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The process of increasing the functionality of poly(glycidyl azide) GAP
Proces zwiększenia funkcyjności poli(azydku glicydylu) (GAP)

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Abstract: *Poly(glycidyl azide) (GAP) is a synthetic polymer with energetic properties due to the presence of an azide group in its structure. It is used in industry primarily as a component of binders for rocket fuel. Classically produced GAP has secondary hydroxyl groups, which react much more slowly with the crosslinking agents diisocyanates found in high-energy materials. It has been confirmed that methods can be used which modify the structure of GAP thereby obtaining a polymer with an increased number of functional groups. Furthermore, such processes produce a polymer with more desirable primary hydroxyl groups. Using such a polymer is economically advantageous and allows easier control of processes using GAP. Attempts were made to obtain such a modified polymer. The polymers obtained were subjected to FTIR analysis, viscosity measurements and hydroxyl group values.*

Streszczenie: *Poli(azydek glicydylu) to syntetyczny polimer o właściwościach energetycznych, które zawdzięcza posiadaniu w swojej strukturze grupy azydkowej. Znajduje zastosowanie w przemyśle przede wszystkim jako składnik lepiszczy do paliw rakietowych. Klasycznie wytwarzany GAP posiada drugorzędowe grupy hydroksylowe dużo wolniej reagujące z występującymi w materiałach wysokoenergetycznych czynnikami sieciującymi – diizocyjanianami. Potwierdzono możliwość zastosowania metod, które pozwalają zmodyfikować strukturę GAP i uzyskać polimer ze zwiększoną ilością grup funkcyjnych. Ponadto w procesie tym wytwarzany jest polimer o bardziej pożądanych pierwszorzędowych grupach hydroksylowych. Używanie takiego polimeru jest korzystne ekonomicznie i pozwala na łatwiejszą kontrolę procesów z użyciem GAP. Podjęto próby otrzymania tak zmodyfikowanego polimeru. Otrzymane polimery poddano analizie FTIR, pomiaru lepkości i wartości grupy hydroksylowej.*

Keywords: *GAP, poly(glycidyl azide), PECH, polyepichlorohydrin, epoxidation, modification, functional groups, hydroxyl groups*
Słowa kluczowe: *GAP, poli(azydek glicydylu), PECH, poliepichlorohydryna, epoksydacja, modyfikacja, grupy funkcyjne, grupy hydroksylowe*

1. Introduction

Glycidyl polyazide – GAP – is a synthetic polymer first synthesised in 1972. Due to the presence of an azide group in its structure, it has explosive properties. The molecular weight of GAP ranges from 500 g/mol to as much as 36,000 g/mol for the most branched polymers. It is a viscous, amber liquid. It has a low glass transition temperature (–45°C), low viscosity and a density of approximately 1.3 g/cm^3. The enthalpy of formation of GAP is +957 kJ/kg, while the heat of reaction for the decomposition of the azide group into nitrile and nitrogen is 685 kJ/mol. In addition, it shows low sensitivity to mechanical and thermal stimuli [1-3].

Its application is based on the use of the characteristics of macromolecular compounds which, when added to explosives, reduce sensitivity to common stimuli and improve their mechanical properties. This makes GAP one of the most well-known and frequently used energetic binders; its use in rocket fuel increasing their calorific value. The hydroxyl groups it contains react with the isocyanates used in solid heterogeneous rocket fuels, which act as crosslinking agents in them. The most commonly synthesised GAP is bifunctional and has secondary hydroxyl groups which react much more weakly with diisocyanates than the primary groups. GAP functionality ranges from 1.6 to 3.1, depending on the catalyst used, the initiator and the ratio of initiator to substrate (ECH – epichlorohydrin). The functionalization of the linear polymer is approximately 2. To achieve better results in the crosslinking process of polymer matrices, crosslinking agents such as triols or trioisocyanates are added to the blends to produce products with better mechanical properties. The polymer has secondary hydroxyl groups which react more slowly than primary hydroxyl groups with the –NCO group, so polymers having secondary groups require the additional introduction of catalysts or the use of reduced pressure during mixing and crosslinking. GAP with primary hydroxyl groups will crosslink faster even at lower temperatures. Increasing the functionality of the polymer allows the use of catalysts or crosslinking agents to be omitted [4]. Obtaining polymers with enhanced functionality therefore makes it possible to eliminate the use of such additives. In addition, the use of GAP with primary hydroxyl groups eliminates the need for catalysts and other additives, which contributes to minimising costs and eliminating process control issues. Increasing the functionality is therefore one direction of modification of a well-known and useful polymer which can be used on both laboratory and industrial scales. Figure 1 shows the structural formula of GAP.

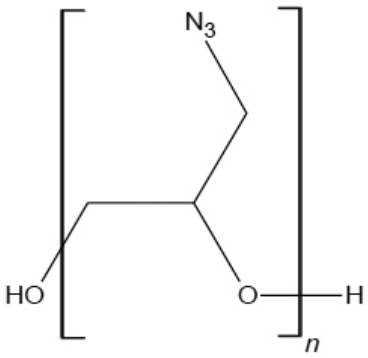

Figure 1. GAP structural formula

2. GAP synthesis

The simplest method for the synthesis of GAP, well described in literature, is the nucleophilic substitution reaction (SN2) of a chlorine atom contained in polyepichlorohydrin (PECH) by an azide group. The method consists of two stages, the first of which involves polymerisation of epichlorohydrin (ECH) with

an initiator and catalyst. Figure 2 shows the reaction using ethylene glycol as initiator; BF_3 etherate can be used as the catalyst. The second stage is the actual SN2 reaction carried out using sodium/potassium/lithium azide in organic solvents such as *N*,*N*-dimethylformamide (DMF) or dimethylsulphoxide (DMSO) at approximately 100 °C. Depending on the use of the GAP target application location, a polymer of different molecular weights can be used. In order to shorten the synthesis process, ready-made intermediates or custom synthesised products can be used, e.g. PECH of any molecular weight available on the international market [5]. The length of the process and thus the degree of chlorine substitution with azide groups, is influenced among other things, by the temperature of the reaction and the ratio of substrates used [1, 3]. Based on the reaction indicated in Figure 2, under the same conditions, a trifunctional GAP can also be obtained (after using glycerol as an initiator), but still having secondary hydroxyl groups.

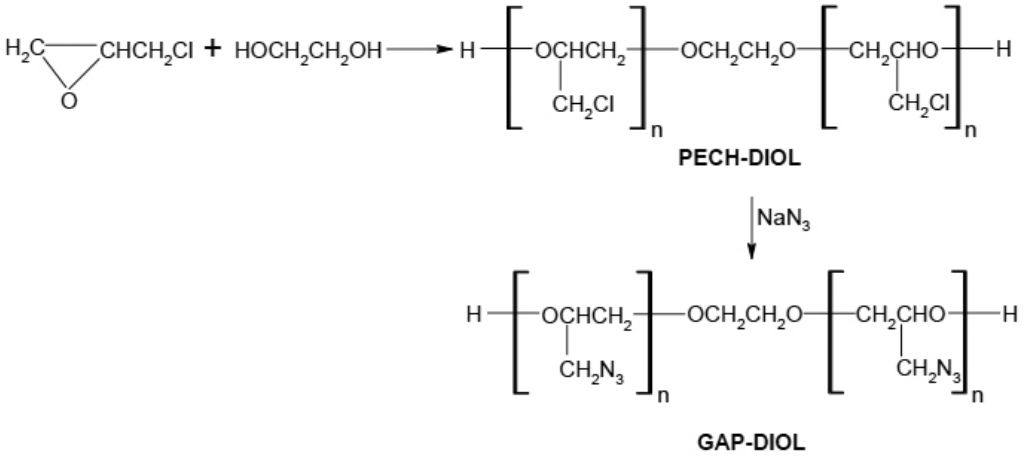

Figure 2. Reaction scheme to obtain GAP

3. Modification of GAP

In order to avoid the problems described above for the production of GAP-based polyurethanes, methods for obtaining modified GAP by modifying the substrate used for its synthesis, PECH, were developed and tested. Modification of the PECH chain makes it possible to obtain GAPs with two-, three- and fourfold increased functionality (increased number of hydroxyl groups at the ends of the chain).

The PECH chain modification process takes place in three stages. The most important of these is the regiospecific epoxidation reaction of linear PECH under alkaline conditions. The second stage, epoxy ring opening, is carried out using water with the addition of an acid, triol or tetraol to produce a polymer with functionalities 2, 3 and 4, respectively. Due to the fact that the last stage, the azidation stage, being an SN2 reaction, does not change the functionality of PECH any further, but only involves a direct substitution of a chlorine atom by an azide grouping, the GAP obtained having the same functionalities as the PECH used for its synthesis [4, 6].

To produce the epoxide, PECH dissolved in tetrahydrofuran (THF) is heated to solvent boiling point and then sodium hydride or sodium hydroxide is introduced. A schematic of the epoxidation reaction is shown in Figure 3.

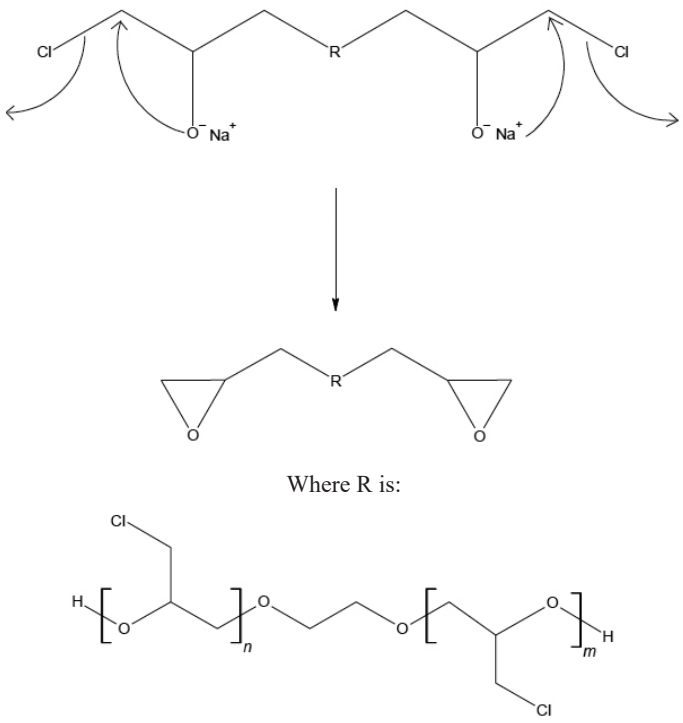

Figure 3. PECH epoxidation reaction scheme

4. Own research

The present study investigated the possibility of modifying the chain termination of polyepichlorohydrin by reacting with sodium hydride or potassium hydroxide to remove the hydroxyl groups. The polyepichlorohydrin chain thus obtained is terminated with epoxy groups. In a subsequent stage, such chain termination was modified by reaction with polyols. At this preliminary stage of the research, only confirmatory studies were carried out to obtain these compounds. Using FTIR analysis, the disappearance of hydroxyl groups was confirmed, followed in a subsequent stage by the reconstruction of the chain termination with more hydroxyl groups. In the future, this research will allow such modified GAP to be used as a component of solid heterogeneous rocket fuels.

4.1. Raw materials and methods of analysis

The process studied consisted of 3 stages in which the following reagents were used:
(i) for stage 1:
– THF (p.a. grade, POCH)
– polyepichlorohydrin (produced and tested in ZMW PW) – L_{OH} = 37 mgKOH/g
– potassium hydroxide (p.a. grade, POCH)
– sodium hydride (p.a. grade, Sigma-Aldrich)
(ii) for stage 2:
– THF (p.a. grade, POCH)
– DMF (p.a. grade, POCH)
– distilled water

– sulphuric acid (95%, p.a. grade, Chempur)
– 1,1,1-(trihydroxymethyl) ethane (Sigma-Aldrich)
– pentaerythritol (98%, Acros Organics)

(iii) for stage 3:

– DMF (p.a. grade, POCH)
– sodium azide (p., POCH)

The DMF and THF used for the reaction were previously subjected to drying-cooking under a reflux condenser over CaH_2, followed by straight distillation and, in the case of DMF, distillation under reduced pressure.

In order to confirm the effectiveness of the reactions carried out, the samples obtained were subjected to FTIR analysis after each stage, using a Thermo Nicolet 6700 instrument with ATR attachment and OMNIC software to record and process the spectra obtained. This made it possible to observe successively the disappearance of the –OH groups, then their reconstitution in increased amounts, and then the effectiveness of the substitution of the –Cl groups with azide groups in stage 3. Viscosity measurements were made for stage 1 samples using a Brookfield HB DV2T viscometer with a small-volume sample attachment and Rheocalc software. A hydroxyl number determination is essential in confirming the obtained results. The most commonly used method for determining the hydroxyl number is the titration method, which involves acylation of the hydroxyl groups of the polymer with acetic anhydride in the presence of pyridine.

4.2. Stage 1 – PECH epoxidation

The raw material in this reaction is polyepichlorohydrin:

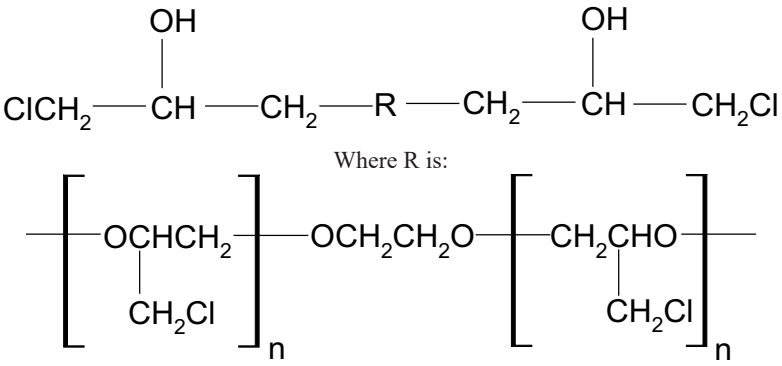

Figure 4. PECH structure

The reaction setup consisted of a 1 l three-neck flask, a reflux condenser, a thermometer, an oil bath and a magnetic stirrer. Approximately 50 g of PECH, THF were placed in the flask and the oil bath heated to the boiling point of THF (66 °C). When this was reached, an appropriate amount of KOH or NaH was added. In the first reaction carried out, sodium hydride was used. The reaction of sodium hydride with water is violent, so even the inadequate drying of system components is a potential hazard, especially when using solvents such as THF, which is highly flammable. The product of both reactions was the same, therefore at the stage of laboratory work and taking into account the prospective transfer of the scale of the process and the difficulties associated with the properties of NaH, further reactions were carried out using potassium hydroxide. Once the temperature had stabilised, the reaction was run continuously for 24 h. After this time, the mixture was cooled to room temperature, 100 ml of water was added and transferred to a 500 ml round-bottomed flask. The flask was placed on a rotary evaporator and the THF was evaporated. The mixture was then transferred to a separating funnel and extracted with 100 ml of methylene chloride, washed three times

with 100 ml of distilled water and 100 ml of a 10% aqueous NaCl solution. The extracted organic phase was transferred to a 500 ml round-bottomed flask and after, placing on a rotary evaporator, the methylene chloride was evaporated and the resulting product weighed. Table 1 shows the parameters of the reactions carried out in stage 1. After carrying out the above reactions, the compound with the following structure is obtained (see Figure 5).

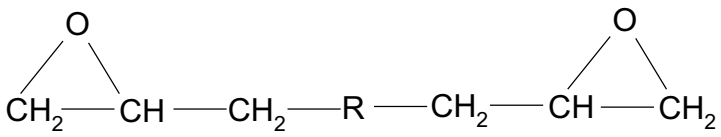

Figure 5. Structure of epoxidised PECH (α,ω-diepoxypolyepichlorohydrin)

Table 1. PECH epoxidation reaction parameters

Sample number	Temperature [°C]	PECH [g]	THF [ml]	KOH [g]
1	66	50	500	5.3
2	66	50.29	210	7.9
3	66	50.41	210	8.0
4	60	51.96	310	8.0
5	66	50.68	310	8.0
6	66	50.32	250	7.9
7	66	50.61	110	8.0
8	66	50.16	210	9.0

All the reactions used PECH produced at Department of High-Energetic Materials, Warsaw University of Technology, Faculty of Chemistry (ZMW PW). Reaction one used the most THF and used sodium hydride. The possibility of using solvent of different purity was investigated (dried and commercial solvent supplied directly from the manufacturer was used). Reactions 2 and 3 were characterised by the same amounts of substrate used; however, the solvent in reaction 2 was pre-dried and in reaction 3 a commercial solvent was used. Reactions 4 and 5 also have the same amounts of substrate but only reaction 4 was carried out at a temperature 6 °C lower than the others. In reactions 6 and 7, only the amount of solvent used was modified again, and in reaction 8, the amount of KOH used was increased by 12.5% compared to the other reactions in which it was used. The use of a commercial solvent did not reduce the yield (amount of polymer obtained). If NaH is used, it is necessary to use only pre-dried solvent. Replacing sodium hydride with potassium hydroxide simplifies the reaction, eliminating the need for dried solvent. In addition, handling large quantities of sodium hydride when carrying out large-laboratory or industrial-scale reactions is much more dangerous than using potassium hydroxide. The yield was approximately 85%.

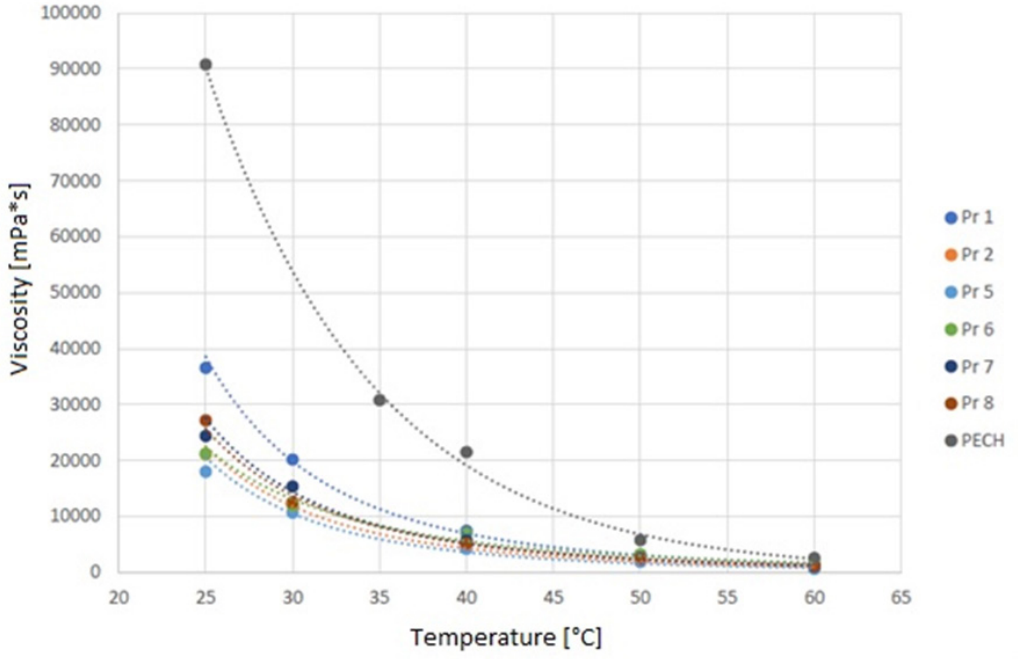

Figure 6. Diagram of temperature dependence of viscosity of PECH and epoxidised PECH

The viscosity of the obtained polymers is shown in Figure 6. The modified PECH had a viscosity almost twice as low at the test temperatures. The epoxy group-terminated polymers obtained have similar viscosity values; however, sample 1 (Table 1, sample 1), which was synthesised using sodium hydride, shows higher viscosity at higher temperatures than those synthesised using potassium hydroxide. In stage 1, FTIR spectra of the obtained products were performed, examples of which and a comparison with the initial PECH are shown in the Figure 7.

The most important signal considered in the above spectra is the soft peak at wavelength 3477 cm^{-1} corresponding to the stretching vibrations of the –OH group. It is present on the spectrum of pure PECH in Figures 7 and 8. The peak at wavelength 2873 cm^{-1} in all spectra corresponds to the stretching vibrations of the C–H bonds of the aliphatic chain. The wavelength of 1092 cm^{-1} corresponds to the stretching vibration for the C–O bond. The peak at around 743 cm^{-1} is also characteristic of the stretching vibration of the C–Cl bond. The disappearance of the band at 3400 cm^{-1}, corresponding to the –OH groups in the EPECH spectrum, confirms the removal of these groups from the polymer chain.

4.3. Stage 2 – opening up the epoxy to increase PECH functionality

4.3.1. Doubling functionality

The reaction setup consisted of a 500 ml three-neck flask, a reflux condenser, a thermometer, an oil bath and a magnetic stirrer. The EPECH obtained in stage 1 (10 g) was placed in the flask and dissolved in THF (commercial) (200 ml) by heating the mixture to the boiling point of THF. Water is used in these reactions, so there is no need to use dried and distilled THF. Distilled water (5 ml) and concentrated sulphuric acid(VI) (2 drops) were added to the mixture before heating. The mixture was heated continuously for 24 h. The mixture was then cooled to room temperature, transferred to a 500 ml round-bottomed flask, 50 ml of water was added and the THF was evaporated on a rotary evaporator. The mixture was then transferred to a separating funnel, where it was extracted with 50 ml of methylene chloride, washed three times with 50 ml

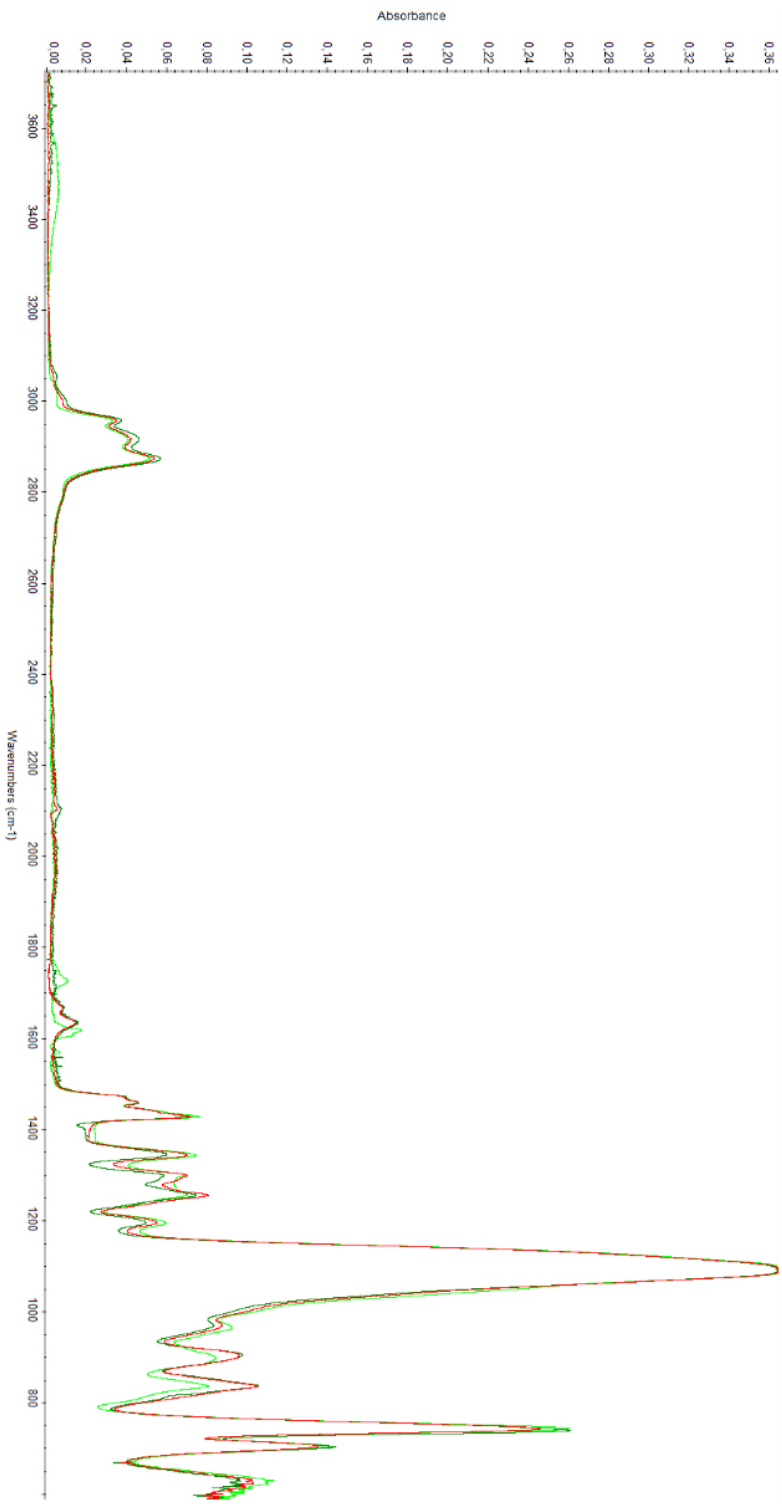

Figure 7. Comparison of the FTIR spectra of PECH (in green) and epoxidised PECH (in red)

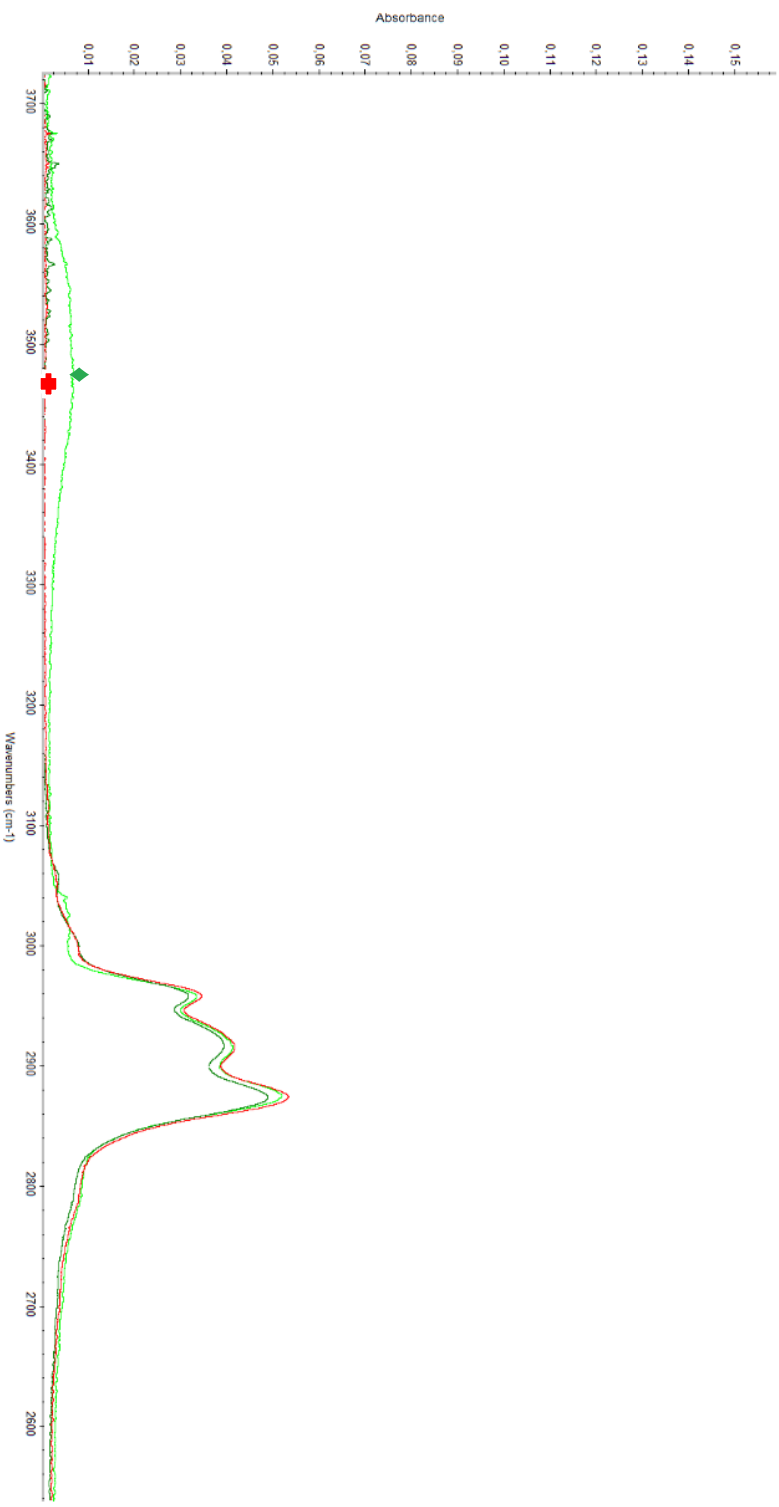

Figure 8. Comparison of the spectra of PECH (◆) and epoxidised PECH (✚) in terms of the occurrence of the –OH group signal

of distilled water and 60 ml of 10% NaCl solution. The extracted organic phase was transferred to a round-bottomed flask to evaporate the methylene chloride. The resulting product was weighed. Reactions were carried out several times using the EPECH obtained in stage 1. The yield was approximately 93%. The use of different types of epoxidised PECH had no significant effect on reaction yield. The hydroxyl number value of this polymer is approximately 48 mgKOH/g. A product with the following structure (Figure 9) was obtained.

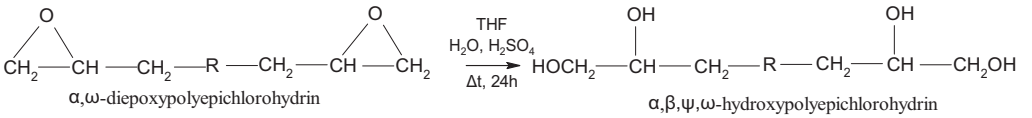

Figure 9. Reaction scheme for the doubling of the number of OH groups in PECH

4.3.2. Triplication of functionality

The reaction setup consisted of a 500 ml three-neck flask, a reflux condenser terminated with a balloon tube to protect the system from moisture, a thermometer, an oil bath and a magnetic stirrer. EPECH (10 g), DMF (200 ml) were placed in the flask with the EPECH being dissolved by heating the mixture in an oil bath to 140 °C. After dissolving the EPECH, 1,1,1-(trihydroxymethyl) ethane (3.4 g) was added, the temperature was stabilised and the mixture was left to stand for 24 h with continuous heating. The contents of the flask were then cooled to room temperature using an ice water bath and transferred to a 200-ml round-bottomed flask to evaporate the DMF using a rotary evaporator. Then, 100 ml of methylene chloride were added to dissolve the polymer, the unreacted thiol being removed by filtration on a fluted filter. The organic solvent used was evaporated on a rotary evaporator and the resulting product weighed. The yield of the process was around 95%. The hydroxyl number value of this polymer is approximately 55 mgKOH/g. A product with the following structure was obtained:

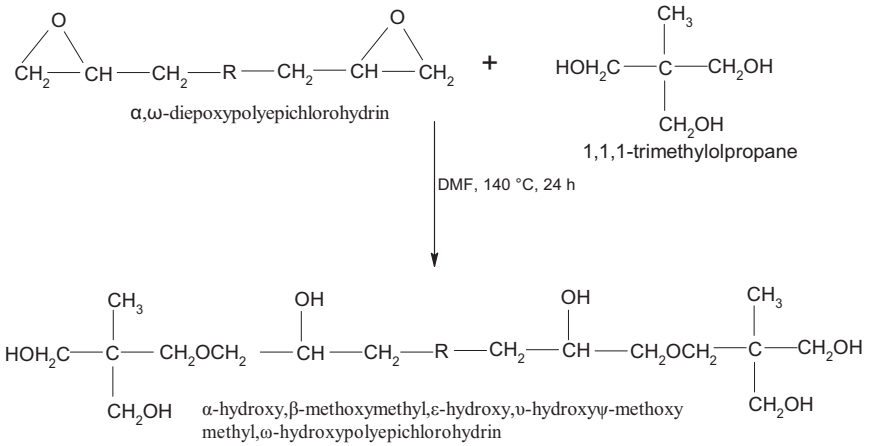

Figure 10. Reaction scheme for tripling the number of OH groups in PECH

4.3.3. Fourfold increase in functionality

The reaction setup consisted of a 500 ml three-neck flask, a reflux condenser terminated with a balloon tube to create an anhydrous environment, a thermometer, an oil bath and a magnetic stirrer. The steps performed are the same as described in the previous section with the difference that tetraol – pentaerythritol (4 g) EPECH (10 g) DMF (200 ml) was added instead of triol. The yield of the process was around 95%. The hydroxyl number value of this polymer is approximately 62 mgKOH/g. A product with the following structure was obtained:

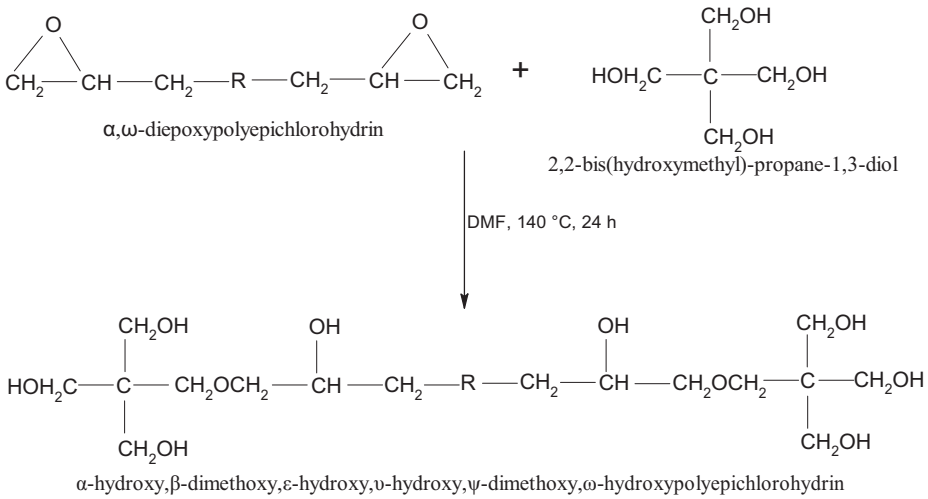

Figure 11. Reaction scheme for the quadrupling of –OH groups in PECH

The polymers obtained in the second stage were visually different. Epoxides opened with water and sulphuric acid gave transparent mixtures in which the organic and aqueous phases could be easily distinguished. Samples with triol turned brown after a few hours to give products which were slightly black in colour. During the purification process, these gradually turned lighter in colour. Samples using tetraol showed a brown colour, changing to orange during the purification process. In order to confirm that the reactions carried out allowed the epoxide from stage 1 to be opened and produce PECH with a modified chain having a multiplied number of functional groups, FTIR spectra were also performed for the samples subjected to all modifications, i.e. reactions with acid and water, triol and tetraol. The spectra taken are shown in the Figures 12 and 13, respectively. It is necessary to thoroughly purify the product of unreacted substrates and the solvent used.

Evidence that the ring-opening reaction of the epoxide has occurred is the appearance of a peak at 3479 cm^{-1} on the spectrum shown, which again corresponds to the stretching vibration of the -OH group. However, peaks characterised by a higher absorbance value are observed in the figure, indicating the correct derivation of a molecule with an increased number of hydroxyl groups compared to the PECH sample where the number of hydroxyl groups was doubled. Furthermore, it should be noted that the signals from the PECH chain and the chlorine substituent did not change after opening the epoxides. This is confirmed by the structural behaviour of the polymer.

4.4. Stage 3 – azidising

The reaction setup consisted of a 50 ml three-neck flask, a reflux condenser, a thermometer, an oil bath and a magnetic stirrer. A suitably modified PECH was placed in the flask. The amounts of raw materials used were recalculated in relation to the PECH used and the reactions were carried out at 90 °C. DMF (15 ml) was added to the PECh (10 g), with the whole mixture being stirred and heated. Once the target temperature was reached, sodium azide (8.5 g) was added. After stabilisation of the temperature, reactions were carried out for a total of 12 h. After this time, the mixture was cooled to room temperature and filtered under reduced pressure, after which the organic solvent was evaporated from the filtrate. The mixture was then transferred to a separating funnel and extracted with dichloromethane (200 ml) and washed three times with distilled water. The organic phase was placed in a round-bottomed flask and the solvent used in the extraction process was evaporated. The resulting GAP was weighed and subjected to further analyses. The yield was 85%. Losses in the resulting product occur in the purification and filtration stages. Here, the

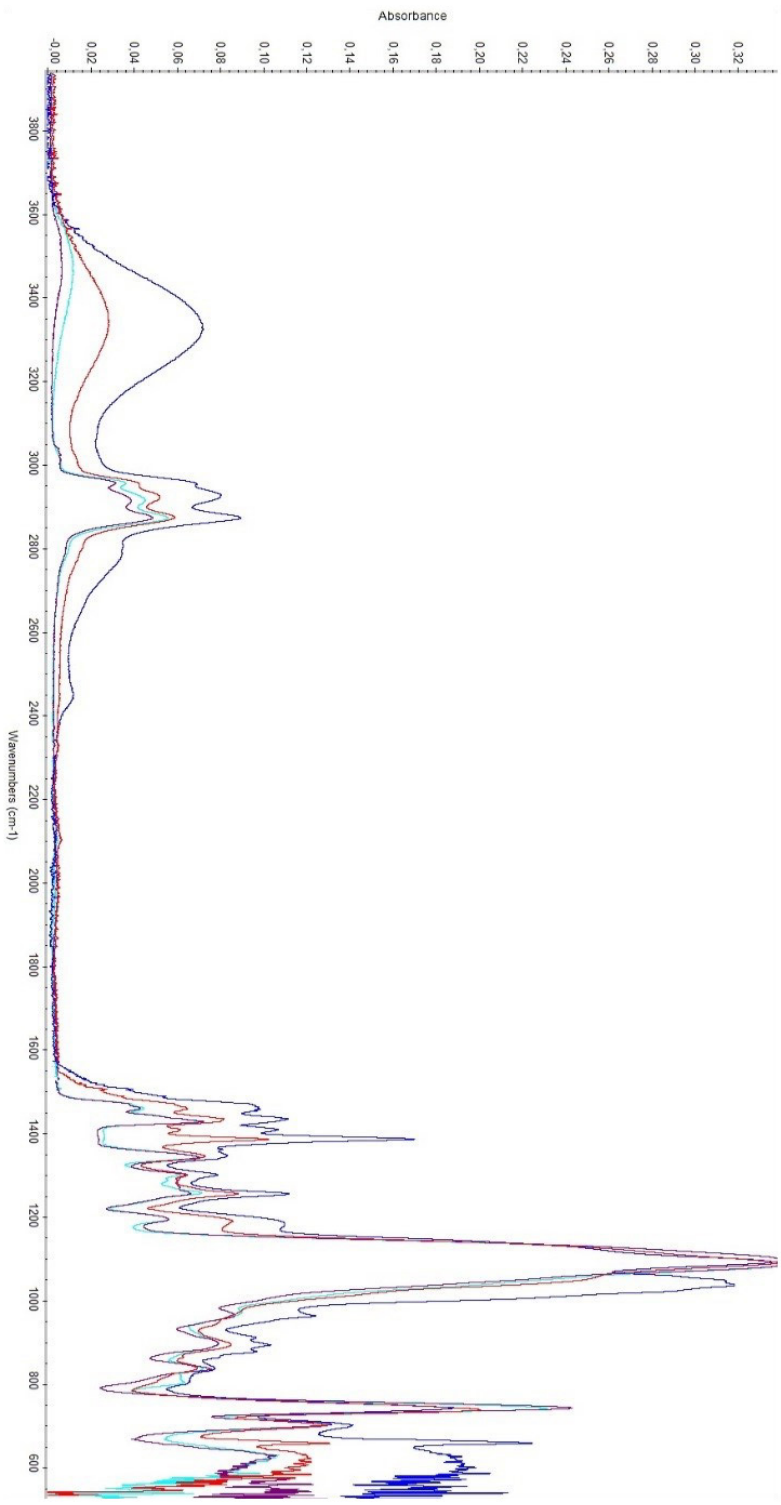

Figure 12. A compilation of FTIR PECH spectra after functionalisation enhancement

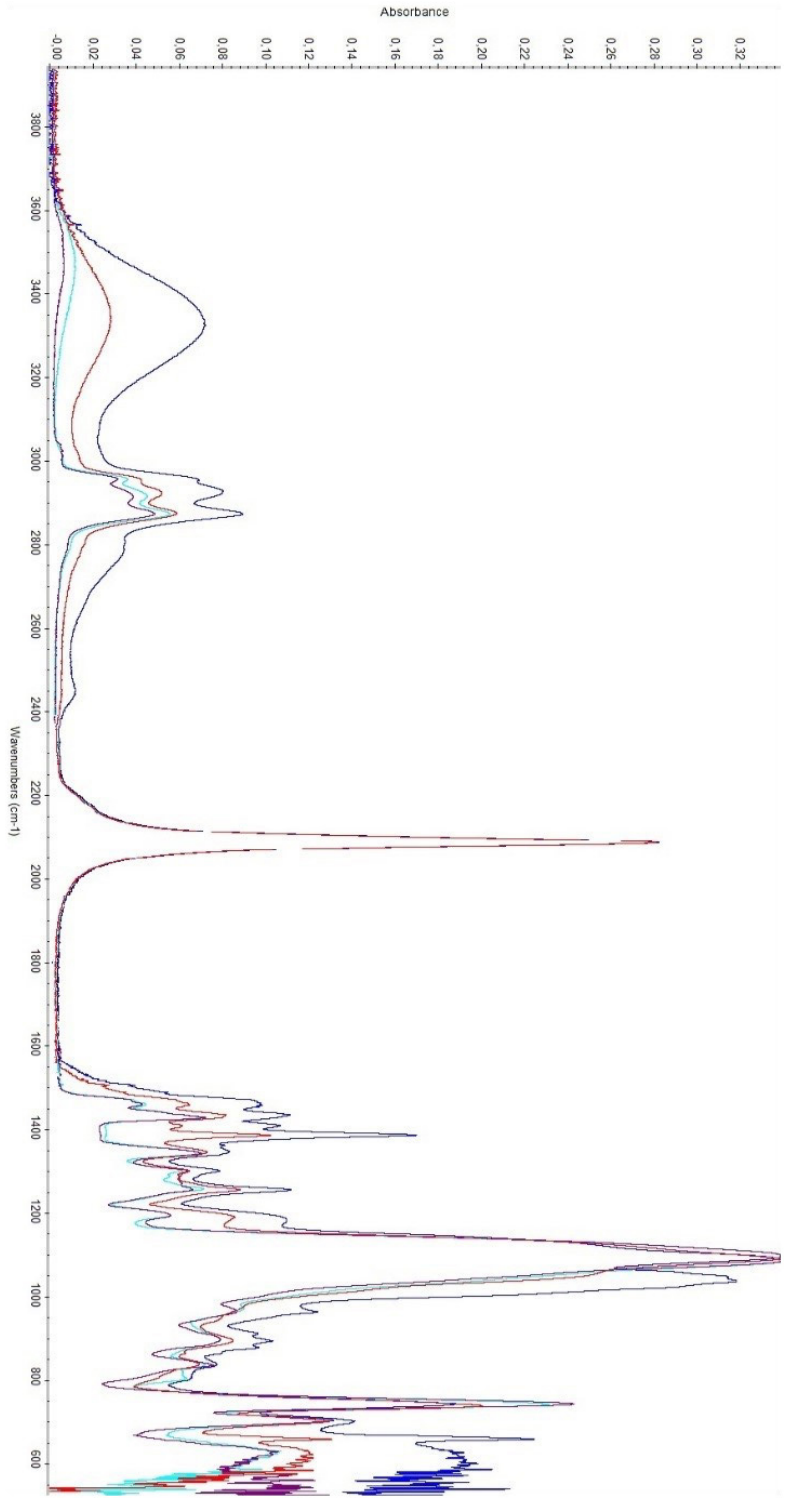

Figure 13. FTIR spectrum of GAPs obtained from PECH with enhanced functionality

viscosity of the polymer and the use of its solutions had a significant impact on the purification process. FTIR analyses were performed showing the presence of –OH groups and introduced $–N_3$ groups. The spectra obtained are shown in Figure 13.

In the Figure 13, it should be noted that the peak at 2092 cm^{-1}, which corresponds to the azide group and which, in all samples, confirms that the azidation reaction has been successfully carried out, whereas the disappearance of the signal at 740 cm^{-1}, which corresponded in earlier stages to the binding of carbon to chlorine, indicated that the chlorine was completely substituted by the $–N_3$ grouping. In addition, peaks are visible at 3479 cm^{-1} – characteristic of the -OH group. Further, bands are also visible at 2872 cm^{-1}, confirming that the polyester chain of the starting polymer has not broken down.

5. Summary

- The possibility of enhancing GAP functionality by modifying the PECH chain, the starting component for GAP synthesis, was investigated. To this end, a three-stage process was carried out.
- In the first stage, the PECH produced in the ZMW PW was subjected to a regiospecific epoxidation reaction using sodium hydride and potassium hydroxide. The samples obtained were subjected to viscosity tests and FTIR analysis, which concluded that the expected effect – the disappearance of the –OH groups present in the starting substrate – had been achieved. In the second stage, selected samples were subjected to opening reactions of the produced epoxides in order to increase the polymer functionality and to obtain primary hydroxyl groups. To do this, 3 routes were used – reactions were carried out in the presence of water and H_2SO_4 to produce a GAP with doubled functionality. 1,1,1-Tri(hydroxymethyl) ethane was used to obtain a GAP with three times the functionality of the epoxide opening reaction, and pentaerythritol was used to obtain a compound with four times the amount of –OH groups. FTIR studies of the samples modified in this way showed the opening of the epoxides and an increase in the amount of –OH groups in their chains. The samples were then subjected to an azidation process to substitute the –Cl groups with $–N_3$ groups, thereby obtaining a modified GAP. The occurrence of the above reactions was confirmed by analysing the disappearance of the peak corresponding to the chlorine substituents and the appearance of a peak characteristic of the azide group.
- This way of modifying PECH to obtain a GAP containing first-row hydroxyl groups will eliminate the problems of producing polyurethanes with suitable mechanical properties.

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