

Various Types of Polyurethanes in the process of Chemical Recycling

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Abstract

Increasing raw material costs and more stringent regulations have led to more pressure to develop customer-oriented recycling processes for polyurethanes. Furthermore, waste disposal runs into increasing costs for the producers while old methods of disposal are prohibited legally, both in the US and Europe. One way to solve this problem is to develop a well-suited process and plant for a customer specialised procedure to re-use the waste material obtained for each type of polyurethane product. Based on the previously described simultaneous glycolysis and aminolysis of polyurethanes in this paper, we will report on first results on larger scale recycling of some polyurethane products. While we were initially focused on the use of the recycling products (recycling polyols) to produce new types of polyurethanes, e. g. from cold moulded foams sealants or coatings, the philosophy had to be changed to use the recycling polyols as much as possible to produce the same materials as originally. This route was consequently developed further to other polyurethane products and the incorporation of the recycling polyols into original premixes to be reacted with isocyanates.

Zusammenfassung

Steigende Materialkosten und verschärfte regulatorische Anforderungen sind Stressoren hin zu einem anwenderorientierten chemischen Recycling von Polyurethanen. Ferner ist die Abfallablagerung in den USA und Europa weitgehend nicht mehr möglich und die Entsorgung mit steigenden Kosten verbunden. Eine Möglichkeit, das Problem zu lösen, besteht darin, für jeden Polyurethan-Typ einen entsprechend angepassten Prozess einschließlich Anlagenauslegung für die Wiederverwendung des Abfallmaterials zu entwickeln. Aufbauend auf einer kombinierten Glykolyse und Aminolyse wird im vorliegenden Artikel über erste Ergebnisse einer Maßstabsvergrößerung an konkreten Polyurethan-Produkten berichtet. Die Zielrichtung zu Beginn war die Verwendung von Recycling-Produkten (Recycling-Polyolen) zur Herstellung von neuen Polyurethan-Typen, z. B. ausgehend von Kaltformweichschäumen zu Dichtmassen oder Beschichtungen. Mit der nunmehr verfolgten Philosophie werden so viel wie möglich Recycling-Polyole in der Original-Rezeptur verwendet. Dieser Weg wurde konsequent für Polyurethanprodukte unter Einbeziehung von Recycling-Polyolen in ursprünglichen Mischungen zur Reaktion mit Isocyanaten weiterentwickelt.

1. SHORT REVIEW OF THE PROCESS

The combined glycolysis and aminolysis reaction make use of the re-esterification at the urethane group by the glycols present to liberate the polyetheralcohol originally employed and an amidation reaction with cleavage of the urethane group to produce a trisubstituted urea and the originally present alcohol (Stoychev et al. 2010). The polyureas present remain mainly unchanged, only on extended addition or reaction times the cleavage by the glycolic hydroxyl groups to form primary aromatic amines occurs as an undesirable side reaction

(Stoychev et al. 2011).

Depending on the type of polyurethane to be treated, the glycol is either only a monomer or an oligomer or, as in most cases, is a mixture of several glycols so as to produce optimum product quality and ease the dissolution of the solid particles. As has been shown previously (Langenstraßen et al. 2001), the type of glycol determines the rate of reaction to some extent but more the viscosity of the recycling polyol and the final properties of the new polyurethane produced from it. An additional feature is the particle size of the grafted polymers from grafted polyols used

which may be established by proper choice of the glycol mixture (see further chapters).

The recycling polyols may be produced by the batch, or continuously (Schmidt et al. 2001). The batch process makes use of jacketed stainless steel reactors with a volume up to 6 metric tonnes with specially designed periphery equipment and a specially designed dosage unit so as to receive a continuous flow of solid particles with optimum rate into the reactor. The reactor outlet is connected to a filtering unit to filter off any insoluble material and additionally

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to be able to apply a certain reduced pressure to degas the recycling polyol if necessary. There is no need for further treatment of the recycling polyol, moreover, it is used as produced (Behrendt & Pohl 1999, 2004b, 2004a). In the continuous process, a twin screw reactor is typically used where the shafts of the screws and the mantle are both heated to the reaction temperature by a heat transfer medium, usually thermal oil. The feed is made by a screw to densify the material and by dosage pumps and the outlet is again connected to a filtering unit and a suction pump.

2. MATERIALS AND METHODS

2.1 MATERIALS

Diethylene glycol (DEG), dipropylene glycol (DPG), polyethylene glycols (PEG) of molecular weight 200 and 400, and polypropylene glycol (PPG) of molecular weight 400 were obtained by Fluka AG and used without further purification, polypropylene glycol 2000 was a gift of Elastogran AG, Germany, dinbutyl amine (DBA) was purchased from Merck KGaA, Darmstadt, Germany, and used without further treatment. Catalysts used were Dabco 33 LV as a gift from Air Products and Polycat NP 40 from Performance chemicals GmbH. Stabilizers of various types were generously given by Th. Goldschmidt AG.

The various types of polyurethanes were samples from producers of Germany, Japan, Mexico, Poland, the USA, Bulgaria, or Portugal.

2.2 METHODS

First experiments were generally performed in small-scale lab glass ware: a 750 ml four necked glass flask with stirrer, thermometer, reflux and solids inlet. The liquids were placed into the reactor, heated to 180°C, and the solids introduced with stirring as fast as possible while the temperature was slowly increased to the final reaction temperature. At this, the mixture was kept after completion of the addition another 30 to 60 minutes. The reaction mixture was allowed to cool down, filtered, and subjected to analysis.

The next step was the first scale up to a 1.75 kg batch in a 2.5 l glass reactor. The apparatus was as before and so is the process. For filtering, in this case was used a pressurized filter with a 120 mesh screen where the pressure was obtained from compressed nitrogen and applied with up to 25 kp/cm².

The third step in up-scaling was the use of a 100 l stainless steel reactor heated by thermal oil and stirred by a blade stirrer at 60 rpm. The process was the same as before, for filtering a suction filter was directly connected to the bottom outlet and used together with a membrane vacuum pump. The reactor was equipped with a three stage heat exchanger consisting of demister, first heat exchanger adjusted to a predetermined temperature and a second heat exchanger to collect any low boiling liquids.

3. RESULTS

3.1 RECYCLING POLYOLS FROM AUTOMOTIVE PRODUCTS

From automotive wastes, mainly seat cushions, i.e. cold moulded foams, ceiling elements, i.e. rigid reinforced foams, and wheel mould flashes, i.e. microcellular elastomers or flexible integral foams, were reacted to form recycling polyols.

Cold moulded foams were delivered by two main German manufacturers as complete cushions that did not meet standards. These were cut to flakes of about 8 cm size by a shredder. The flakes were introduced into the respective reactor without further treatment or separation.

The seats were used in an amount between 50 and 75% by weight to produce recycling polyols with viscosities ranging from 2,000 to 30,000 mPas (25°C) and hydroxyl numbers of 350 to about 270 mg KOH/g. The aim was to add the recycling polyols to premixes to result in elastic products again. Mainly, the recycling polyols were used as additives with 15 to 25% by weight in premixes to produce flexible cold moulded foams. Additionally, they were used to produce new types of material, e. g. sealants or steel tank coatings (Evtimova et al. 2004) or

composites with wood fibers (Belke et al. 2003). Table 1 depicts some examples of recycling polyols as derived from cold moulded foams.

By the process described from cold moulded flexible foams, recycling polyols can be prepared with a viscosity in the range between 3,500 and 27,000 mPas (25°C) with waste loads of the mixture between 60 and 75% by weight. In the range of about 65% by weight of solids the viscosity is established in the range between 4,000 and 11,000 mPas with hydroxyl numbers of about 300 mg KOH/g. These recycling polyols maybe used as an additive to commercial premixes or added as an additional feed to the foaming mixture up to 30% by weight. The resultant foams increase somewhat in hardness but do not suffer a loss in low temperature performance or comfort.

Integral foams processed were polyether based systems used to produce steering wheel shells of which the mould flashes were shredded to pieces of about 5 cm thickness. The flakes were subjected to several investigation of the system in which the amount of solids, the amine content, and the reaction time were systematically investigated.

As in the case of the cold moulded Foams, the optimum amount of polyurethane solids is again in the range of 60 to 65% by weight where the viscosity is of a magnitude allowing the recycling polyol to be added to a premix or processed as one of the components of the foaming mixture. The addition of the secondary amine leads to a rather high amine number in the lab scale experiments. This does not significantly affect the processing times, but may in some cases lead to a decrease in the amount of catalyst.

The investigation of several amine concentrations is presented in table 3. As shown in table 3, the amine concentration does not significantly affect the amine number. It only results in a further increase at concentrations beyond 4% by weight. This limit is different for any type of polyurethane and depends on the concentration of urethane groups present in the polymer. Most effect is contributed by the reaction time as shown in table 4.

Tab. 1: Recycling polyols from flexible cold molded foams

Item/No.	191	192	194	198	130
PUR (% by weight)	65,0	70,0	63,0	62,5	75,0
DPG (% by weight)	30,0	25,0	32,0	32,5	23,3
DBA (% by weight)	5,0	5,0	5,0	5,0	1,7
Reaction temperature (°C)	210	210	210	210	200
Reaction time (min)	55	60	55	45	115
Appearance	turbid	viscous	clear	clear	inhomogeneous
OH-No. (mg KOH/g)	299	251	310	303	213
Amine No. (mg KOH/g)	48	15	17	18	21
Viscosity (25°C) (mPas)	11,500	17,800	4,100	3,680	27,000

Tab. 2: Recycling polyols made with varying the amount of polyurethanes

No.	PUR (% by weight)	Reaction time (min)	OH No. mg KOH/g	Amine No. mg KOH/g	Viskosity (25°C) (mPas)
149	70,0	190	225	29	15,030
158	65,0	110	266	27	6,600
146	63,0	90	310	28	10,800
150	60,0	100	269	22	5,130
143	55,0	105	351	23	4,850
151	50,0	80	336	20	2,020
152	40,0	65	413	16	1,230

Tab. 3: Systematic variation of the amount of di-n-butyl amine in batches with 60 % by weight polyurethane solids load

No.	DBA (% by weight)	Reaction time (min)	Hydroxyl No. (mg KOH/g)	Amine No. (mg KOH/g)	Viskosity (25°C) (mPas)
153	1,0	95	336	24	6880
154	2,0	95	335	25	7700
155	3,0	95	336	28	5640
156	4,0	95	338	31	5280
157	5,0	95	335	36	5340

Tab. 4: Systematic variation of the reaction time in batches with constant polyurethane solids load at 200°C

No.	DBA (% by weight)	Reaction time (min)	Hydroxyl No. (mg KOH/g)	Amine No. (mg KOH/g)	Viscosity (25°C) (mPas)
159	63,2	50	246	17	9650
160	63,2	65	241	20	8360
161	63,2	80	243	25	5900
162	63,2	95	244	26	6600
163	63,2	110	254	24	5500
164	63,2	125	230	20	9610

The reaction time of the mixture after completing the addition of the polyurethane foam flakes increases corresponding to the increasing the reaction time, reaching a limit after about 90 minutes. Shorter reaction times (addition and post reaction) such as 50 minutes could not be established under lab conditions with suitable amounts of reactands (i. e. a batch size of 500 g). In continuous production, this number maybe decreased further by establishing reaction times of 20 minutes. Shorter reaction times will not be suitable even at temperatures exceeding 250°C as demonstrated and proven by experiments conducted with a continuous and a semi-continuous reactor, as the reaction is not complete. The experiments performed to this point with up to a batch size of 90 kg demonstrate the integral foams to be processable to recycling polyols with suitable properties. The somewhat higher viscosity as compared with the polyols received from the cold moulded foams may be attributed to the different formulation and the load of solids (pigments and fillers). The wastes employed were glass fibre reinforced high density foams as used in car ceilings having an estimated density of 65 g/dm³. The glass fibres were of 20 to 48 mm length before the experiment and decreased to 12 to 27 mm length after. The fibres were separated by simple filtration via a Buchner funnel. The unknown formulation of the rigid foam led to lower degrees of solids content in the experiments as shown in table 5.

The rigid foams were transformed with 40 % by weight into polyols of hydroxyl numbers of about 400 mg KOH/g and viscosities in the range of 8,000 mPas (25°C) when any solids were filtered off. The solids were glass long fibres or solids consisting of other polymers (mainly polyolefins) which had to be separated before they could further processed to give rigid foams without reinforcements under lab scale conditions. The increases of the reaction temperature. In this case lead to a tremendous increase in viscosity. The source of this increase is not yet clear but may be attributed to finely dispersed solids and fillers of the original foam to produce structural viscous liquids.

3.2 FLEXIBLE SLABSTOCK FOAMS

Flexible slabstock foams are produced from polyether systems, polyester systems, and mainly based on grafted polyether systems. Each of these types needs a detailed investigation and a specially developed solvolysis mixture and processing technology. Furthermore, the final product properties need to be carefully determined by the customer according to his technology before process development to adjust both viscosity and hydroxyl content (Behrendt & Naber 2009).

Flexible slabstock based on polyester systems was solvolysed using a typical mixture to give viscous recycling polyols of light amber colour. They were produced by batch technology in small and 6 kg batches. The results are depicted in table 6.

With this type of slabstock foam, the viscosities of the recycling polyols are generally high as are the original polyester polyols. They may be processed into the premixes at higher temperature to result in flexible foams again. The limit of application into a typical premix was determined to be 15% by weight at present. Further experiments were performed to reduce the viscosity and to be able to use more than the limiting 15 % by weight in a premix. Some results of such experiments are presented in table 7.

The addition of only a few percent into the reaction mixture reduces clearly the viscosity to values suitable for use in the production. The recycling polyols are clear, amber liquids without any solid side products. The incorporation of these recycling polyols into slabstock foam formulations (free rise under lab conditions) led to a decrease in hardness and a higher degree of softness with lower ball rebound. This may be attributed to the interference of the short chain triols with phase build up during foaming and polymer formation.

The materials used in further experiments were flexible slabstock foam residues from the outer part of the block with densified skins having a determined density of 34.5 g/dm³ of the foam part. Some results are shown in table 8.

The results with polyether flexible

slabstock foams are similar to those obtained with cold moulded foams, i. e., in a range of solids, lead to the reaction mixture of a bout 60 % by weight recycling polyols with suitable viscosities can be attained. The increase in the solid content as shown with batch 116 leads to a sharp increase in viscosity while the hydroxyl number accordingly decreases. In application of such recycling polyols, an optimum for viscosity and hydroxyl content has to be found to have both a maximum amount of recycling polyol added to the foaming mixture and optimum processing conditions. Flexible slabstock foams based on grafted polyether polyols are the main product in this field today, but present the greatest issue as well. The problem is centered on the solids content which maybe either separated and disposed of or dispersed in the recycling polyol as fine particles. As the reaction temperature typically exceeds the melting temperature of the grafted polymer chains, a special technology had to be developed to produce stable dispersions. A further limitation may arise from the polyureas present in the recycling polyol resulting in the combination of both viscosity problems through the build-up of tixotropy or of a high portion of non-Newtonian viscosity (structural viscosity). When developing a technology to separate the grafts, the solvolysis mixture needs to have a well-adjusted surface tension which is established by the use of a carefully selected mixture of short chain glycols. Some examples are presented in table 9, using batches that were produced on 1 kg basis to receive the grafts as filterable solids.

The technology and solvolysis mixture used in these experiments resulted in homogeneous recycling polyols of clear, light amber appearance with a viscosity as low as 1,500 mPas (25°C) due to the low solids content. A precipitate formed of solid needles of about 4 to 6 mm length and 0.5 to 1.5 mm thickness or particles of about 0.2 mm diameter which turned out to be the grafted polymers. The needle-like and the particulate material could be easily filtered off both at room temperature and at 75°C while the latter temper-

Tab. 5: Recycling polyols from reinforced rigid foams

Item/No.	166	168	169
Foam (% by weight)	40,1	40,1	40,1
DPG (% by weight)	29,2	29,2	29,2
DEG (% by weight)	35,2	29,2	29,2
DBA (% by weight)	1,5	1,5	1,5
Temperature (°C)	200	220	230
Time (min)	40	45	40
OH-No. (mg KOH/g)	381	387	473
Amine No. (mg KOH/g)	36	32	38
Viscosity (25°C) (mPas)	7,750	28,500	>50,000

Tab. 6: Recycling polyols from polyester slabstock foam

Item / No.	110	111	112	115	113
Foam (% by weight)	53,8	57,7	62,3	65,0	67,5
DPG (% by weight)	44,8	40,9	36,3	33,5	31,0
DBA (% by weight)	1,4	1,3	1,4	1,5	1,5
Temperature (°C)/time (min)	180/60	220/60	220/80	220/85	220/60
Hydroxyl No. (mg KOH/g)	303	331	292	290	275
Amine No. (mg KOH/g)	45	46	46	42	43
Viscosity (25°C) (mPas)	10,530	8,690	19,370	16,880	32,300

Tab. 7: Modified recycling polyols from polyester slabstock foam

Item / No.	122	124	130	131	132
Foam (% by weight)	65,0	71,0	75,0	57,7	57,7
DPG (% by weight)	33,5	27,4	23,3	38,9	36,8
Short chain triol(% by weight)	0	0	0	2,0	4,1
DBA (% by weight)	1,5	1,6	1,7	1,3	1,4
Temperature (°C)/time (min)	200/80	220/80	220/80	220/80	220/80
Hydroxyl No. (mg KOH/g)	304	278	213	348	346
Amine No. (mg KOH/g)	42	45	41	42	42
Viscosity (25°C) (mPas)	12,500	32,400	27,000	6,200	7,600

Tab. 8: Recycling polyols from polyether slabstock foam

Item / No.	116	117	119	121
Foam (% by weight)	70,0	57,7	57,7	57,6
DPG (% by weight)	28,3	40,9	40,9	40,9
DBA (% by weight)	1,6	1,4	1,4	1,5
Temperature (°C)/time (min)	200/80	220/80	220/60	220/95
Hydroxyl No. (mg KOH/g)	241	355	361	356
Amine No. (mg KOH/g)	41	41	41	41
Viscosity (25°C) (mPas)	57,750	4,200	3,880	3,780
Appearance	amber, with particles	light amber, clear	yellow, clear	yellow, clear

ature was preferred because of the much lower viscosity of the recycling polyol. The filtered recycling polyol was used as an additive up to 25% by weight in a typical formulation to produce polyether slabstock foams again.

When aiming at dispersed solids in the recycling polyols the technology and the solvolysis mixture had to be changed: the rate of the stirrer was increased to about 1200 rpm and the solvolysis mixture adjusted to a higher surface tension by the choice of the glycols. Some results are presented in table 10.

As shown in the table, by the process and technology developed recycling polyols with homogeneously dispersed non-settling solids and rather low viscosities could be obtained when applying a solids load between 55 and 70% by weight. The viscosities as measured by oscillation or rotation mode (Haake Rheostress® 300) possess a difference of roughly 800 mPas at 25°C which shows a high degree of structural viscosity originating from the combined action of the grafted polymers and the oligoureas present in the mixture.

The polyols thus obtained were introduced into a simple flexible foam mixture in the free rise mode (see formulation S1065 for details). In this formulation, part of the polyether polyol Lupranol® 2085 was substituted by the recycling polyols. The composition and some properties of the foams obtained are shown in table 11.

Tab. 9: Solvolysis of grafted polyether based flexible slabstock foam aimed at filterable solids (temperature always 220°C, reaction time 30 minutes)

Item/No.	141	142	145
PUR foam (% by weight)	40,0	40,0	40,0
DPG (% by weight)	43,1	48,1	51,7
Short chain triol (% by weight)	14,4	9,4	5,8
DBA (% by weight)	2,5	2,5	2,5
Appearance	Grey liquid with needle-like solids	Yellow liquid with solid phase	Yellow liquid with solid particles
Hydroxyl No. (mg KOH/g)	445	437	450
Amine No. (mg KOH/g)	44	45	43
Viscosity (25°C) (mPas)	1,480	1,670	1,560

Tab. 10: Solvolysis of grafted polyether based flexible slabstock foam aimed at homogenous polyols

Item/No.	139	105	195	196	197
Foam (% by weight)	50,0	50,0	60,0	55,0	65,0
DPG (% by weight)	36,0	37,6	29,75	34,85	26,4
DEG (% by weight)	12,0	9,4	5,25	6,15	4,6
DBA (% by weight)	2,0	3,0	5,0	4,0	4,0
Temperature (°C)	200	200	220	220	220
Time (min)	80	60	70	85	60
OH-No. (mg KOH/g)	381	434	329	374	284
Amine No. (mg KOH/g)	-	62	24,4	24,5	44
Viscosity oscillation mode (25°C) (mPas)	-	-	10,600	5020	7050
Viscosity rotation mode (25°C) (mPas)	-	8,100	10,500	4300	6200
Appearance	slurry	homogeneous, amber	homogeneous, dispersion	homogeneous, dispersion	homogeneous, dispersion

Tab. 11: Free rise foam composition and properties with the addition of the recycling polyols received from flexible slabstock foam based on grafted polyether alcohols (amounts given in % by weight)

Item/No.	S1040	S1045	S1046	S1042	S1043
Polyol 195	0	15.8	23.1		
Polyol 196	0	0	0	7.85	15.8
Lupranol® 2095	78.8	63.0	53.9	71.0	63.1
Polycat® NP40	0.33	0.33	0.32	0.33	0.33
TEGOSTAB® 8433	0.06	0.06	0.06	0.06	0.06
Water	1.05	1.06	1.02	1.05	1.05
Lupranat® M20A	19.7	19.7	19.2	19.7	19.7
Start (s)	20	17	21	17	17
Index	90	60	50	70	57

Tab. 12: Recycling polyols obtained from polyester shoe soles

Item/No.	172	173	174
PUR (% by weight)	65	70	70
DPG (% by weight)	32,5	27,5	26,5
DBA (% by weight)	2,5	2,5	3,5
Reaction temperature (°C)	200	200	200
Reaction time (min)	60	60	60
Hydroxyl No. (mg KOH/g)	296	248	257
Amine No. (mg KOH/g)	23	16	18
Viscosity (25°C) (mPas)	22,370	87,500	66,000

The compression strength of the foam is decreased by only 12% when adding up to 20% by weight of the recycling polyol while compression set shows no change. When adding larger amounts of the recycling polyols the foams tend to get a higher proportion of closed cells and to shrink. The reason for this phenomenon has not been elucidated but maybe attributed to the cell stabilizers originally present in the foam formulations. The demoulding times turn out to be under lab conditions somewhat shorter than the formulation based on primary polyols.

When using recycling polyols of this type the hardness of the free rise foams is efficiently controlled by the isocyanate index (Behrendt & Pohl 1998). It has to be pointed out that the higher the amount of recycling polyol added the lower the isocyanate index should be formulated so as to produce maximum flexibility of the foams. When

employing 30% by weight of the recycling polyol the index may kept as low as 50 in the total stoichiometric balance (including water). Thus, the formulation is produced more economically by reducing the amount of polymeric MDI necessary for foaming.

3.3 SHOE SOLE PRODUCTION WASTES

Wastes of the shoes sole production are of polyether or polyester type (Stoychev et al. 2010). Both types were subjected to solvolysis and introduced into the original systems again. The solvolysis did not need a change in batch technology but in the continuous mode. The following table 12 shows some results obtained with both polyether and polyester shoe soles at various degrees of solids content.

The originally employed polyester diols used in shoe sole production are at room temperature semi solid or

solid materials. The viscosity is measured and presented at 25°C while the temperature at working conditions is in the range of 55°C. Hence, the viscosities of the recycling polyols are at 55°C in the range of the original polyesters. Depending on the technology of the customer, the amount of solids in the mixture maybe as high as 80% by weight to give a material being semi solid (paste-like) at room temperature and having a viscosity of about 2500 mPas at 55°C.

Polyether based shoe sole wastes were solvolysed in the same way. As in any other case, also with this material the conditions had to be developed and adjusted to the material. Some of the results with higher proportions of solids are depicted in table 13.

Tab. 13: Recycling polyols obtained from polyether shoe soles

Item/No.	056	057	059	060	061
PUR (% by weight)	60	55	70	63	65
DPG (% by weight)	35,5	40,5	26,5	33,0	30,5
DBA (% by weight)	4,5	4,5	3,5	4,0	4,5
Reaction temperature (°C)	200	200	200	200	200
Reaction time (min)	30	30	30	30	30
Hydroxyl No. (mg KOH/g)	380	383	257	279	254
Amine No. (mg KOH/g)	15	18	27	31	18
Viscosity (25°C) (mPas)	2,720	1,780	11,930	2,430	8,800

Due to the general lower viscosities of the polyether polyols there are two choices: either the viscosity can be kept low, e. g. at about 3000 mPas (25°C) having a solids content of about 63 % by weight, or the amount of solids is high, e. g. 70% by weight, when the viscosity is apt to be processed by the technology employed by the applicant and easily reaches 15,000 mPas (25°C). Even higher percentages of solids are possible. It was shown that even at 85 % by weight of solids a semi solid recycling polyol can be produced showing a viscosity at 25°C of about 80,000 mPas. In any case, the applicant of such recycling polyols has to carefully determine the parameters aimed at which should be completely in concordance with the technology employed.

The recycling polyols were introduced into typical shoe sole systems at rates up to 40% as calculated on the basis of the premix component. If the premixes are changed by the applicant or supplier, especially by eliminating some of the chain extenders ethylene glycol and/or butane-1,4-diol, the glycol of the solvolysis mixture may take over part of their function in establishing a certain phase segregation in the polyurethane and further adding to the rigidity of the material (Stoychev et al. 2011). Such experiments are under way.

4. CONCLUSIONS

The combined glycolysis/aminolysis is the basis of a new polyurethane recycling process well suited to produce recycling polyols of good quality

from various polyurethane sources. It has been shown by a multitude of lab and semi-technical scale experiments that for each type of polyurethane a special formulation has to be developed, that a formulation fitting for one product cannot be transferred without problems to another product even of the same type but the solvolysis mixture has always to be carefully reformulated and adjusted to the product under consideration. Further, it has been shown that the recycling polyols maybe produced at various scales with identical parameters as shown with the hydroxyl numbers and viscosity. The reaction conditions further influence the quality of the product with respect to homogeneity and colour. The colour of the recycling polyols – in general yellow to dark amber – does not affect the foam properties and is not a result of oxidation during the process but more that of a side reaction of minor contaminants and does not deepen on longer addition or reaction times. Fillers or pigments remain in the recycling polyols, thus leading to products with the colour of the original polyurethane or – in case of mixtures of several colours – of a mixed colour. In some cases a solids content of the polyurethanes up to 20 % by weight was found and stabilized in the recycling polyol either by the viscosity (where the appearance of tixotropy has to be avoided) or at lower viscosities (e. g. 2000 mPas) with agitation of the polyol in the storage container. The polymers grafted to polyether alcohols as in the grafted polyols may either be formed into a needle-like material and filtered off or finely dis-

persed and remain in the recycling polyol to be introduced into the new polyurethane again.

The solids content of the recycling polyol is in case of elastic types usually in the range of 60 % by weight to meet viscosity requirements. It maybe increased to up to 85 % by weight but in these cases the viscosity at 25°C exceeds processing conditions so that processing is possible only at elevated temperatures. The latter holds especially in the case of polyester based shoe soles. With rigid foams the amount of solids is limited to about 50% by weight to meet acceptable viscosities.

The recycling polyols maybe used as single components in the production of composites, coatings, or sealants, i. e. a new type of material. Attempts to introduce them into formulations similar to the original products have shown that depending on the type of polyurethane produced between 15 and 40 % by weight of the premix component maybe substituted by the recycling polyol without detrimental effects on the final product properties.

Thus, the solvolysis by combined aminolysis and glycolysis represents not only a much faster and simpler way to produce recycling polyols from a variety of polyurethane products but also gives recycling polyol with qualities allowing them to be introduced into formulations of the original products as well as in such for completely different products. The process and the apparatus to perform the process are available up to volumes of 6 met-

ric tonnes thus allowing for an annual production of up to 4,500 metric tonnes in the three shift system. The process is economical in that way as the production costs at an annual production exceeding 250 metric tonnes are far below the primary raw materials and usually in the range of € 0.50 (or equivalent \$ 0.62).

Remark: Article based on a presentation held at STI Conference Nyeri (Kenia), 04.-07.11.2014

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