

# Oxazoline-functionalized hydrogenated nitrile rubber as impact modifier for polyamide-6

J. Piękowski\*, I. Gancarz, M. Właźlak

*Institute of Organic Technology and Polymers, Wrocław University of Technology, ul. Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland*

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## Abstract

Hydrogenated nitrile rubber (Therban) was modified in the solution and in the melt to introduce oxazoline units into the chain. Conversion of nitrile groups reached about 40% what corresponds 13.6 mol% of oxazoline units in the modified sample. The chemical structure of product was confirmed by FTIR and 2D NMR spectra. To calculate the degree of conversion from IR spectra, correlation between <sup>1</sup>H NMR and IR data was found.

Blends of modified samples with polyamide-6 were prepared. DSC data seem to indicate the partial miscibility of blend components as a result of the creation of covalent bonds between them. By addition of modified rubber, impact strength of the polyamide was highly improved. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Functionalized polymers; Polymer blends; Reactive processing

## 1. Introduction

For many years oxazoline and its derivatives played an important role in organic chemistry. They were used, for example, as chiral catalysts or optically active reagents. Of all of the possible isomers 1,3-oxazoline (2-oxazoline) was the most frequently used. There are many methods for its synthesis—the new review paper [1] presents more than 20 of them. The oxazoline rings are very reactive, especially for the reactions with nucleophiles. Detailed review on reactions of 1,3-oxazoline can be found in the papers of Kronek et al. [2] and Wörner [3].

The last few years have brought a growing interest in oxazoline compounds among polymer chemists. Polymers with oxazoline ring functionality could be obtained by the following methods:

1. Free-radical polymerization or copolymerization of monomers bearing oxazoline ring, like 2-isopropenyl-2-oxazoline (IPO) [4] or 5-oxazolinyln-pentylmethacrylate [5,6].
2. Free-radical grafting of oxazoline monomers onto polymers. In this way IPO was grafted onto polypropylene (PP), ethylene–propylene rubber (EPR) and styrene polymers [4]. Ricinoloxazoline maleinate was used for grafting polycaprolactone [7], polyethylene (PE), EPR,

styrene block copolymers [8] and poly(organophosphazenes) [9].

3. Conversion of functional groups existing in polymer into oxazoline functionality. One can imagine many such reactions, however the one most often applied is the catalyzed reaction of nitrile groups with 2-aminoalcohols. Copolymers of acrylonitrile with butadiene or hydrogenated butadiene [3], styrene [10] or polymers bearing –CN end-groups [3,4,11] were modified in this way.
4. Reaction between polymer functional groups (acidic, amine) with oxazoline derivatives or bis-oxazoline compounds [11].

Polymer chemistry profits from very high reactivity of oxazoline groups in many ways. The examples of using oxazoline functionality for grafting [5] or introducing double bonds into polymer [12] are described. Bis-oxazoline compounds were applied as linear chain extenders for polyesters [3,13] and polyamides [14]. Oxazoline macromonomers [15,16] were used to synthesize hyperbranched polymers of various structures [17]. Oxazoline-grafted polymer was used as a nonionic hydrogel for metal complexation [18]. Oxazoline polymers and copolymers [19–22] as well as oxazoline functionalized polymers [4,8,10] were found to be useful also as reactive compatibilizers for polymer blends.

Blending of polymers offers attractive opportunities for

\* Corresponding author. Fax: +48-71-3203678.

Table 1  
Parameters of modification in the solution and crude estimation of modification degree

Synthesis number	Solvent	Solution conc. (wt.%)	Amount of catalyst (mol/mol C≡N)	Amount of aminoalkohol (mol/mol C≡N)	Heating time (h)	$H_{1662}/H_{2239}$
1	Chlorobenzene	7.7	0.19	7.8	4.5	0
2					11.0	0.097
3					18.0	0.13
4					24.5	0.15
5		15.3	0.19	7.8	24.5	0.29
6					42.5	0.47
7		23.1	0.19	10.3	20.5	0.28
8					48.5	0.52
9		15.3	0.31	12.8	13.0	0.34
10					29.0	0.60
11					41.5	0.71
12					65.0	0.92
13					79.0	1.06
14					102.5	1.25
15	<i>o</i> -Dichlorobenzene	16	0.31	12.8	11.0	1.13
16					27.0	2.00
17					41.0	2.87
18					55.0	3.30
19		16	0.31	12.8	10.0	0.85
20					27.0	1.33
21					50.0	2.75
22					89.5	2.77

developing new materials. Most polymer blends however are thermodynamically immiscible and compatibilization seems to be necessary to obtain desired properties. The role of compatibilizers so far was played by block- and graft-copolymers. Last few years reactive compatibilization became very popular. In this process the polymers to be blended have to possess the suitable functional groups. In the blending process these groups react, chemically linking both ingredients of the mixture, creating in this manner a copolymer compatibilizer in situ. As a result, new materials possessing better mechanical properties and stable morphologies are obtained. An oxazoline-group containing polymers can be utilized in such process. A well-known example is that of poly(styrene-*co*-vinyl oxazoline) which was used in the blends with modified PE, nitrile rubber and polyamide-6 [4]. Oxazoline-functionalized polymers like SAN [10], PE, PP and their copolymers [8] were investigated as compatibilizers for blends with PA or PBT. It was found that in these blends interfacial reactions involving oxazoline rings resulted in much finer, stable morphology and had dramatic effect in increasing interfacial adhesion even when the concentration of the reactive groups was very small. Increase in the tensile strength and improvement of the impact properties were also observed [4].

In the present paper we will report the improved route to oxazoline modification of hydrogenated butadiene-acrylonitrile copolymer that allowed to get a higher degree

of functionalization than previously reported [3]. The properties of blends of such modified nitrile rubber with polyamide-6 was also investigated.

## 2. Experimental

### 2.1. Materials

Hydrogenated nitrile rubber—Therban 1707 (Bayer AG) containing 34 wt% of acrylonitrile was used for modification. 2-Aminoethanol (Reachim, Russia) was distilled under reduced pressure in an argon atmosphere. Cadmium acetate (catalyst) (POCH, Gliwice, Poland) was dried for 24 h at 80°C in a vacuum oven. Chlorobenzene and *o*-dichlorobenzene (U.C.B. Belgium) were used as received. Cyanox 425 (American Cyanamid Co.) served as an antioxidant. Polyamide-6 (Stilamid S-27) was kindly supplied by Z.W.Ch. Stilon S.A., Poland. Chloroform was purchased from POCH (Poland) and deuterated chloroform from Dr Glaser AG Basel, Switzerland.

### 2.2. Modification in solution

Nitrile rubber (5 g) was dissolved under reflux in the chosen solvent (chlorobenzene or *o*-dichlorobenzene) to which antioxidant (0.1 wt.% of polymer) was added. The desired amounts of aminoalcohol and catalyst were added

Table 2  
Degree of modification calculated from  $^1\text{H}$  NMR data and estimated from FTIR data (correction on Fig. 6)

Synthesis number <sup>a</sup>	$D_{\text{oxa}}$ (NMR) % <sup>b</sup>	$A_{1662}/(A_{2931} + A_{2858})$	$D_{\text{oxa}}$ (IR) % <sup>c</sup>
1	–	0.0037	0.60
2	–	0.0068	1.1
3	1.45	0.010	1.6
4	–	0.0095	1.5
5	–	0.019	3.1
6	–	0.035	5.7
7	–	0.060	1.0
8	–	0.033	5.3
9	–	0.024	3.9
10	5.0	0.035	5.6
11	–	0.048	7.7
12	–	0.062	9.9
13	–	0.070	11.3
14	14.2	0.078	12.6
15	–	0.076	12.4
16	–	0.127	20.4
17	–	0.190	30.6
18	32.0	0.208	33.4
19	7.4	0.05	8.0
20	18.2	0.09	14.5
21	24.0	0.15	24.1
22	–	0.24	38.5

<sup>a</sup> As in Table 1.

<sup>b</sup> From  $^1\text{H}$  NMR data.

<sup>c</sup> Calculated from correlation in Fig. 6.

and the mixture was continuously stirred and refluxed under a stream of argon bubbling through the solution. After a pre-determined time, the polymer solution was sampled, diluted with chloroform and poured into a large (ten-fold) amount of methanol. The precipitated polymer was washed with fresh methanol several times, redissolved in chloroform and the whole procedure of product purification was repeated. Finally, the polymer was dried in the vacuum oven at room temperature. The detailed reaction parameters

Table 3  
Parameters and results of modification in the melt

Synthesis number	Amount of catalyst (mol/mol C≡N)	Amount of aminoalcohol (mol/mol C≡N)	Temp. (°C)	Heating time (min)	$A_{1662}/(A_{2931} + A_{2858})$	$D_{\text{oxa}}$ <sup>a</sup> (%)																						
23	0.033	1.38	155	45	0.010	1.6																						
			155	45			24	0.066	2.76	160	45	0.023	3.6	155	45	25	0.066	2.76	160	45	0.029	4.7	165	90	26	0.033	1.38	160
24	0.066	2.76	160	45	0.023	3.6																						
			155	45			25	0.066	2.76	160	45	0.029	4.7	165	90	26	0.033	1.38	160	45	0.011	1.8	170	45				
25	0.066	2.76	160	45	0.029	4.7																						
			165	90			26	0.033	1.38	160	45	0.011	1.8	170	45													
26	0.033	1.38	160	45	0.011	1.8																						
			170	45																								

<sup>a</sup> Calculated from correlation in Fig. 6.

and results are given in Tables 1 and 2. Successive syntheses were just numbered. Samples 19–22 were synthesized on a larger scale (from 10 g of rubber) without taking samples during reaction course.

### 2.3. Modification in melts

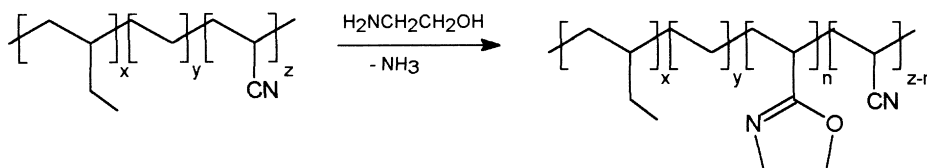
A home-made, Brabender like mixer was used for oxazoline functionalization of Therban in the melt. The chamber of the mixer had a capacity of 40 cm<sup>3</sup>. Rubber was crumbled and plasticized in the mixer chamber. Successively antioxidant and solution of catalyst in 2-aminoethanol were slowly added. Mixing was continued for the desired time at a chosen temperature, then the sample was taken off from the mixer and cooled. In procedure 26 (Table 3) rubber was swelled for 24 h in the solution of aminoalcohol with catalyst and antioxidant before loading into the mixer. Parameters of these processes are given in Table 3.

For analysis, all samples were purified by dissolution in chloroform and precipitation into methanol. Such procedure was repeated twice and then samples were dried in vacuum oven at room temperature.

### 2.4. Analysis

For FTIR analysis 0.1 g of modified polymer was dissolved in 2 ml of chloroform. Spectra were recorded on Perkin–Elmer System 2000 apparatus. Thirty-two scans with 4 cm<sup>-1</sup> resolution were taken. Absorbance at wave-number 1662 cm<sup>-1</sup> (C=N in oxazoline groups), 2239 cm<sup>-1</sup> (C≡N from acrylonitrile), 2858 and 2931 cm<sup>-1</sup> (CH– stretching bonds) were measured. The last two peaks come from the non-reacting part of the molecule so their intensity should not change during the modification process. They were used as standard peaks.

NMR spectra were recorded on AMX 300 MHz Bruker apparatus. About 0.03 g of polymer was dissolved in 0.6 ml of deuterated chloroform. Samples of low solubility in this solvent were dissolved in non-deuterated chloroform and



Scheme 1.

then a small amount of deuterated solvent was added to lock the signal on the NMR instrument. For qualitative estimation of the modification degree,  $^1\text{H}$  NMR peaks at 2.4 ppm (protons in CH groups in polymer chain from both oxazoline and nitrile mers), 3.8 and 4.2 ppm (protons from  $\text{CH}_2$  groups of oxazoline rings) were integrated [3]. Degree of modification was defined as the molar ratio of oxazoline rings and the sum of oxazoline and nitrile groups:

$$D_{\text{oxa}} = \frac{[\text{oxa}]}{[\text{oxa}] + [\text{C}\equiv\text{N}]} 100\%.$$

The thermal properties of all samples were measured calorimetrically using a Metler-Toledo Model TA 821<sup>e</sup> differential scanning calorimeter with a Metler thermal analysis data station Model Star<sup>e</sup>. Temperature calibration was performed using zinc and indium as standards. Heating cycles were conducted at a heating rate of  $10 \text{ K min}^{-1}$ , with a sample size between 10 and 18 mg with standard aluminum sample pans. An air atmosphere surrounded the sample. The  $T_g$  was taken as the temperature at which the heat capacity reached one half of the entire step change as observed on the thermogram. Crystallinities were calculated using an extrapolated value of enthalpy corresponding to the melting of 100% crystalline polyamide sample:  $\Delta H_f = 190 \text{ J/g}$  [23].

## 2.5. Blending procedures and properties of the blends

The chosen samples, used for blending with polyamide were marked as “Th-oxa X” where X is the molar content of oxazoline units in acrylonitrile–butadiene rubber. They were blended at  $220^\circ\text{C}$  for desired time with polyamide-6 in the mixer described above. The material was then compression-molded into 4 mm thick plates ( $220^\circ\text{C}$ , pressure: 0 for 2 min, 50 Pa for 1 min and  $>200 \text{ Pa}$  for 1 min) from which standard shape samples were cut and their Charpy notch impact strength was measured. The values in Table 5 are average from at least 10 measurements.

## 3. Results and discussion

### 3.1. Modification in solution

As has been mentioned above, the method and preliminary parameters of introducing 1,3-oxazoline ring into hydrogenated nitrile rubber was taken from Ref. [3]. This method is based on the reaction of nitrile group with 2-aminoalcohol in the presence of the catalyst (cadmium acetate). The scheme of reaction is shown in Scheme 1 (conversion of nitrile groups into oxazoline functionality).

Wörner [3] was able to convert only 6% of nitrile groups to oxazoline rings and all attempts to get higher degree of modification resulted in crosslinked, insoluble material.

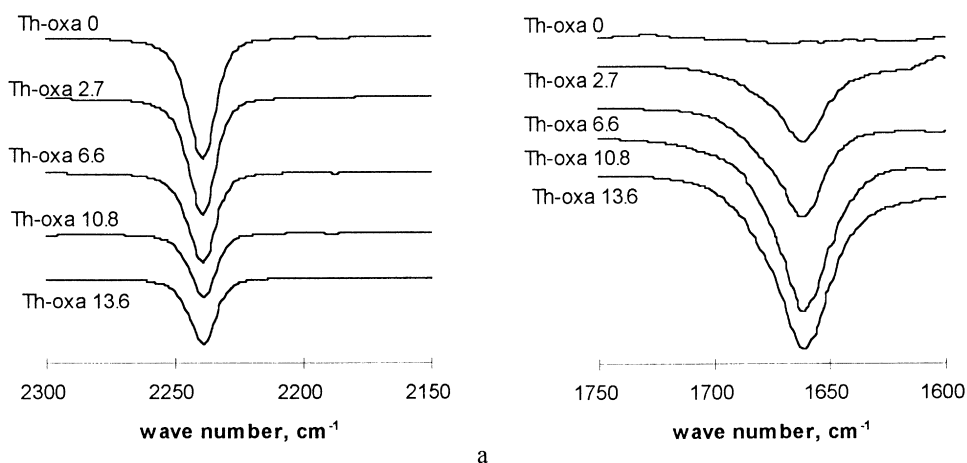


Fig. 1. Absorption band of (a) nitrile ( $\text{C}\equiv\text{N}$ ) groups and (b) oxazoline ( $\text{C}=\text{N}$ ) groups for Therban 1707 and some modified samples.

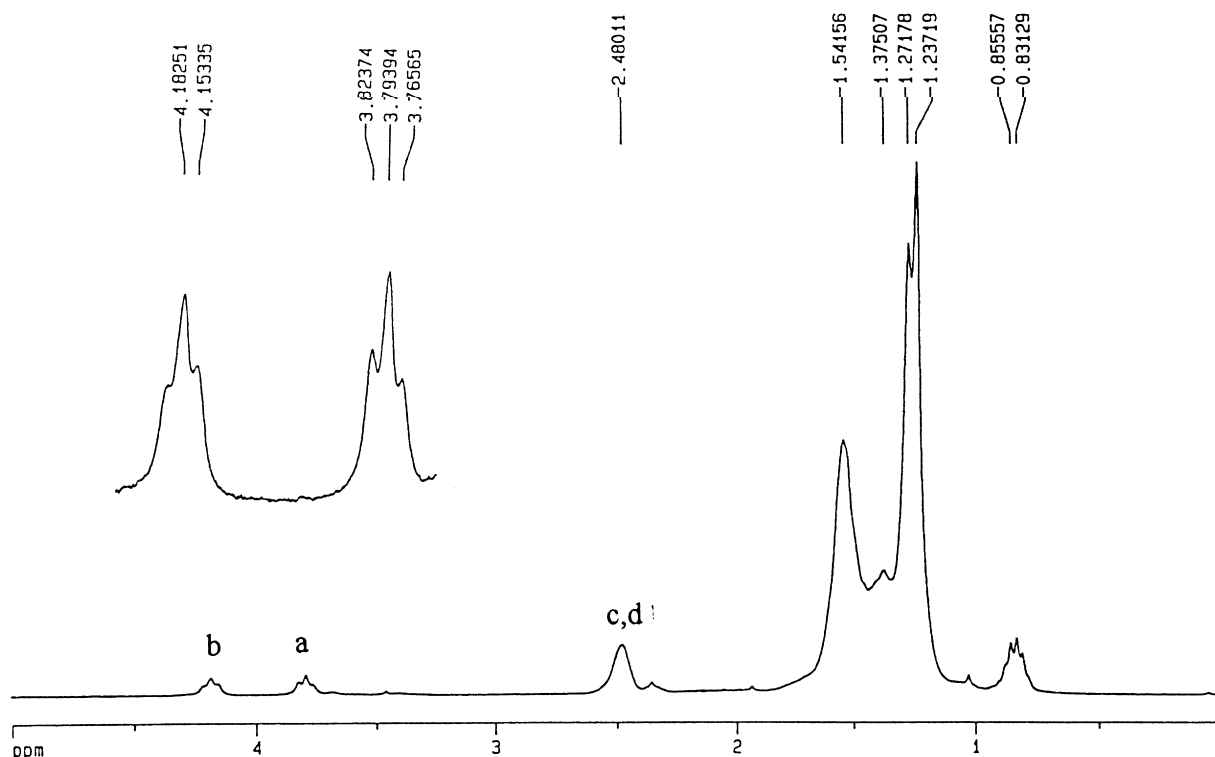


Fig. 2.  $^1\text{H}$  NMR spectrum of oxazoline-functionalized hydrogenated nitrile rubber (sample oxa 14).

Assuming that this could happen due to the presence of residual double bonds in the polymer, we decided to add a small amount of antioxidant to the reaction mixture. We also tried to make the reaction proceed in a higher boiling solvent—dichlorobenzene. Chosen reaction parameters—solution concentration, amount of aminoalcohol and catalyst, kind of solvent are given in Table 1.

The reaction course was monitored by recording FTIR spectra of samples taken after certain time of heating. In the modified polymers a new strong peak at  $1662\text{ cm}^{-1}$  is characteristic for the  $\text{C}=\text{N}$  group in oxazoline rings (Fig. 1b). Clear diminution of nitrile group absorption at  $2239\text{ cm}^{-1}$  (Fig. 1a) was also observed. Ratio of intensities of these two peaks was used as a crude estimation of modification degree (Table 1).

From the data in Table 1 one can see that large increase in modification degree was achieved after changing solvent from chlorobenzene (b.p.  $132^\circ\text{C}$ ) to higher boiling dichlorobenzene (b.p.  $180^\circ\text{C}$ ). In all the studied cases prolongation of reaction time gave higher conversion degree. It should be

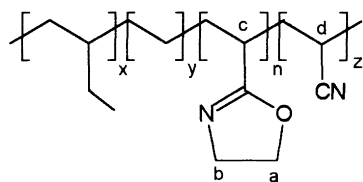
pointed out that within applied conditions the crosslinking effect was not observed. Samples with higher content of oxazoline functionality however became insoluble when kept some time in the air atmosphere.

### 3.2. Detailed analysis of modified polymers

For some chosen samples of modified polymers  $^1\text{H}$  NMR spectra were recorded to calculate degree of conversion of  $\text{C}\equiv\text{N}$  groups into oxazoline functionality more precisely. According to Ref. [3] the peaks of interest for that purpose were those of chemical shift  $\delta$  3.8, 4.2 and 2.4 ppm (Fig. 2). The first two come from  $\text{CH}_2$  protons of oxazoline rings (a and b in Scheme 2, assignment of peaks in  $^1\text{H}$  NMR spectrum of the modified polymer) while the last—from protons of  $\text{CH}$  group in polymer chain from both oxazoline and nitrile containing mers (c and d in Scheme 2).

All four  $\text{CH}_2\text{--CH}_2$  protons are in fact diastereotopic and should be seen as ABCD spin system. Chemical environment however for geminal protons attached to the same carbon is not very different, so they in fact form  $\text{A}_2\text{B}_2$  spin system that is manifested by two triplets.

The typical  $^1\text{H}$  NMR spectrum of modified polymer is given in Fig. 2. The assignments of these signals were confirmed by us after analysis of 2D NMR spectra (Figs. 3 and 4). From the HH Cosy spectrum (Fig. 3) it is clearly seen that the peaks at 3.8 and 4.2 ppm (appearing after modification) are coupled to each other (manifested by the off-diagonal peaks). Other crosspeaks indicate the coupling



Scheme 2.

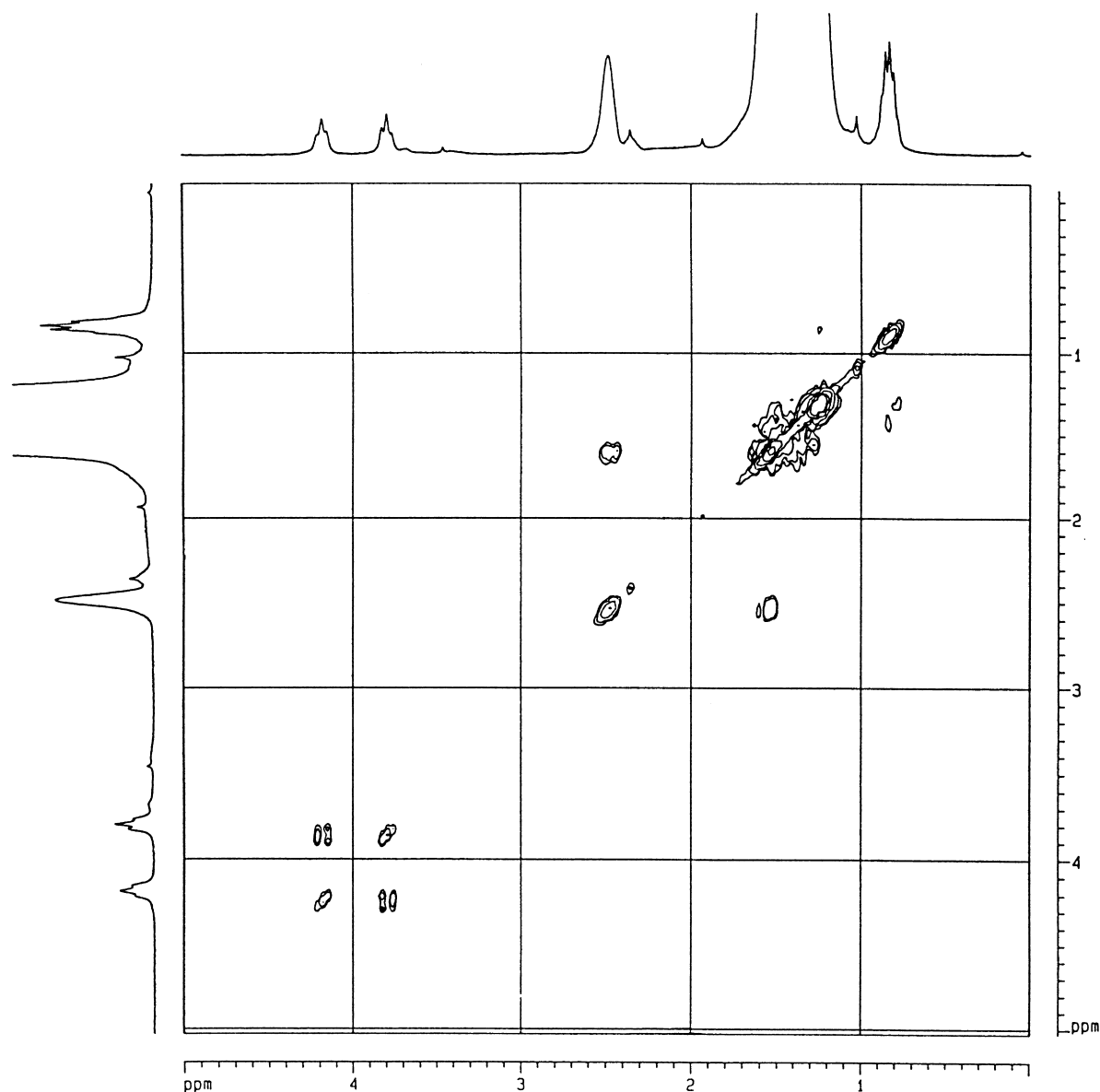


Fig. 3. HH Cosy spectrum of oxazoline-functionalized hydrogenated nitrile rubber (sample oxa 14).

of CH protons at 2.44 ppm to CH<sub>2</sub> protons at 1.59 ppm as well as CH<sub>3</sub> protons at 0.83 ppm to CH<sub>2</sub> protons at 1.23 ppm. From HC Cosy (Fig. 4) it can be seen that protons at 3.8 and 4.2 ppm are attached to carbons with chemical shift 54.1 and 66.9 ppm, respectively. These values are in agreement with the tabulated data for carbon atoms of CH<sub>2</sub> groups deshielded by nitrogen and oxygen, to which they are directly connected.

Results of calculation of modification degree for chosen samples from <sup>1</sup>H NMR data are given in Table 2. We tried to correlate NMR results with those obtained from FTIR analysis. Unexpectedly, band intensity ratio of C=N to C≡N appeared to be quite good estimation for conversion degree in the whole investigated range. The ratio of  $H_{1662}/H_{2239}$  as a function of calculated modification degree

is linear function ( $y = 0.102x$ ) with correlation coefficient equal 0.9872 (Fig. 5). One would expect more reliable results however, by correlating the modification degree with the ratio of absorption of the group C=N (1662 cm<sup>-1</sup>) or C≡N (2239 cm<sup>-1</sup>) to the absorption of the bands coming from stretching CH bonds (2931 + 2858 cm<sup>-1</sup>). These last absorption bands were assumed to stay unchanged during process. In both cases we have got good linear correlation with the correlation coefficient equal 0.9949 and 0.9638, respectively. As one can see the best estimation for the modification degree seems to be the absorption ratio of C=N groups to CH stretching bonds (Fig. 6) and this function ( $y = 0.00622x$ ) was used to calculate conversion degree in all modified samples. Results are given in Table 2.

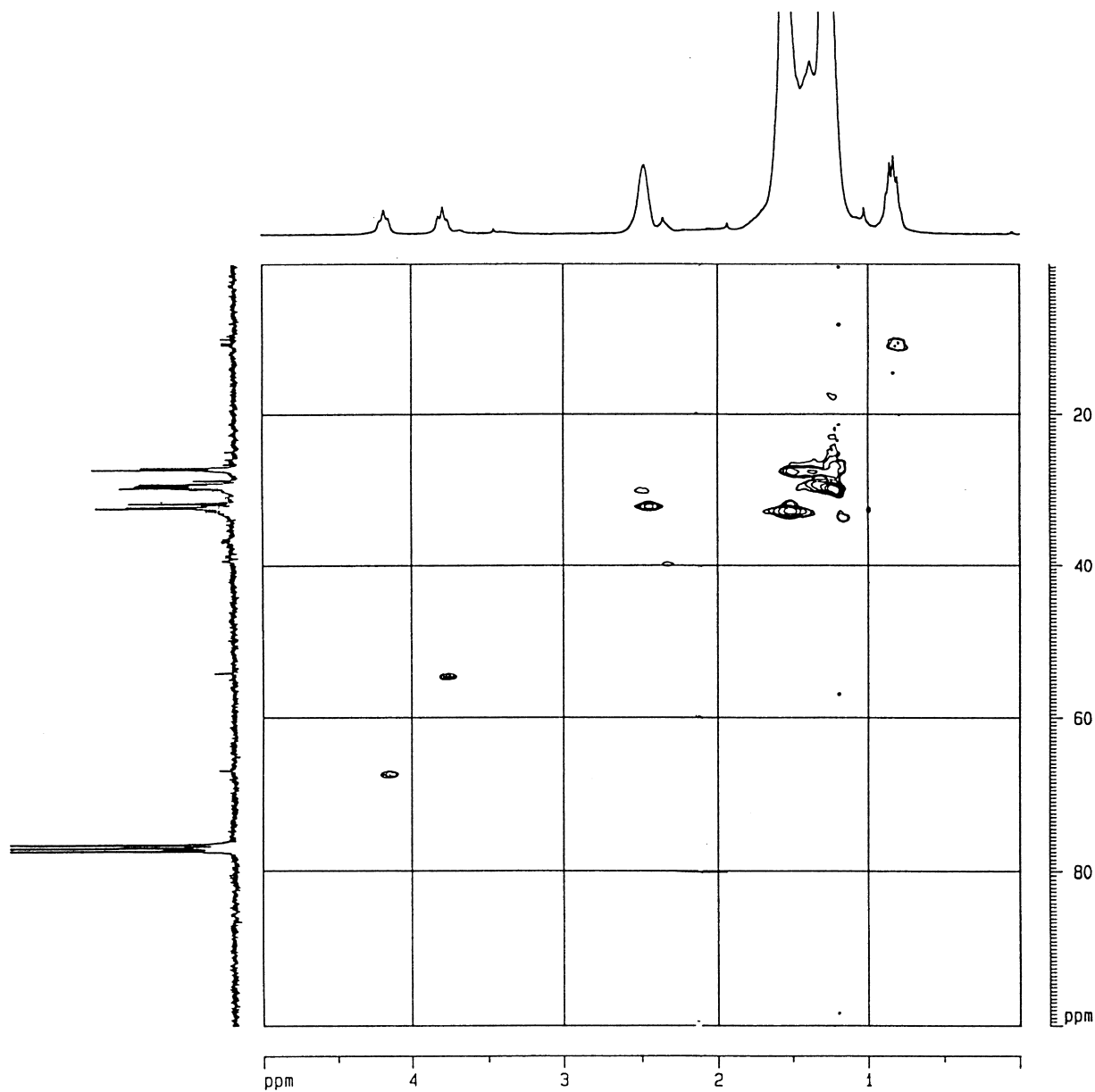


Fig. 4. HC Cosy spectrum of oxazoline-functionalized hydrogenated nitrile rubber (sample oxa 14).

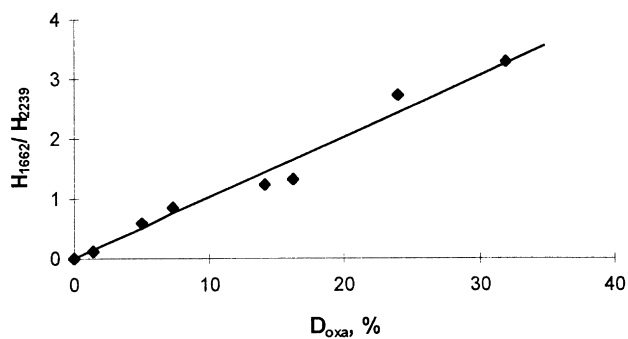


Fig. 5. Correlation between the ratio of intensity of absorption bands C=N to C≡N and modification degree calculated from  $^1\text{H}$  NMR.

Dependence of estimated degree of modification on reaction time for two temperatures is shown in Fig. 7. Deviation from linearity is clearly observed for long reaction time. It would mean that there is some limiting modification degree that can be achieved.

### 3.3. Modification in the melt

Modification in the melt would have numerous advantages over that in the solution. It would allow avoiding the usage of solvents and the whole precipitation procedure after reaction. Some experiments were done to check the

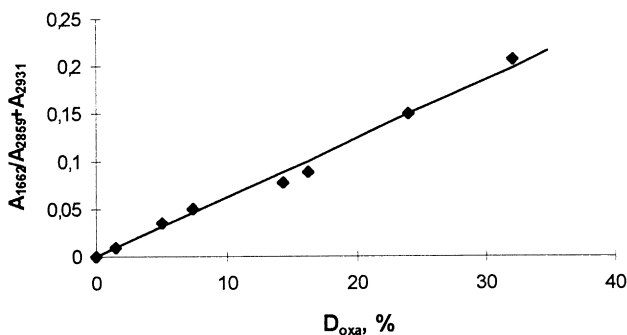


Fig. 6. Correlation between degree of modification and absorption ratio of C=N ( $A_{1662}$ ) to stretching CH ( $A_{2931} + A_{2858}$ ).

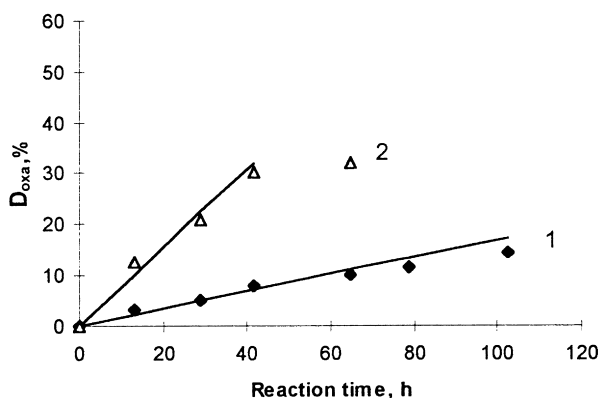


Fig. 7. Dependence of conversion degree on reaction time: 1—modification in chlorobenzene (samples oxa 9–14, Table 1), 2—modification in *o*-dichlorobenzene (samples oxa 17–20, Table 1).

modification possibility in such conditions. The parameters and results of such process are given in Table 3.

As one can see, we were able to get some conversion (up to 4.7%) of nitrile groups into oxazoline groups. The obtained modification degrees though small, are higher than in solution for such short time. They seem to increase with amount of aminoalcohol and catalyst, temperature and time. There were however limits that did not allow to go to higher values of these parameters. Higher temperature and longer times caused polymer degradation. Mechanochemically induced radicals and imperfect oxygen removal from reaction chamber could be the reasons of various undesired side reactions. The product was black and brittle and did not remain that after reaction in solution. Some technical problems with addition in the mixer of fluid ingredients to the plasticized polymer also appeared. There was some maximum amount of ingredients added to plasticized rubber above which they were thrown off from the mixer.

### 3.4. Blends of modified Therban with polyamide-6

Data obtained with DSC are summarized in Figs. 8 and 9 and Table 4. As could be seen in Table 4, the glass transition of butadiene–acrylonitrile rubber increases with increasing amount of CN-groups converted into oxazoline units. One can conclude that cyclic oxazoline side groups hinder chain motions and increase their stiffness.

Nitrile rubber and polyamide are incompatible as is demonstrated by two glass transition temperatures:  $T_{g2}$  associated with rubber-rich region and  $T_{g4}$  associated with PA-rich region. In all studied blends the  $T_g$  of rubber phase (both

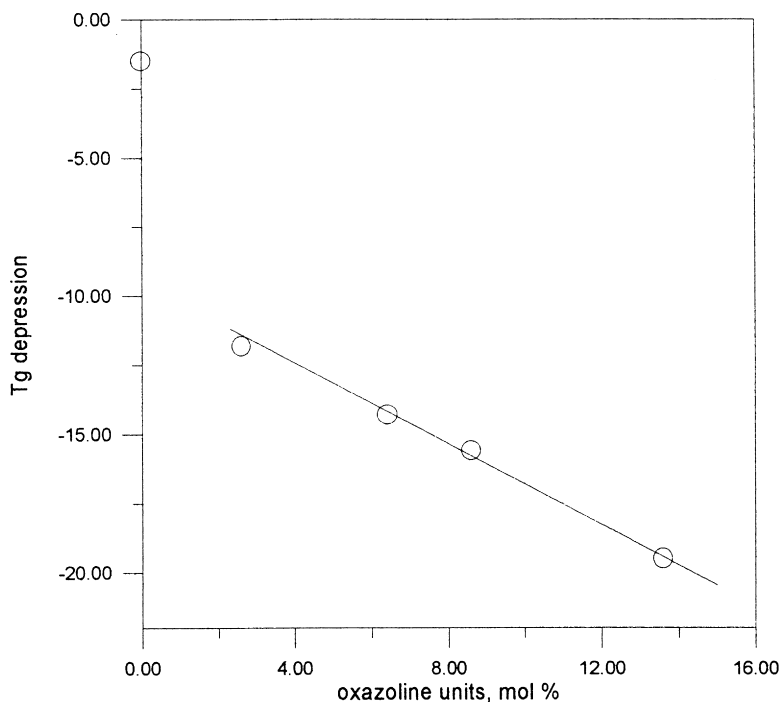


Fig. 8. Dependence of  $T_g$  depression of PA in the blend with modified Therban on content of oxazoline units in rubber.



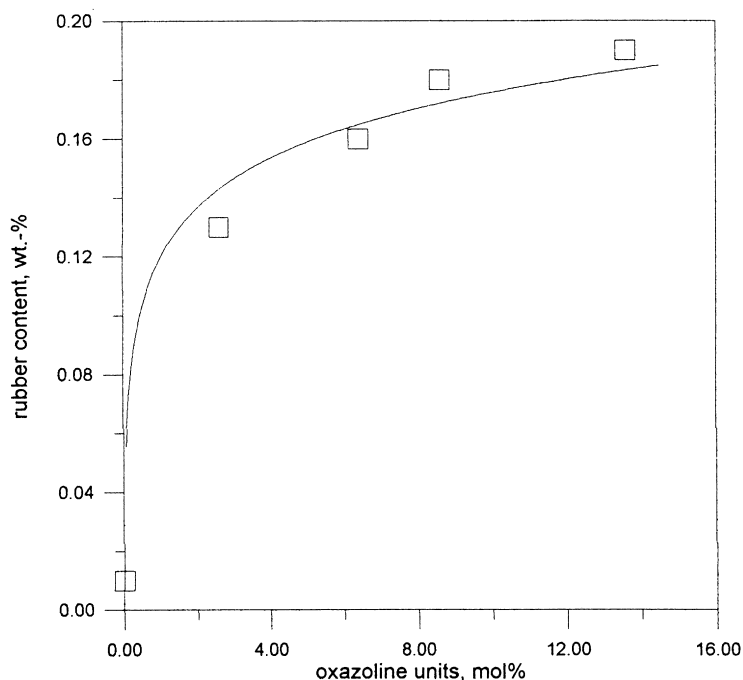


Fig. 9. Rubber content in the PA mixed phase vs. content of oxazoline units in the rubber.

unmodified and after oxazolation) was found to occur at about the same position as in the rubber alone. The small differences (between  $-1.2$  and  $+1.4$  K) may be attributed to the error of experimental data.

The glass transition of amorphous polyamide phase in the investigated range (excluding unmodified Therban) seems to decrease linearly with increasing molar fraction of oxazoline units in the rubber (Fig. 8). Data were fitted by least-squares regression technique; the slope of the straight line was found to be  $-0.7321$  and correlation coefficient equal to  $0.9964$ . No significant change of  $T_g$  of polyamide-rich region was observed in the blend with the unmodified Therban (corresponding glass transition temperature is marked on the  $T_g$ -axis). These results confirm the incompatibility of polyamide-6 and butadiene–acrylonitrile rubber and suggest at least partial miscibility in PA/Th-oxa blends. Blends containing nitrile rubber modified with oxazoline seem to have a microstructure that is a composite of the PA crystalline phase coexistent with two amorphous phases. Our results suggest that Th-oxa macromolecules could react with the end groups of polyamide forming graft copolymers dissolved in the polyamide amorphous phase but not in the rubber phase. Using the empirical inverse rule of mixtures (Fox equation) [24] one can roughly estimate the composition of the mixed phase of amorphous polyamide. The calculated weight fraction of the rubber content in the mixed phase increases from 0.01 to 0.19 for PA/Therban and PA/Th-oxa 13.6 blends, respectively (Fig. 9). The miscibility enhancement due to the introduction of covalent bonds between the constituents of the blend is observed. Crystallization reduces the quantity of polyamide associated

with the Th-oxa in the compatible amorphous phase. Data in Table 4 show that actual (calculated) rubber/amorphous PA ratio is higher than the prepared blend ratio of rubber and PA (15/85).

It is interesting to compare the actual rubber/amorphous polyamide ratio with those predicted by Fox equation. As we can see from Table 4 the amount of rubber in the blends is significantly higher than could be dissolved in the PA matrix. One can state that the PA/Th-oxa system exhibits a narrow range of miscibility and the excess of rubber in the blends form a separate phase. By suitable reduction of rubber content one can expect total disappearance of rubber phase and creation a two-phase system consisting of PA crystalline and PA amorphous mixed regions. Further research is necessary to confirm this hypothesis.

Some of the modified samples were added to the

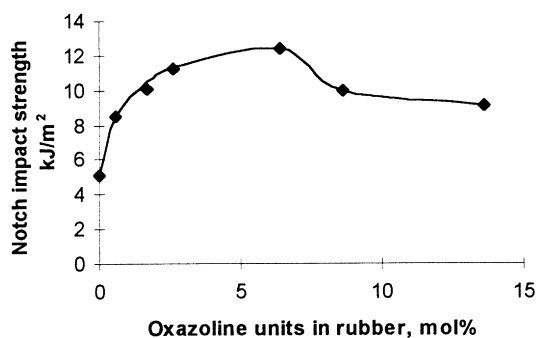


Fig. 10. Dependence of notch impact strength of blends of modified Therban with polyamide-6 on oxazoline content in the rubber (rubber content in the mixture, 15 wt.%; blending time, 3 min).

Table 4  
DSC measurements of the blends of polyamide-6 with modified nitrile rubber

Blend	$T_{g1}$ (neat rubber)	$T_{g2}$ (rubber in the blend)	$\Delta T (T_{g2} - T_{g1})$	$T_{g3}$ (neat PA)	$T_{g4}$ (PA in the blend)	$\Delta T (T_{g4} - T_{g3})$	Rubber content in the mixed phase (wt. fraction)	Heat of fusion (J/g)	Crystallinity degree (%)	Rubber/amorphous PA (wt. ratio)
PA	—	—	—	52	—	—	—	75.4	40	—
PA/Th-oxa 0	-24.9	-26.1	-1.2	—	50.5	-1.5	0.01	62.2	39	0.29
PA/Th-oxa 2.6	-22.6	-24.7	-2.1	—	40.2	-11.8	0.13	57.8	36	0.28
PA/Th-oxa 6.4	-21.8	-23.2	-1.4	—	37.7	-14.3	0.16	56.9	35	0.27
PA/Th-oxa 8.6	-20.1	-18.7	1.4	—	36.4	-15.6	0.18	54.9	34	0.27
PA/Th-oxa 13.6	-17.9	-17.4	0.4	—	32.5	-19.5	0.19	53.7	33	0.26

Table 5

Impact strength of blends of modified Therban with polyamide-6

Symbol of the sample blended with PA-6	Rubber content in the blend (wt.%)	Notch impact strength (kJ/m <sup>2</sup> )
Th-oxa 0	0	4.46
	15	5.12
	20	7.57
Th-oxa 0.6	15	8.45
		14.7 <sup>a</sup>
Th-oxa 1.7	15	10.1
	20	9.04
Th-oxa 2.6	15	11.24
Th-oxa 6.4	15	12.37
Th-oxa 8.6	15	9.92
Th-oxa 13.6	15	9.14

<sup>a</sup> Blending time, 25 min; all other samples, 3 min.

polyamide-6 and the impact strength of such blends was measured. Results are given in Table 5. Unmodified nitrile rubber practically does not improve the impact properties of polyamide-6. For oxazoline-modified rubber we got clear dependence of impact strength on modification degree (Fig. 10). First, impact strength increases with conversion degree, an optimum is observed, then seems to slowly decrease. Under the investigated conditions optimum is achieved for modification degree about 18% what corresponds about 6 mol% of oxazoline units in modified rubber.

The chosen time of blending (3 min) does not seem to be sufficient. As we can see for sample oxa-26 (Table 5) prolonged mixing dramatically increases the impact strength of the sample.

#### 4. Conclusions

Under the chosen reaction conditions we were able to get modified hydrogenated nitrile rubber in which up to almost 40% of nitrile groups were converted into oxazoline units. This corresponds to about 13.6 mol% of oxazoline units in the chain. Modification in the melt did not appear to be as efficient as in the solution.

FTIR and 2D-NMR data confirmed the chemical structure of the modification product and made possible the calculation of modification degree.

DSC results confirm partial compatibility of modified nitrile rubber with polyamide-6 which may be the result of creation of covalent bonds between constituents in the blend.

Impact strength of polyamide-6 was highly improved by the addition of modified nitrile rubber. Optimization of blend composition and blending parameters seems to be necessary.

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