



Closed Loop of Polyurethane Flexible Slabstock Foam Wastes by a Chemical Process

Martin Belke, Roseta Evtimova, Rainer Langenstraßen, Iris Pniok, Vladimir Peshkov, Gerhard Behrendt

1 Introduction

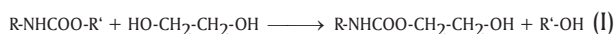
Presently, about 8 million metric tons of polyurethanes are produced in the world annually. During production of precursors, semi-finished products and final products about 5 to 10 % of this amount is waste, i. e. an amount of about half a million tons. To this add the products after their life cycle. This is a large source of material which should not be given to landfills or incinerators but be used as secondary materials for the production of new polyurethanes.

To recycle waste polyurethanes several processes have been developed. These in general make use of a transesterification at the carbamic acid ester group by diols to produce carbamic esters with hydroxyl end groups and liberate the originally employed polyhydroxyl compound which might be a polyester, a polyether, a polycaprolactone, or an polyaminoalcohol [1]. In case of water used as a foaming agent polyureas are produced which are believed not being changed during the transesterification but actually are partly cleaved by the diols used to produce aromatic primary amines [2].

Such transesterification reactions are used with a catalyst or without employing mainly glycols like diethylene or dipropylene glycol in discontinuous batch reactors up to 6 metric tons volume. The reaction proceeds in average during six hours at temperatures in the range of 200 to 260 °C. About 2 to 3 hours are needed only to dissolve the necessary amount of polyurethane wastes in such a six cubic meter reactor. The long reaction time and the formation of the primary aromatic amines have led to the consequence to search for an alternate way to produce polyols from polyurethane wastes.

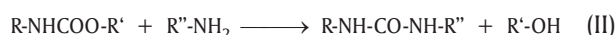
2 The combined aminolysis/glycolysis process

The transesterification of the carbamic ester group is well known for long proceeding formally analogous to the transesterification of carboxylic esters and may be described by the following formulae:



In this, R means the residue of the aromatic di- or polyisocyanate and R' the residue of the polyetheralcohol, which is in soft foams mainly a triol based on glycerol or trimethylol propane onto which propylene oxide and optionally ethylene oxide are added by anionic polymeri-

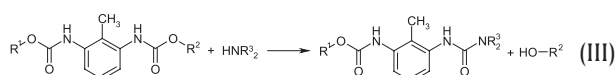
zation. Further, it is well known that the carbamic acid group may be transamidated by any amine to produce a urea according to the general scheme:



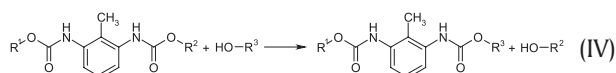
In this reaction, formally only the urea and the alcohol originally present in the carbamate are formed. The rate of this reaction depends to a great extent on the basicity of the amine and the solvent used [3]. In hydrophobic solvents like toluene the reaction rate is rather low while it becomes fast in hydrophilic solvents like dimethyl formamide or dimethyl sulfoxide. In hydroxyl compounds the reaction rate is still favorably high so that mixtures of hydroxyl compounds and certain suitable amines could be used to cleave polyurethanes.

The process based on this reaction was developed with secondary alkyl amines and mixtures of glycols by which process only trisubstituted ureas are produced and the original alcohol is liberated. Due to the short reaction times the cleavage of the polyureas can be disregarded. The process of the aminolysis of the urethane group by transamidation to form trisubstituted ureas may be described as follows:

The transamidation in the case of toluylen-2,6-diisocyanate:



and the simultaneous transesterification by any alcohol:



The transamidation by a secondary amine like di-n-butyl amine proceeds very fast at elevated temperatures in properly selected glycols. Typical reaction temperatures are in the range of 200 °C and typical dissolution times of polyurethane soft foams are in the range of less than a minute.

The secondary amine has two functions in this type of reaction: first, it is a reaction partner in the transamidation reaction to form a trisubstituted urea and secondly, it is a catalyst for both the transesterification and transamidation. Thus, after dissolution of the polyurethanes by a first cleavage of bonds to produce soluble, only partly crosslinked or entangled macromolecules the actual reaction times become very short and are typically in the



range of 15 to 45 minutes to reach the desired result of oligomeric products including soluble oligoureas. By the comparably low temperatures and short reaction times, the cleavage of ureas does not play any role and the content of primary aromatic amines can be kept very low, i. e. in the range of less than 0.1 %.

Furthermore, this combined aminolysis/glycolysis reaction can be applied to any type of material containing urethane groups. Using the conditions described this group is always rapidly transformed into the corresponding urea thus cleaving the material under consideration. Hence, any polyurethane product like soft foam, elastomers, semi-rigid foam, rigid foam, rigid casts, or even polyisocyanurate foams are rapidly dissolved to produce polyols. Depending on the type of polyurethane material used, the percentage of polymer in the solvent may be as large as 80 % by weight.

3 Recycling of flexible polyurethane slabstock foams

Object of the present investigation was to provide an improved process to close the loop in the production of flexible slabstock polyurethane foams by reacting the wastes produced with such a solvolysis mixture to produce first polyols from the polyurethane wastes and secondly introduce these polyols into the premix system of the slabstock process at certain proportions so as to produce the same elastomeric polyurethanes from them. In this process, the polyurethane wastes are generally introduced into a specially developed mixture of diols and a secondary alkyl amine and reacted at temperatures in the range of 200 to 220 °C by which process a mixture of polyether alcohols and trisubstituted polyureas dissolved or dispersed in them is formed.

The glycols used in case of the flexible slabstock foams represent a mixture composed of a short chain glycol and a long chain one in a proportion optimized for short dissolution and reaction times and adjusted to the amount of the secondary amine used. The following table 1 gives some examples of glycol mixtures used in this process:

Material/ No.	W116	W138	W139	W155	W157	W338	W332
Foam flakes (parts)	59.2	50.0	50.0	60.0	60.0	53.5	64.1
Dipropylene glycol (parts)	38,6	0	36,0	33,0	30,0	9,9	24.8
Diethylene glycol (parts)	0	48,0	12,0	0	0	0	0
PPG 400 (parts)	0	0	0	0	0	35,4	0
PPG2000 (parts)	0	0	0	0	6,0	0	7.3
PEG 600 (parts)	0	0	0	3,0	0	0	0
Di-n-butyl amine (parts)	2,2	2,0	2,0	4,0	4,0	1,2	3.8
Reaction time (min)	75	230	290	135	145	265	210
Reaction temperature (°C)	190	200	200	200	210	210	210
Hydroxyl No. (mg KOH/g)	355	408	397	391	354	173	290
Viscosity (mPas, 25°C)	3,240	>50,000	>50,000	16,460	2,210	9,560	8,500

Table 1: Aminolysis/glycolysis of flexible polyurethane slabstock foam using various glycol mixtures

As can be seen from the table, some effects arise from mixing the glycols: the lower the hydroxyl content of the mixture (i. e. the higher the amount of high molecular weight glycols such as polypropylene glycol 2000) the longer the reaction time and the higher the viscosity of the recycling polyol. The introduction of the more hydrophilic oligomeric ethylene glycols leads as well to longer reaction times but these are in some cases necessary for proper dissolution of the polyurethane material. Especially diethylene glycol prolongs the reaction time significantly.

From such experiments, a typical formulation was selected to give short dissolution and reaction times as well as reasonable properties of the resultant recycling polyol and slabstock foam properties when added in proportions up to 30 parts by weight. The compositions of the dissolution medium selected for larger scale experiments with foam residues obtained by the courtesy of Hickory Springs Manufacturing Co. (Hickory Springs, SC, USA) are presented in the following table 2:

Substance	Composition (parts by weight)		
	A	B	C
Dipropylene glycol	70	75	82,5
Polypropylene glycol 2000	20	15	0
Polyethylene glycol 600	0	0	7,5
Di-n-butyl amine	10	10	10

Table 2: Selected solvolysis mixtures for flexible slabstock foams

The ratio of polyurethane soft foam waste to the dissolution medium was investigated in the range of 40 to 60 to 80 to 20 parts by weight to find a suitable ratio for the desired viscosity of the recycling polyol. In the following table 3 the results of some of these experiments are shown.

	W117	W311	W337	W375	W376
Composition	B	B	C	A	A
Foam (pts by weight)	74,1	60,0	55,0	50	40
Time (min)	130	120	60	240	200
Temperature (°C)	210	210	200	200	200
OH-No. (mg KOH/g)	224	356	371	55	65
Viscosity (mPas, 25 °C)	8,100	3,370	2,480	10,500	9,580

Table 3: Aminolysis/glycolysis experiments with selected solvolysis mixtures



The dissolution time of polyurethane flexible slabstock foam in such mixtures was 30 seconds for a foam flake of about 8 cm in diameter. The dissolution time in a 100 l reactor by manual addition into a 5" feed is about one hour which is mainly a consequence of the low weight and bulkiness of the foam particles. Consequently, the dissolution of the polyurethane flexible foams is controlled by the rate of introduction into the reaction vessel and not by the chemical reaction.

It turned out that the solvolysis composition B with various amounts of slabstock foam is well suited to produce recycling polyols with viscosities in the desired range while composition A is well suited to obtain products with the aimed hydroxyl number.

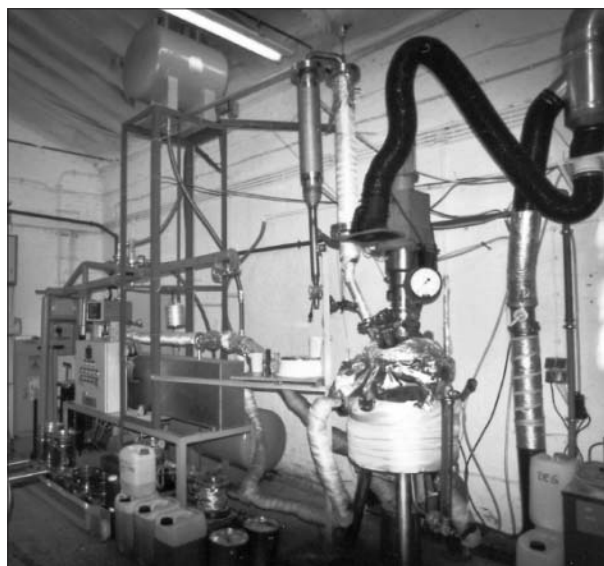
After complete addition of the foam flakes the reaction mixture is kept between 20 and 120 minutes at the reaction temperature depending on the nature of the solvolysis mixture and the slabstock foam. The formulation selected for experiments in the 100 l batch reactor was adjusted to 74 % by weight in case of composition B and 48 % by weight for composition A to receive a recycling polyol corresponding to the necessities of the production process. The products obtained clear amber solutions showing a viscosity in the case of the selected formulation below 10.000 mPas (25 °C).

It was found that wastes of flexible polyurethane slabstock foams dissolve comparably rapidly in mixtures of diols adjusted to the properties of the original slabstock foam and a carefully selected secondary alkyl amine and lead to recycling polyols being mixtures of several components including the originally used polyol(s), the catalyst(s) and the oligomeric ureas from the amine urethane reaction. They maybe directly introduced into the premixes in slabstock production so far suitable ratios of reactants are used to receive applicable viscosities and hydroxyl numbers being in the range of the materials typically used in such systems.

4 Technology of the process

The solvolysis of this type may be performed batchwise [4] or continuously [5]. In any case, from the flexible polyurethane slabstock foam wastes a high quality recycling polyol is produced, which may be added to the formulation with a high percentage. The product properties of the polyurethane produced from such mixtures equal those of the original product.

In the batch process, a jacketed stainless steel reactor of suitable volume equipped with bottom outlet, screw feed from the foam storage container, stirrer, demister, and heat exchanger is employed (see picture 1). The volume of the reactor depends on the anticipated annual production rate. The solvolysis mixture of glycols and amines is introduced into the reactor and heated up to the desired temperature, e. g. 200 °C, by an external thermal oil heater. At this temperature, the defined amount of polyurethane waste is introduced as rapidly as possible. The addition needs in a 100 l reactor about 20 minutes



Picture 1: Experimental batch reactor

and proceeds at temperatures between 200 and 220 °C for another 30 minutes. During the addition and reaction a nitrogen blanket is applied. After completion, the reaction mixture is allowed to cool to about 160 °C and recovered by the bottom outlet directly into a barrel. There is no need of further purification if the wastes applied do not contain any contamination or other plastics materials. In case of solid particulate contaminants a mechanical filter is positioned between the outlet and the storage container. The recycling polyol is allowed to completely cool down in the storage container or barrel and is ready to be used as it is.



Picture 2: First 6 t production unit (courtesy H&S Anlagentechnik)

Higher volumes of the reactor maybe used. Experiments in a 1000 l reactor showed five batches to be performed in 24 hours giving a daily amount of recycling polyol of nearly 4 t. In case the reactor has a higher capacity, e. g. 5 metric tones (see picture 2), a different layout of the plant is used. In such cases specially designed feeds and recovering sites are constructed to give optimum performance of the reaction. The reactor volume depends on the waste material available and the shift system of the customer. In the following table 4 some examples of such batch reactions are given.



	W318	W326	W223	W225
Composition	A	B	C	B
Slabstock foam (parts)	75	70	48	71
Reaction time (h)	100	90	110	105
Reaction temperature (°C)	220	220	220	220
OH-No. (mg KOH/g)	81	210	83	328
Viscosity (mPas)	23,500	12,560	7,860	7,700
Recovered amount of product (kg)	77	76	78	75

Table 4: Data on batch reactions in semi scale reactors

The products obtained from flexible slabstock foams by both process variants are homogenous, light amber liquids. The hydroxyl number is determined by the following factors:

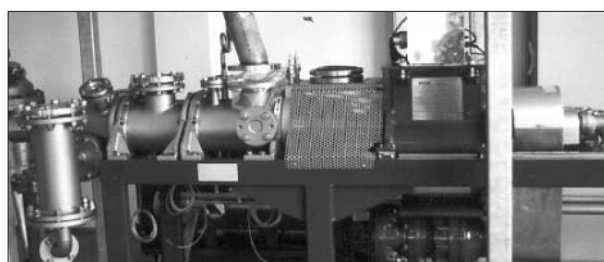
- nature of the polyurethane waste,
- mixture of the glycols/polyols,
- percentage of polyurethane used

and may vary between 80 and 240 mg KOH/g by adjusting the above mentioned factors. The primary aromatic amine content as measured in samples of the lab scale reactors is in the batch process due to the longer dissolution time between 0.25 and 0.75 % by weight and in the continuous process between 0.1 and 0.7 % by weight. The viscosities are in relation to the hydroxyl number between 2,000 and 10,000 mPas at 25 °C. The recycling polyols show a high reactivity, the pot life with polyisocyanates like Lupranat® M20A of the BASF AG is between 1 and 3 minutes.

The polyols are in any case produced by reacting polyurethane foams by their successive introduction into a mixture of lower polyalkylene glycols and a secondary alkyl amine at a temperature ranging from 180 °C to 240 °C. In the solvolysis process of flexible slabstock foams, a mixture of a short chain diol such as dipropylene glycol and a longer chain diol such as polyethylene glycol 600 or polypropylene glycol 2000 optionally with small amounts of diethylene glycol or a higher ethylene glycol is used. To this mixture a secondary amine such as dibutyl amine is added in a range of 2 to 8 % by weight and further the elastic polyurethanes up to 150 % by weight related to the solvolysis mixture and the desired viscosity. The ratio of the diols and of these to the amine(s) depends on several parameters among which are most essential the average molecular mass of the reactants and the type of polyurethane used and to be produced. It should be kept in mind that the secondary alkyl amine is both catalyst of the depolymerization reaction and reactant and hence must not be used in excess. The amount of the amine(s) maybe calculated roughly from the theoretical urethane group content according to the polyurethane formulation. Depending on the type of polyurethane, the reaction product nearly does not contain free amine reactant so that further work-up is not necessary.

The series of recycling polyols produced in the batch process variant covers a range of hydroxyl numbers between 80 and 400 mg KOH/g, of which table 4 presents only few typical examples.

Combining different glycols of various chain length and structure allows to produce recycling polyols of determined properties which are adjusted to the needs of the polyurethane products subsequently produced from them. In case of flexible slabstock foams there is the need not to increase the hydroxyl number of the polyol component of the system or to increase the viscosity of it because of the metering pumps in-line to the mixing head. Thus, a recycling polyol with a hydroxyl number as low as 80 mg KOH/g having a viscosity not beyond 10,000 mPas (25 °C) is desirable and can be obtained by this process.



Picture 3: Continuous experimental reactor

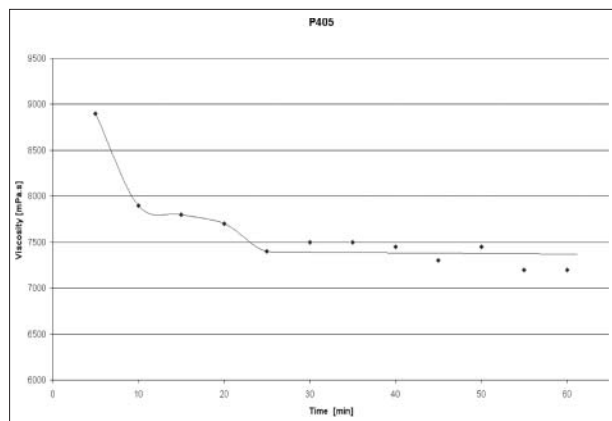
In the continuous process as developed on a laboratory scale with a throughput of about 600 kg per eight hour shift, all steps proceed sequentially. Into a specially designed twin-screw reactor with heated jacket and hollow shaft with screw feeder, dosage units for liquids and degassing unit (see picture 3) are introduced into a first zone the solvolysis mixture and the polyurethane wastes as particles up to a size of 8 cm while the mixture is kept at a temperature between 175 and 200 °C and nitrogen is purged in at a low rate. The dissolution proceeds within a very short time keeping this zone rather short. The second zone is designed as the reaction zone where the reaction proceeds. The third zone is the degassing zone from which the solvolysis product is recovered via a filtering unit into any storage container. The processing time in the reactor is in case of the flexible slabstock foam between 15 and 20 minutes. Depending on the nature of the polyurethane and the reaction temperature used with other polyurethane materials time and temperature have to be adjusted. The size of the plant is mainly determined by the polyurethane waste amount available and by the residence time necessary in the reaction zone. To produce about 500 metric tons per year the reactor itself has an effective length of 1.20 m.

Component/rate	P 416	P 422	P 409	P 405
Block foam flakes (kg/h)	55.0	60.6	61.2	65.3
Dipropylene glycol (kg/h)	40.0	26.0	19.2	32.6
Hexapropylene glycol (kg/h)	0	3.0	1.6	0
Di-n-butyl amine (kg/h)	5.1	6.4	6.8	2.1
Residence time (min)	23	22	20	18
Heater Oil Temperature (°C)	195	198	200	224
Nitrogen consume (l/h)	45	51	44	43
Output (kg/h)	99	95.4	88.1	94.5
Filter residue (kg/h)	0.38	0.42	0.56	0.25
Product properties:				
Hydroxyl number (mg KOH/g)	371	284	249	313
Viscosity (mPas, 25 °C)	2485	9620	12,800	7,150
Amine number (mg KOH/g)	6	3	9	5.2
Water content (% by weight)	0.14	0.17	0.22	0.23

Table 5: Recycling polyols produced by the continuous process



The examples of running the process continuously in the experimental reactor were performed usually during a period of an hour or less due to the high amount of consumed polyurethane. The experiment P405 was continued for 120 minutes to obtain the product data over a longer time period. By running the experiment (No. P405) over two hours, the viscosity of the product as measured in intervals of five minutes was constant after a short starting period of 20 minutes (see picture 4).



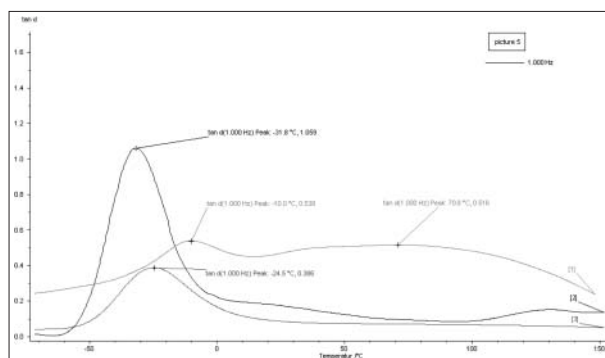
Picture 4: Viscosity measurement in the continuous process

5 Polyurethane production

By this process a composition of the recycling polyol results which for the first time allows the direct production of elastomeric polyurethanes of various types by reaction with a di- or polyisocyanate or its use as an additive to premixes for highly elastic products. Elastic products are obtained by reaction of 100 % of recycling polyol with the polyisocyanate Lupranat® M20A in a Shore-A-hardness range between 47 to 98 depending on the formulation used. If certain recycling polyols are added to the polyol component of two component systems as used for slabstock production up to 50 % by weight maybe added without a loss in mechanical properties. For the recycling polyols no work-up step is necessary in these cases. The small amount of free amine rapidly reacts and does not lead to any odor of the final polyurethanes or VOC emissions.

Some polyurethanes were produced as films to investigate the thermomechanical properties by dynamic-mechanical analysis (DMA). To this end, the foamed materials were subjected to pressing in a heated mould at 160 °C and 20 kp/cm² pressure for 10 minutes to give homogeneous clear films (see picture 5 for the DMA curves). In picture 5 are presented three curves of the loss factors (tan δ) of which one sample is prepared from a typical flexible foam polyether triol and diphenylmethane diisocyanate (MDI) (3) showing the glass transition at -31.8 °C and two lower broad maxima at about +20 °C and +135 °C. The latter maybe attributed to hard segment formation while the first one may result from short chain polyethers present in the polyol. Sample (1) was prepared from a typical flexible foam formulation and exhibits the glass transition at -10 °C, which is an unusual shift to higher temperatures, and

a broad maximum between +35 °C and +100 °C as a result of further formulation components. The maximum at 135 °C or at higher temperatures is not visible so that the formation of hard segments seems not to take place in this formulation. Curve (2) depicts the loss factor of a polyurethane foam made only from the recycling polyol P409 and MDI showing the glass transition at -24.5 °C, i. e. somewhat shifted to a higher temperature as compared with the formulation from a primary polyether but at lower temperatures than the original formulation. There is shown a broadening of the high temperature slope of the main transition region hinting to somewhat inhomogeneous structures. The missing of the high temperature maximum suggests the absence of phase separation in this material.



Picture 5: DMA analysis of compressed polyurethane foams

The DMA analysis shows that with a high percentage of long chain polyether alcohols in the recycling polyols due to a high content of polyurethane in the solvolysis mixture after reaction with polyisocyanates the glass transition temperature of the resulting polyurethanes is shifted to lower values as in a typical formulation, i. e. the material is at room temperature in the elastic region. Surprisingly, this value is not moved to markedly higher temperatures by the low molecular weight diols. By choosing these low molecular weight diols with respect to type and amount the upper and lower service temperature of the resultant polyurethanes may be controlled and predetermined already during the depolymerization reaction.

The reaction of the recycling polyols with di- and/or polyisocyanates to form elastic polyurethanes is usually faster as with standard polyether polyols because of their higher reactivity and remaining catalysts from the original polyurethanes. This reduces in general the amount of catalysts necessary in the premixes. If added to commercial premixes the total reaction times, i. e. start and rise times, may shorten up to 15 %. Usually, there is no effect on the physical foam properties.

Lupranol 2045	100	90	80	70	80
Recycling Polyol W 326		10	20	30	
Recycling Polyol P 409					20
Density (kg/m ³)	35	34	35	34	36
ILD 25 % (N)	108	109	111	112	110
50 % compression set	6	4	4	4	5

Table 6: Effect of recycling polyols on physical properties of a block foam formulation based on Lupranol® 2045 (BASF AG)



6 Discussion

The combination of glycolysis and aminolysis in the recycling of polyurethane flexible foams leads to a different reaction mechanism of the depolymerization of polyurethanes compared to the state of the art glycolysis. During glycolysis the cleavage proceeds preferably by transesterification at the urethane groups and as secondary reactions with a nucleophilic cleavage of the polyureas and a decarboxylation of the urethane groups, both with the formation of primary aromatic amines. Contrary to this, by cleaving the polyurethanes by a combination of glycolic hydroxyl groups and secondary amino groups the urethane groups are transformed both to trisubstituted urea groups and hydroxyl containing oligourethanes. Because of the basic reaction conditions a nucleophilic reaction at the urea groups of the polyureas takes place only in the trace range. During the reaction of the combination of glycol and secondary alkyl amine with the polyurethane, hence, are produced mainly the long chain polyether alcohols from the polyurethanes and trisubstituted polyureas from the isocyanate or the oligoureas from the isocyanate water reaction and the secondary alkyl amine, i. e. a very low content of primary aromatic amines. The polyureas are present in the mixture of lower molecular weight glycol and long chain polyether alcohol usually in a dissolved form up to 70 % by weight of polyurethane waste in the mixture, at higher proportions a stable dispersion maybe formed. By carrying out the process this way the resulting reaction mixture has not only a new composition, i. e. a polyether polyol mixture containing active low size fillers, but also the amount of short-chain glycol used may be drastically decreased and be as low as 20 % of the total reaction mixture.

This new process may be performed as a batch reaction in common jacketed reactors with a volume up to 10 m³. Alternatively, when larger amounts of waste are continuously available the process may be carried out continuously in a specially designed twin screw reactor. In any case, the reaction proceeds fast and the rate limiting step is usually the feed of the soft foam flakes into the reactor. The residence times in the batch reactor are about 30 minutes and in the continuous reactor only 20 minutes. This process produces recycling polyols which can be used without additional working-up steps, e. g. a post-reaction or a purification step.

By this process a composition of the polyether component results which for the first time allows the direct production of slabstock polyurethane foams especially from the recycling polyols without a work-up step. The polyol component with its high percentage of long chain polyether alcohols from the original polyurethane and from the solvolysis mixture after reaction with polyisocyanates does not affect the glass transition temperature of the resulting polyurethanes so that they remain at low values. From DMA measurements it can be seen that the high temperature slope of the polyurethane is broadened leading to better response in this temperature range and extending the elastic region. The glass transition is not

moved to markedly higher temperatures by the low content of low molecular weight diols. By choosing these diols with respect to type, chain length, and amount the upper and lower service temperature of the resultant polyurethanes may be controlled and predetermined already by the depolymerization reaction mixture.

This reaction maybe extended to any type of elastic polyurethanes or microcellular elastic polyurethanes but carefully selected mixtures of diols and secondary alkyl amines as well as the reaction conditions, especially temperatures and residence times, have to be used. For any polyurethane waste, the solvolysis mixture and conditions are to be carefully adjusted to receive optimum recycling polyols.

The polyols produced in this way exhibit a hydroxyl number in the range of 300 to 70 mg KOH/g and a viscosity between 2500 to 12,000 mPas (25 °C). The amine content as determined by amine number can be adjusted to values as low as 3 to 6 mg KOH/g and further decreased by the continuous process. The low amine content does not adversely affect the catalytic system or the properties of the resultant foams. The content of primary aromatic amines is usually kept as low as 0.02 % by weight depending on the performance of the process.

During the investigations described here only flexible slabstock foams without additives of any kind were used in the solvolysis process. Up to now, we see some limitations of the process in cases of solid fillers as used in slabstock foams, such as solid flame retardants like antimony oxide or chalk, where in the recycling polyols the solids may settle and cause problems in tubes and pumps. In few experiments, flame retarded slabstock foams were introduced, but only in cases of halogen bearing aromatics the reaction proceeded without problems. Further flame retardants, e. g. phosphonamides or the like, may influence the course of the reaction. Another problem was envisaged by the use of grafted polyols in the slabstock foams. When such are present, the grafts separate as solids. These solids may have a different nature depending on the composition of the solvolysis mixture: they maybe in the form of needle-like material with a length of up to 10 mm or a fine dispersion in the polyol which is stable over at least three months. The filler materials derived from the original grafting are introduced into the formulation and, consequently, into the new slabstock foam leading to somewhat increased hardness. In such cases a special development has to be performed.

7 Costs

The production costs of the recycling polyols are calculated according to a conservative German scheme and include raw materials, personal costs, energy costs, interest rates, costs for the building, equipment costs, and repair. The costs depend on the amount of waste available and the throughput of the plant with slight differences in the raw materials depending on the type of polyurethane to



be recycled and have been calculated for the production of recycling polyols from slabstock flexible polyurethane between 500 and 5000 metric t annually while it seems economically convincing to use this process with an amount as low as 80 t annually.

Discontinuous Process (Batch Process)			Continuous Process		
500 t/a	1000 t/a	5000 t/a	1000 t/a	3000 t/a	7500 t/a
0,80 €/kg	0,56 €/kg	0,40 €/kg	0,50 €/kg	0,40 €/kg	0,35 €/kg

Table 7: Production costs of recycling polyol (conservative German calculation scheme)

8 Conclusions

By the development of a new type of solvolysis mixture containing a mixture of short chain and long chain diols as well as at least one aliphatic secondary amine the recycling of polyurethane slabstock foams is performed at moderate temperatures continuously or discontinuously in reaction times as short as 20 minutes to completion resulting in recycling polyols to be either added to premixes for the same type of foams without affecting their physical properties or to form elastic polyurethanes from 100 % of the polyols or by blending with other hydroxyl components for adjustment of properties. The process may be run batchwise in typical stirred jacketed reactors or in a specially designed continuous reactor. The latter process should be applied in cases of higher amounts of polyurethane wastes produced continuously and the polyols produced to be introduced continuously at a ratio of up to 35 % to the premix so as not to have an essential effect on the properties of the flexible slabstock polyurethane foams produced.

References

- [1] G. Behrendt, M. Pohl, P. Wagner, H. Huth, K.-H. Schmidt: Drei neue Synthesewege zur Herstellung von Polyolen für Polyurethane, *Wiss. Beitr. Techn. Fachhochschule Wildau* 1/2000, S. 73-78
- [2] K.-H. Schmidt, H. Koch, M. Pohl, H. Huth, S. Ivanyi, O. Stürmer, G. Behrendt: Entwicklung von Polyurethan-Beschichtungssystemen auf der Basis von Recyclat-Polyolen aus Polyurethan-Weichschaumstoffen, *Wiss. Beitr. Techn. Fachhochschule Wildau* 1/2001, 28-37
- [3] G. Behrendt, unpublished results (1972)
- [4] G. Behrendt, M. Pohl: Verfahren zur Herstellung von Polyolen und diese Polyole, DE-OS 199 17 932 (1999), EP1086169, USP 6.683.119 (27. 01. 2004)
- [5] G. Behrendt, R. Langenstraßen, B. Gebert, H.-D. Hunger: Verfahren und Vorrichtung zur Herstellung von Recyclat-Polyolen aus Polyurethanen, DE-Pat.-Anm. 103 13 150.7 (2003)

Acknowledgement

This paper is an extended version of a paper read on the annual meeting of the Polyurethane Foam Manufacturers Association (PFA) at Montreal (Canada) in October 2003.

V. P. gratefully appreciates a visit to Technische Fachhochschule Wildau to perform work on the continuous process funded by the Deutscher Akademischer Austauschdienst (DAAD) within the project of the Stability Pact South East Europe.

Authors names and addresses

Dipl.-Ing. Martin Belke

H&S Anlagentechnik GmbH
Sandstraße 19, 27232 Sulingen
Tel. +49 4271 1011
E-Mail: info@hs-anlagentechnik.de

Prof. Dr. Roseta Evtimova

University of Chemical Technology and Metallurgy
Bl. K. Ohridski 8, 1756 Sofia, Bulgaria
Tel. +359 2 6254295
E-Mail: rozetaevt@yahoo.de

Dr. Rainer Langenstraßen

Technische Fachhochschule Wildau
Fachbereich Ingenieurwesen/Wirtschaftsingenieurwesen
Tel. +49 3375 508-502
E-Mail: rlangens@igw.tfh-wildau.de

Dipl.-Chem. Iris Pniok

Technische Fachhochschule Wildau
Fachbereich Ingenieurwesen/Wirtschaftsingenieurwesen

Dipl.-Ing. Vladimir Peshkov

University of Chemical Technology and Metallurgy
Bl. K. Ohridski 8, 1756 Sofia, Bulgaria
Tel. +359 2 6254295
E-Mail: peshkov_v@abv.bg

Prof. Dr. Gerhard Behrendt

Technische Fachhochschule Wildau
Fachbereich Ingenieurwesen/Wirtschaftsingenieurwesen
Tel. +49 3375 508-591
E-Mail: behrendt@vt.tfh-wildau.de