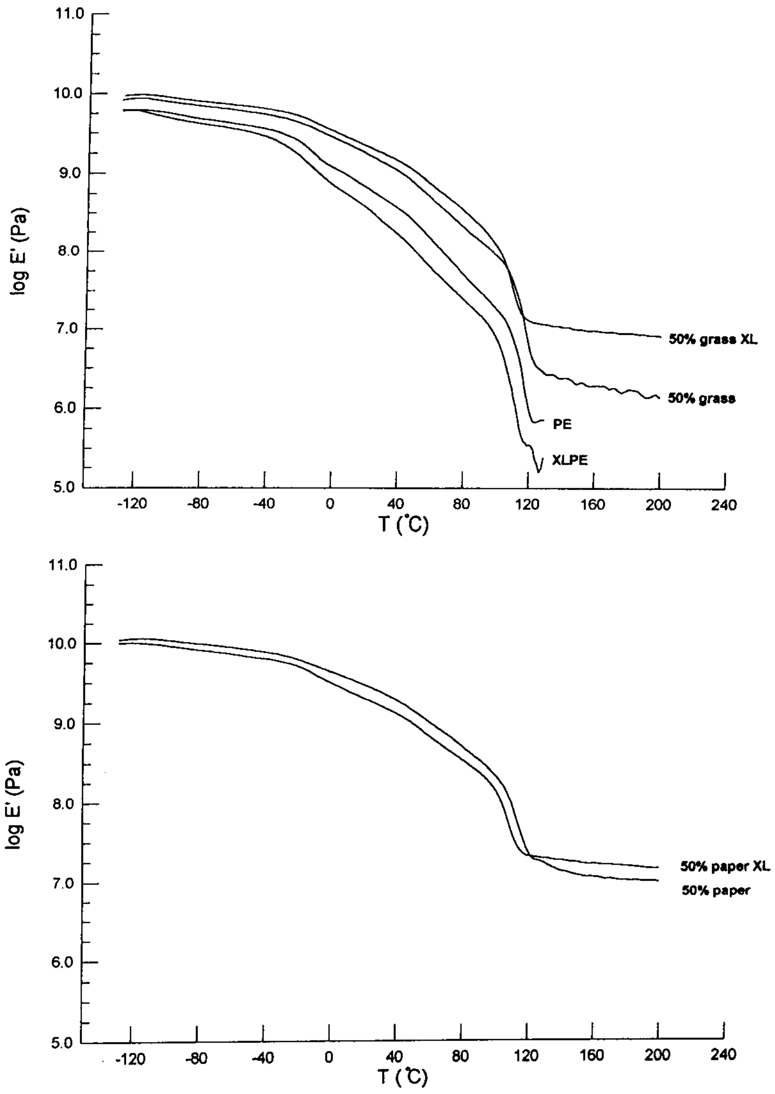


Fig. 4 : Temperature dependence of storage modulus for the crosslinked and uncrosslinked samples of LDPE unfilled and filled with grass (a) or paper fibres (b).

low polymer - filler interaction resulting from low surface area of the filler. Assumed formation of matrix - filler covalent bonds due to crosslinking leads to increased tensile properties.

3. Addition of starch - based fillers does not have any extensive reinforcing effect since the filler itself is rather soft compared to other fillers investigated. Therefore the increase in tensile strength and modulus, as well as the decrease in elongation at break is much lower than for the materials filled with the other fillers. The changes due to crosslinking reflect mainly the effect on the polymeric matrix itself.

In crosslinked samples the polymer - filler interaction can be estimated from equilibrium swelling data (Ref. 18). Empirical interaction parameter can be calculated according to the Kraus equation (Ref. 19) assuming that at high interactions physical crosslinks are formed, which contribute to overall crosslink density resulting in lower swelling degree. Thus, the ratio between swelling degree of unfilled matrix and that of filled composite can be considered as a measure of the interaction. Usually the interaction parameter is calculated as a slope of the swelling degree dependence on concentration of the filler. In our case, since the samples with only two concentrations were prepared, the interaction parameter was not calculated and the interactions were estimated according to the swelling degree expressed as a volume portion of matrix polymer in swollen gel. The results are shown in Table 3.

Table 3 : Equilibrium swelling parameters (content of solvent Q, and portion of polyethylene in swollen gel V_R) after swelling of crosslinked LDPE filled with various filler at 110 °C in xylene.

Filler	Q, wt % of the dry sample			V_R, volume %		
beech	827	724	273	7.6	7.6	9.4
grass	827	430*	205	7.6	11.5*	11.9
starch	827	620	295	7.6	8.8	8.9
mod.starch	827	635	314	7.6	8.6	8.5
aspen	827	597	137	7.6	9.0	14.8
paper	827	550	158	7.6	9.7	13.6
filler, %	0	10	50	0	10	50

* 20 wt % of the filler

The data in Table 3 support the conclusion drawn from mechanical properties. The swelling is the lowest for cross-linked composites filled with fillers with high aspect ratio (highest V_R

values in the presence of 50 % filler). It means that physical crosslinks are formed and rather high polymer - filler interaction is effective even if the material is not crosslinked. According to swelling data lower polymer - filler interaction is to be expected with milled grass and beech wood flour. Very poor reinforcing effect can be achieved in the presence of starch in spite of rather small particle size of this filler. Apparently, the hydrophilicity of the filler surface is too high. The effect of crosslinking is negligible in this case, probably because of insufficient degree of crosslink formation on the filler surface indirectly indicated by high gel as shown in Table 2. Since the crosslinking of the matrix is highest in the presence of starch, it can be concluded that crosslinking is initiated by peroxide preferentially in bulk polyethylene matrix and not on the filler surface. Surprisingly, the propylation of the starch does not improve the interaction.

CONCLUSIONS

Reasonable mechanical properties can be achieved for composites of LDPE filled with various organic fillers. The fillers with the fibric shape behave similarly to inorganic reinforcing fillers. The fillers with low aspect ratio do not have any reinforcing effect and the properties of the composites are inferior. The properties can be substantially improved by crosslinking of the matrix. The addition of starch leads to poor mechanical properties which can not be improved via crosslinking. The formation of covalent bonds between the polymeric matrix and the filler surface is proposed as an explanation for the obtained results. Polymer - filler interactions for various fillers were estimated from the equilibrium swelling data of crosslinked samples. The results calculated from swelling data correspond with the other conclusions.

ACKNOWLEDGEMENT

The authors from Polymer Institute, Bratislava are grateful to Slovak grant agency VEGA (grant No. 2/1144/96) for financial support of this research.

REFERENCES

(1) S.H. Morrell, *Plastic and Rubber Proc. Application* **1**, 179 (1981)

(2) A. D. Beshay, B.V. Kokta, C. Daneault, *Polymer Composites* **6**, 261 (1985)

(3) F.M.B. Coutinho, T.H.S. Costa, D.S. Carvalho, *J. Appl. Polymer Sci.*, **64**, 1227 (1997)

(4) A.Y. Coran, R. Patel, *US patent 4 323 635* (1982)

(5) P. Zadorecki, P. Flodin, *J. Appl. Polymer Sci* **30**, 3971 (1985)

(6) P. Zadorecki, P. Flodin, J. *Appl. Polymer Sci.* **31**, 1699 (1986)

(7) L. Hua, P. Zadorecki, P. Flodin, *Polymer Compos.* **8**, 199 (1987)

(8) M.M. Sain, B.V. Kokta, Polym. *Plast. Technol. Engn.* **33**, 89 (1994)

(9) D. Maldas, B.V. Kokta, *J. Adhesion Sci. Technol.*, **8**, No 10, 1 (1994)

(10) B.V. Kokta, C. Daneult, A.D. Beshay, *Polymer Composites* **7**, 337 (1986)

(11) B.V. Kokta, L. Araneda, C. Daneault, *Polymer Engn. Sci.* **24**, 950 (1984)

(12) P. Bataille, P. Allard, P. Cousin, S. Sapieha, *Polymer Composites* **11**, 301 (1990)

(13) P. Cousin, H.P. Schreiber, P. Bataille S. Sapieha, *J. Appl. Polymer Sci.* **37**, 3057 (1989)

(14) I. Chodak, H. Repin, W. Bruls, I. Janigova, *Macromol. Symp.* **112**, 159 (1996)

(15) E. Borsig, E. Malcherova, M. Lazar, *Polym. Int.* **30**, 367 (1979)

(16) I. Chodak, I. Chorvath, Makromol. Chemie, *Macromol. Symp.* **75**, 167 (1993)

(17) K.A. Kunert, *J. Polymer Sci., Polymer Lett. Ed.* **19**, 479 (1981)

(18) I. Chodak, I. Chorvath, I. Novak, K. Csomorova, *Eur. Polymer J.*, **28**, 197 (1992)

(19) G. Kraus, *J. Appl. Polymer Sci.* **7**, 861 (1963)