

Polyurethane Powder Coatings Crosslinked with Allophanate Structures Containing Polyisocyanates

Barbara Pilch-Pitera

Department of Polymer Science, Faculty of Chemistry, Rzeszów University of Technology, Rzeszów 35-959, Poland

Received 16 January 2009; accepted 4 December 2009

DOI 10.1002/app.31895

Published online 22 February 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: With the use of alicyclic diisocyanates, aliphatic alcohols and dibutyltin dilaurate as well as triethylamine as a catalysts internally-blocked polyisocyanate crosslinkers which contained allophanate bonds were synthesized. The chemical structure of those compounds were characterized by IR, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$ spectroscopy. Their molecular weight distribution (MWD) parameters were determined by gel permeation chromatography (GPC). Those blocked polyisocyanates were used for the

production of ecological lacquer compositions and coatings. The unblocking and curing reactions were investigated on the DTA, TG, and DSC thermograms. The resulting powder lacquers exhibit an excellent appearance; they are transparent, smooth, and nonyellowing. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 3613–3620, 2010

Key words: polyurethanes; coatings; allophanate; polyisocyanates

INTRODUCTION

Polyurethane powder-coating systems have played an important part since the very beginning of the development of the powder coating technology in the period from late 1960s to early 1970s. The reason for the expansion of polyurethane powder coatings is their unique environmental friendliness.^{1,2} R&D efforts were focused exclusively on isocyanate adducts that were deactivated using a blocking agent, to prevent the hardener reacting prematurely with the other reaction component, generally a hydroxy-functionalized polyester, during the powder production process. The form of blocking was chosen so as to obtain sufficiently rapid recleavage into the monomeric blocking agent and free isocyanate group under stoving conditions (temperature range within 190–220°C). The unblocked isocyanate was then able to react with the OH-functionalized resin component to form a thermosetting coating.^{3,4}

The critical disadvantage, however, resulted from the emission of the organic blocking agents used in conventional PU powder coatings. New developments in this field were modern systems that were reduced and free from elimination of by-products. The new crosslinkers were designed to provide the maximum level of isocyanate content for crosslinking, while minimizing the level of blocking agent.^{1,5–26} Structurally, they were based on the combination of

externally and internally blocked diisocyanates. Caprolactam, oximes, and heterocyclic compounds, such as 1,2,4-triazole and 3,5-dimethylpirazole were preferred in these systems for external deactivation of the reactive isocyanate groups. The internal blocking of diisocyanates is based on the formation of uretdione (2,4-diazine-1,3-dione) groups,^{1,5–20} allophanate groups^{21–24} or biuret groups.^{25,26} Although the dimerization process of aromatic diisocyanates is much easier to conduct, the use of those materials in the production of coatings is limited because of the inferior UV resistance of the coatings obtained therefrom. More prospects may thus be expected in that technology from dimers of aliphatic and cycloaliphatic diisocyanates, formation of which is much more difficult versus considerable amounts of isocyanurate structures (25–50% in case of HDI and H_{12}MDI). The crosslinkers requires only uretdione structures and no isocyanurate structures, the first task is to prepare a high purity dimeric diisocyanate. In principle, this can be achieved by way of the reaction regime and by the choice of highly selective catalysts.

The internal blocking reactions, which utilize biuret-type bonds or allophanate-type bonds offer higher yields and they proceed much easier than the dimerization reaction.^{21–26} The former reactions are reversible at lower temperatures (120–180°C) as compared with dimers (180°C), and they may compete with the relatively difficult and time consuming dimerization process. The formation of allophanate blocked polyisocyanate results from the addition of diisocyanates and alcohol. This reaction yields allophanates and isocyanurates, together with ureas and

Correspondence to: B. Pilch-Pitera (barbpi@prz.edu.pl).

biurets if there are traces of water in the reaction medium. The formation of allophanate bonds depends on the reaction conditions, such as temperature, alcohol-to-diisocyanate molar ratio, and the presence of catalysts.^{21–24}

Having the aspects aforementioned in mind, we presented the synthesis method in this article for polyisocyanates that were internally blocked by allophanate bonds. The principal purpose of this work was to select the optimum reaction conditions: diisocyanate-to-alcohol molecular ratio, temperature, time, catalysts, and atmosphere. That optimization was aimed at limiting the formation of by-products. Special attention was paid to the content of isocyanate groups at individual stages of the synthesis process, and to the distribution of molecular weight (MWD) in the produced polyisocyanates. The MWD of those polyisocyanates were investigated by means of gel permeation chromatography (GPC).

The final goal of this work was to employ the obtained polyisocyanates as crosslinkers in the powder coating formulations. The critical issue for said polyisocyanates from the viewpoint of their application is the knowledge on the course of their unblocking and crosslinking processes. The differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TGA/DSC) methods were used to monitor those processes.

EXPERIMENTAL

Raw materials and reagents

1,6-Hexamethylene diisocyanate (HDI)–Desmodur H), isophorone diisocyanate (IPDI)–Desmodur I, and 4,4'-dicyclohexylmethane diisocyanate (H₁₂MDI)–Desmodur W, from Bayer A.G. (Leverkusen, Germany). 2,2',4'- and 2,4,4'-Trimethyl-1,6-hexamethylene diisocyanate (TMDI)–Vestanat TMDI, from Evonik Degussa G.m.b.H. (Marl, Germany). Methanol (ME), ethanol (ET), 2-propanol (PR), 1-butanol (BU), and 1-hexanol (HE), from Aldrich (Buchs, Switzerland). 3,5-Dimethylpirazole (DMP), and imidazole (I), from Aldrich (Buchs, Switzerland). Rucote 102–polyester resin based on isophthalic acid and neopentyl glycol, acid value: 11–14 mg KOH/g, hydroxyl value: 35–45 mg KOH/g, T_g : 59°C, from Bayer A.G. (Leverkusen, Germany). WorleeAdd 902, and Resiflow PV 88, from Worlée–Chemie G.m.b.H (Lauenburg, Germany).

Synthesis of blocked diisocyanates

The diisocyanate feeds were placed in a three-necked flask equipped with a reflux condenser, thermometer, glass stirrer, nitrogen inlet, and dropping funnel. A calculated amount of a blocking agent was

added to reaction mixture in each case. The reactions were carried out in THF, at the temperature of $60 \pm 1^\circ\text{C}$. The end point of the reaction was controlled by the content of $-\text{NCO}$ groups. The products were evaporated under vacuum and dried at the temperature of $100 \pm 1^\circ\text{C}$ to remove the solvent. The obtained products were marked with symbols e.g., HDI-I, where individual segments stand for the names of the feeds used.

Synthesis of allophanate structure containing polyisocyanates

The synthesis covered three stages: synthesis of urethane polyisocyanate, synthesis of allophanate, and blocking reaction.

Synthesis of urethane polyisocyanate

Diisocyanate and dibutyltin dilaurate as well as triethylamine as a catalysts (both at 0.1 wt % with respect to diisocyanate) were placed in a three-necked flask that was equipped with a reflux condenser, thermometer, glass stirrer, nitrogen inlet, and dropping funnel.

A calculated amount of alcohol (to keep the diisocyanate-to-alcohol molar ratio at 2 : 1) was introduced dropwise to diisocyanate. The time of introduction was adjusted to about 30 min. The reaction mixture was then maintained at the temperature of $60 \pm 1^\circ\text{C}$, it was stirred and refluxed for 2 to 3 h, depending on the kind of diisocyanate and alcohol.

The end point of the reaction was controlled by the content of $-\text{NCO}$ groups. The molecular structure of urethane polyisocyanate was presented in Figure 1.

Allophanate synthesis

The reaction mixture was heated up to $130 \pm 1^\circ\text{C}$, stirred and refluxed for 5 up to 10 h, depending on the kind of urethane polyisocyanate. The reaction progress was controlled by the content of $-\text{NCO}$ groups. The molecular structure of allophanate polyisocyanate was presented in Figure 2.

Blocking reaction

A calculated amount of the blocking agent was added to the reaction mixture in each case. The reactions were carried out in THF, at the temperature of $60 \pm 1^\circ\text{C}$.

The products were evaporated under vacuum and dried at the temperature of $100 \pm 1^\circ\text{C}$ to remove the solvent. The molecular structure of blocked allophanate polyisocyanate was presented in Figure 3 and the characteristics of the obtained products were

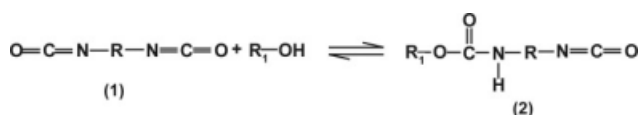


Figure 1 The molecular structure of urethane polyisocyanate.

presented in Table I. The obtained products were marked with symbols, e.g., IPDI-ME-DMP, where individual segments stand for the names of the feeds used.

Preparing lacquer compositions and coatings

The crosslinking agent was mixed with polyester resin RUCOTE 102 (NCO:OH molar ratio = 1 : 1). The mixture was pulverized to the average particle size of 60 μm . The final powder coating was applied manually to steel and glass panels and cured at 150–200°C for 15–50 minutes. The characteristics of so obtained lacquers were presented in Table II.

Measurements

Characterisations of polyisocyanates

Concentration of –NCO Groups. The typical dibutylamine method was employed. Excess of unreacted dibutylamine was titrated with aqueous HCl against bromophenol blue.²⁷

Structural Analysis

IR spectroscopy. The IR spectra were taken by means of an FTIR spectrophotometer from Perkin Elmer, in KBr pellets.

¹H-NMR and ¹³C-NMR spectroscopy. The NMR spectra were recorded using a Bruker Avance^{II} 500 MHz unit.

Gel permeation chromatography (GPC). The GPC apparatus was a Viscotec T60A unit which was equipped with a triple detector: RI, light scattering (LS) and viscosity (DV) based detector. Separation operations were made at $30 \pm 0.1^\circ\text{C}$ on a two SDV columns (size 7.8 mm \times 300 mm), packed with gel of pore diameters 100 \AA and 1000 \AA , from Polymer Standards Service. The eluent (THF) flow rate was 1 cm^3/min , and the volume of inflow circuit – 20 μdm^3 . Operation of the chromatograph was controlled by the original computer software TRISEC Data AcquisitionSystem by Viscotec Corporation; deconvolution was possible for individual peaks that corresponded

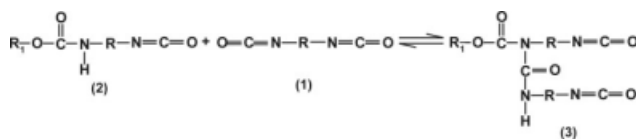


Figure 2 The molecular structure of allophanate bond containing polyisocyanate.

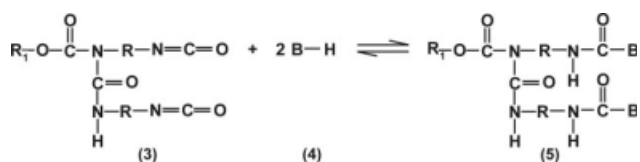


Figure 3 The molecular structure of blocked allophanate bond containing polyisocyanate.

to nonhomogeneous oligomers. The results were interpreted on the basis of conventional calibration of columns with polystyrene standards. The chromatographic analysis of standards yielded the calibration relation for logarithm of mass versus retention volume. The differential curves for distribution of molecular weights as obtained from sample elution curves and from the calibration equation were presented in the form of standardized charts: detector signal divided by the total area below the chromatogram–molecular weights of components.

Thermogravimetric analysis (TGA). The thermal performance of the crosslinking agents was investigated with the use of a Mettler Toledo TGA/DSC1 differential calorimeter, with the Star^e System software. The instrument was calibrated with the use of In standard. The samples (0.0002 g) were placed in alumina crucibles. These were weighed to the nearest 0.000001 g and placed in the measuring chamber. These were weighed to the nearest 0.000001 g and placed in the measuring chamber. The temperature ramp was activated at $10^\circ/\text{min}$., and the temperature was gradually increased from 25 to 500°C. The DTA, TG, and DTG curves were recorded. The measurements were taken under nitrogen blanketing–the gas was passed at the rate of 50 cm^3/min .

Characterisations of powder coatings

Differential scanning calorimetry (DSC). A Mettler Toledo Type 822^e differential calorimeter (DSC) with the Star^e System software was employed to analyze thermal properties of powder coatings. The instrument was calibrated with the use of Zn and In standards. The samples (0.0010 g) were placed in aluminum crucibles. These were weighed to the nearest 0.00001 g and placed in the measuring chamber. The measurements were taken in the heating-cooling-heating cycle within the temperature range of from 25 to 250°C, under nitrogen blanketing, the gas was passed at the rate of 30 cm^3/min . The heating rate was $10^\circ/\text{min}$. The temperatures for phase transitions (T_m , T_g), as well as the unblocking and curing temperatures, were found by means of the generally known method.

Coating thickness. Coating thickness was measured with a micro-TRI-gloss tester from Byk Gardner, according to the standard PN-EN ISO.²⁸

TABLE I
Specifications for the Obtained Polyisocyanates

Number of sample	Type of diisocyanate	Type of alcohol	Type of blocking agent	Symbol of polyisocyanate sample	NCO-group content after deblocking
1	IPDI	Methanol	DMP	IPDI-ME-DMP	17.9
2	IPDI	1-Butanol	DMP	IPDI-BU-DMP	14.0
3	IPDI	1-Hexanol	DMP	IPDI-HE-DMP	14.5
4	H ₁₂ MDI	Methanol	DMP	H ₁₂ MDI-ME-DMP	15.2
5	H ₁₂ MDI	1-Butanol	DMP	H ₁₂ MDI-BU-DMP	14.1
6	TMDI	1-Butanol	DMP	TMDI-BU-DMP	16.8
7	HDI	–	Imidazole (I)	HDI-I	–
8	HDI	Ethanol	Imidazole (I)	HDI-ET-I	21.9
9	HDI	2-Propanol	Imidazole (I)	HDI-PR-I	21.1
10	HDI	1-Butanol	Imidazole (I)	HDI-BU-I	20.4

Gloss. A micro-TRI-gloss tester from Byk Gardner was employed, according to the standard PN-EN ISO²⁹ for the angles of 20°, 60°, and 85°.

Impact resistance strength. The impact resistance strength was determined by using the dart drop method, according to the standard PN-EN ISO.³⁰

Adhesion. Adhesion was determined by using the multi-cut method, in accordance with the standard PN-EN ISO.³¹

RESULTS AND DISCUSSION

Blocked polyisocyanates, which were stable at room temperature, were obtained with the use of alicyclic and aliphatic diisocyanates, aliphatic alcohols, and blocking compounds. Aliphatic and alicyclic diisocyanates were selected for the syntheses since the coatings produced therefrom offer high resistance to yellowing. The synthesis itself involved three stages. The first stage was to form the urethane bond (Fig. 1). Monohydric alcohols, like methanol, ethanol, 2-propanol, butanol and hexanol, were used for that purpose. The use of dihydric alcohols would produce a mixture of urethane oligomers, whereas trihydric alcohols would yield branched structures, which would make it hard to identify the products. The reactions were conducted in bulk, at the alcohol-to-diisocyanate molar ratio equal to 1 : 2. Nitrogen blanketing was employed for the whole process in order to prevent side reactions. Since the allophanate bond was not a fast-forming one, two catalysts were used simultaneously: dibutyltin dilaurate and triethylamine. The first stage, i.e. formation of the urethane bond, was reasonably quick under those conditions (about 1 h), at the temperature as low as 60°C. The second stage, i.e. synthesis of the allophanate bond (Fig. 2), required a higher temperature, 130–150°C. Despite severe process conditions that stage took much longer (a few hours). The reaction progress was monitored by analyzing the content of

free –NCO groups and by comparing the findings to those calculated theoretically. The final stage was designed to block the remaining –NCO groups with the use of heterocyclic compounds: imidazole and 3,5-dimethylpirazole, which were nontoxic and which could be unblocked at relatively low temperatures.

IR and NMR spectra

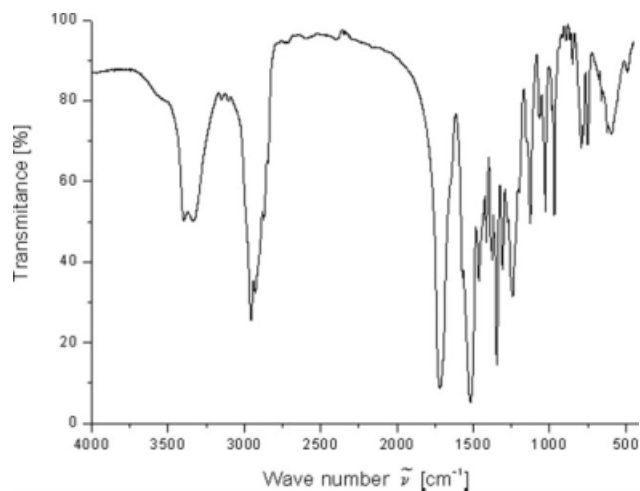
The structures of the obtained products were confirmed by IR (Fig. 4) and NMR spectra (Figs. 5 and 6). The stretching vibration of the C=O group at 1688–1734 cm⁻¹ and of the N–H group at 3262–3414 cm⁻¹ confirm the presence of the urethane linkages for all the adducts. The absence of absorption at 2250–2270 cm⁻¹ indicates that isocyanate groups have been completely blocked. There were no bands in the spectra of the studied compounds at about 2130 cm⁻¹, which were representative of the carbodiimide groups, nor at about 1415 cm⁻¹, which were specific for the isocyanurate ring, and which jointly confirm proper route for the reaction.

The signals coming from allophanate bond protons were present at about 12 ppm (assigned as “b”) in ¹H-NMR spectra (Fig. 5). In samples 7 and 8, weak signals appear for urethane bond protons within 8.66–8.93 ppm, which suggests that not all urethane groups have reacted with diisocyanate to form allophanate structures. In the 3.22–4.20 ppm range, the signals were present from the –CH₂– groups which were neighbors to urethane (“a” and “f”), allophanate (“c”) or urea (“d”) groups.

The ¹³C-NMR spectra clearly confirm the presence of the allophanate bonds which have been formed. Their presence was proven by the signal from the carbon atom of the carbonyl group within the allophanate bond, which can be observed at about 156 ppm (assigned as “i”) (Fig. 6). As opposed to that signal, the one for the carbon atom of the urethane

TABLE II
Specifications for the Obtained Polyurethane Powder Coatings

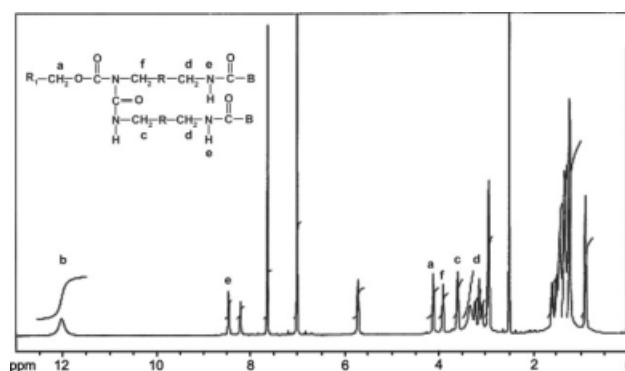
Symbol of polyisocyanate sample	Polyisocyanate content (g)	Polyester resin content (g)	Curing temperature (°C)	Curing time (min.)	Symbol of powder coating	Coating thickness (µm)	Gloss 20° / 65°/80° (%)	Impact resistance strength (cm)	Adhesion to steel surface
IPDI-ME-DMP	1.61	10	180	40	IPDI-ME-RU	132	29/58/52	10	4
IPDI-BU-DMP	1.87	10	180	40	IPDI-BU-RU	152	25/61/55	5	5
IPDI-HE-DMP	1.80	10	180	40	IPDI-HE-RU	249	28/67/74	5	5
H ₁₂ MDI-ME-DMP	1.76	10	150	50	H ₁₂ MDI-ME-RU	200	27/66/58	5	5
H ₁₂ MDI-BU-DMP	1.84	10	150	50	H ₁₂ MDI-BU-RU	151	26/61/54	5	5
HDI-ET-I	2.61	10	200	15	HDI-ET-RU	120	12/52/64	10	4
HDI-BU-I	2.48	10	180	20	HDI-BU-RU	125	5/22/28	10	2


Figure 4 IR spectrum for sample IPDI-BU-DMP. The polyisocyanates were marked according to Table I.

bond appears within 152–153 ppm (“h”), while the urea bond atom was represented at about 148 ppm (“l”).

Gel permeation chromatography (GPC)

The principal task for the analysis of polyisocyanates was not only to confirm the expected chain structure but also to learn the complete distribution of molecular weights as well. Based on the GPC elution curves as recorded with the use of three detectors: RI, LS, and DV, and based on the calibration curve, the molecular weight distribution (MWD) profiles were obtained (Fig. 7). It was concluded with the use of GPC that the composition of the obtained polyisocyanates was more complicated than it follows from the assumed stoichiometry (Table III). The expected products were obtained next to other components, e.g. oligomers with the gradually increasing molecular weights. The content of that fraction, however, was below the figure for the expected product.


Figure 5 ¹H-NMR spectrum for sample HDI-BU-I. The polyisocyanates were marked according to Table I.

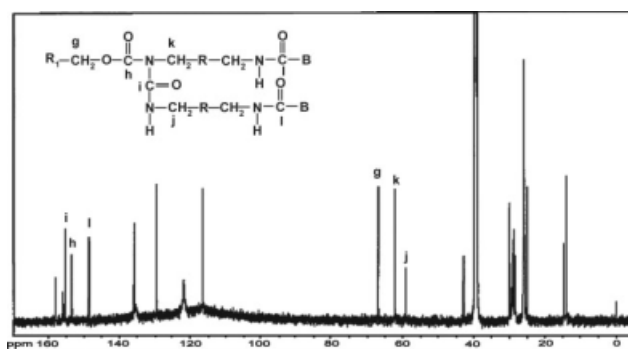


Figure 6 ^{13}C -NMR spectrum for sample HDI-ET-I. The polyisocyanates were marked according to Table I.

Small amounts of low molecular weight compounds were also present in the reaction mixture, and unconverted feedstocks were identified in some cases, too.

Thermogravimetric analysis (TGA)

The thermogram of a selected sample (No 8 HDI-BU-I) was presented in Figure 8. The thermogram was taken for the sample with no allophanate bonds in its structure to properly interpret the transformations which take place during hardening and thermal decomposition processes. The analysis involved the sample with the HDI diisocyanate, blocked with imidazole HDI-I (Fig. 9). Thermal degradation of blocked HDI-I diisocyanate consists of two stages. The sample mass loss at the temperature range of 120–200°C was the consequence of the unblocking reaction. The second stage at the temperature range of 260–370°C leads to the total degradation of the sample. The three-stepped mass loss was observable in the thermogram of the sample HDI-BU-I. The small sample mass loss at the temperature range of 120–200°C was the consequence of the imidazole

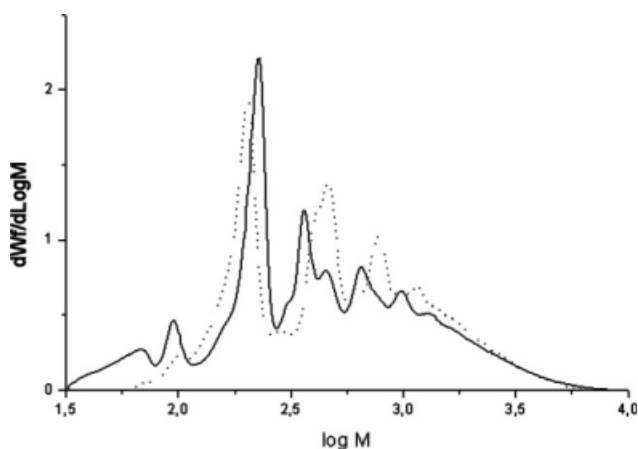


Figure 7 GPC chromatograms for sample HDI-PR-I and HDI-ET-I. The polyisocyanates were marked according to Table I. ---- HDI-PR-I ____ HDI-ET-I.

TABLE III
Interpretation of GPC Chromatograms for Polyisocyanates

Symbol of polyisocyanate sample	Proposed structure of sample compound	M_n in peak maximum as calculated from calibration curve	M_n calculated [g/mol]
HDI-PR-I	(I)	99	68
	(PR)(HDI)(I)	206	294
	(PR) ₂ (HDI) ₂ (I)	417	520
	(PR)(HDI) ₂ (I) ₂	468	530
	(PR)(HDI) ₃ (I) ₃	776	766
	(PR)(HDI) ₄ (I) ₄	977	1002
	(PR)(HDI) ₅ (I) ₅	1169	1238
HDI-ET-I	(I)	98	68
	(ET)(HDI)(ET)	226	260
	(ET)(HDI)(I)	367	282
	(ET)(HDI) ₂ (I) ₂	551	518
	(ET)(HDI) ₃ (I) ₃	656	754
	(ET)(HDI) ₄ (I) ₄	948	990
	(ET)(HDI) ₅ (I) ₅	1318	1226

unblocking reaction. The second stage at the temperature range of 210–260°C was the allophanate unblocking reaction. According to Lapprand et al.,²¹ thermal dissociation of alkyl-aryl allophanate to urethane and diisocyanate begins at 210°C and it was dependent on the type of structure. The next stage (at the temperature over 280°C) leads to the total degradation of the sample.

Differential scanning calorimetry (DSC)

To be able to properly explain the transformations that take place, each sample was investigated in the heating-cooling-heating cycle. At a temperature of 59°C, the glass transition of the polyester resin Rucote 102 can be observed in DSC thermograms (Fig. 10). That transformation shifts toward higher temperatures during the second heating cycle which results from stiffening the resin chain ends by urethane bonds, which in turn makes the evidence for crosslinking of the coat. A short endothermic peak was seen at 100–120°C because of the unblocking reaction. The curing reaction shows a small exothermic effect in the range of 120–140°C. Since deblocking was an endothermic process, and crosslinking was an exothermic one, the thermal effects of those reactions overlap. Hence, those two processes were not clearly visible. The peaks completely disappeared during the second heating—the coating was completely cured.

Analyses of the lacquer coatings performance properties

The resulting powder lacquers exhibit an excellent appearance: they were transparent, smooth and non-

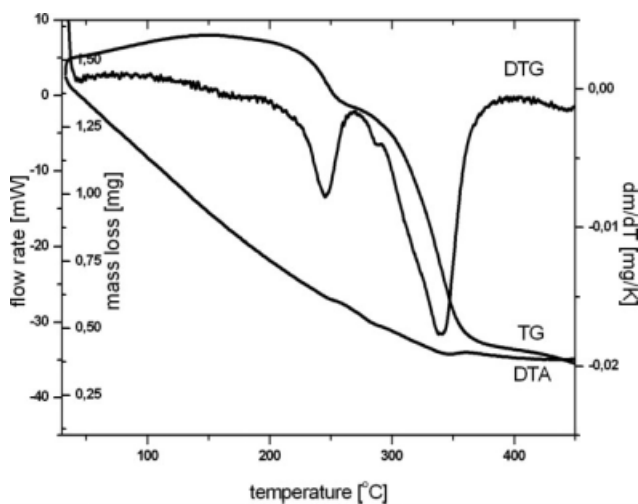


Figure 8 TG, DTG, and DTA thermograms for sample HDI-BU-I. The polyisocyanates were marked according to Table I.

yellowing. The coat thickness fell within 120–249 μm , i.e. it satisfied the standard requirement²⁸ (maximum of 250 μm). The sample of HDI-BU-RU was matt and the other coatings were semi gloss (the values measured for the gloss are in the range 45–70% for the angle of 65°). There was no haze because of insufficient dispersion of the material observed for the obtained coats. Hence, the effects of process factors, like proper dispergation of the components in the blending process or proper application method, on the coat properties may be neglected in this case.

Adhesion to the steel surface was not too high. In the 5-degree scale, it amounts to 2–5 (Table II). During the fall of the weight from 5–10 cm, some bursting was observed. The best adhesion to the substrate and impact resistance strength was offered by the sample of HDI-BU-RU which contains aliphatic 1,6-

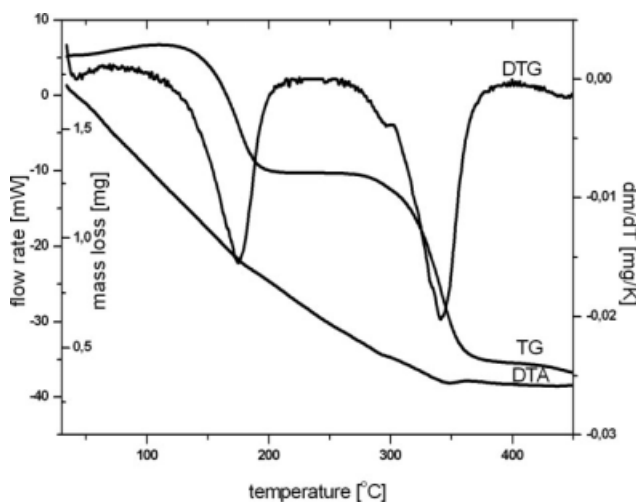


Figure 9 TG, DTG, and DTA thermograms for sample HDI-I. The polyisocyanates were marked according to Table I.

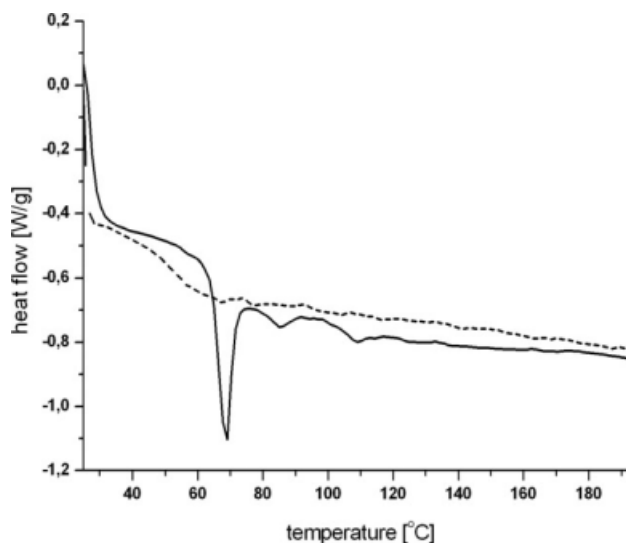


Figure 10 DSC thermograms for sample IPDI-BU-RU. The coatings were marked according to Table II. — First cycle of heating; ---- Second cycle of heating.

hexamethylene diisocyanate and butanol in its structure.

CONCLUSIONS

Internally blocked polyisocyanates, which contained allophanate linkages and which were stable at room temperature, were obtained with the use of alicyclic diisocyanates, aliphatic alcohols, and dibutyltin dilaurate as well as triethylamine as catalysts. Aliphatic or cycloaliphatic structures of the utilized diisocyanates lead to the final coatings with good performance properties as well as high yellowing resistance. Imidazole or 3,5-dimethylpirazole employed for additional external blocking of free $-\text{NCO}$ groups were characterized by low toxicity and low unblocking temperature which is of great importance in the modern powder coating technology. Internal blocking of $-\text{NCO}$ groups, through the formation of allophanate bonds which were unstable under curing conditions, made it possible to minimize the amount of the external blocking agent. The powder coating produced with the use of those polyisocyanates offers much lower emissions in the curing process, which makes it a more environment friendly product, capable of meeting even the stringent environmental requirements.

The GPC analysis gave the qualitative and quantitative insight into the molecular weight distribution in the synthesized polyisocyanates. The obtained products were polydisperse, because of incomplete regioselectivity of diisocyanates (HDI and IPDI) used in this work.

The differential scanning calorimetry and thermal analysis methods were very useful to evaluate the

coating curing process. Those tests were applicable and successful in selecting the parameters (temperature and time) for lacquer stoving. Actually, DSC and TA have been used widely to test also other polymer materials.

The interpretation of the performance properties of the obtained coats made it possible to find good correlations between said properties and chemical structures of polyisocyanates used. The best performance was found for the lacquer which contained aliphatic 1,6-hexamethylene diisocyanate in its formulation. The study on the hazing effect turned out very useful in evaluating the effects of the process factors, like proper dispergation of the components in the blending process or proper application and further treatment methods, on the properties of the lacquer coating.

The author would like to thank Ms Beata Mossety-Leszczak, Ph.D., Ms Małgorzata Walczak, and Ms Małgorzata Kowal, from the Faculty of Chemistry, Rzeszów University of Technology, for taking DSC, DTA, TG thermograms, and GPC chromatograms, as well as Bayer A.G., Evonik Degussa G.m.b.H. and Worlée-Chemie G.m.b.H for sending free samples of raw materials.

References

1. Wenning, A.; Weiß, J.-V.; Grenda, W. *Eur Coat J* 1998, 4, 244.
2. Irfab Chem Consultants; *Focus Powder Coat* 2002, 8, 6.
3. Chen, A. T.; Wojcik, R. T. *Met Finishing* 2000, 98, 143.
4. Subramanian, R. *Met Finishing* 2003, 101, 21.
5. Wicks, D. A.; Wicks, Z. W. Jr. *Prog Org Coat* 2001, 41, 1.
6. Rawlins, J. W.; Feng, S.; Sullivan, C.; Thometzek, P. *Paint Coat Ind* 2002, 18, 38.
7. Dearth, R. S.; Mertes, H.; Jacobs, P. J. *Prog Org Coat* 1996, 29, 73.
8. Schmitt, F.; Wenning, A.; Weiss, J.-V. *Prog Org Coat* 1997, 34, 227.
9. Wenning, A. US. Pat. No 6,849,705 (2003).
10. Wicks, D. A.; Wicks, Z. W. *Prog Org Coat* 1999, 36, 148.
11. Meier-Westhues, H.-U.; Thometzek, P.; Laas, H. J. *Farbe und Lack* 1997, 103, 7.
12. Wenning, A.; Weiss, J. V. EP. Pat. 1,382,649 (2004).
13. Spyrou, E.; Loesch, H. EP. Pat. 1,475,400 (2004).
14. Disteldorf, J.; Huebel, W.; Schmitz, K. EP. Pat. 0,317,744 (1989).
15. Spyrou, E.; Loesch, H.; Wenning, A. EP. Pat. 1,475,399 (2004).
16. Richter, F.; Halpaap, R.; Laas, H.-J.; Hecking, A. US. Pat. 7,151,151 (2005).
17. Richter, F.; Halpaap, R.; Laas, H.-J.; Hecking, A. US. Pat. 7,067,654 (2004).
18. Disteldorf, J.; Gras, R.; Schnurbusch, H.; Huebel, W.; Wolf, E. US. Pat. 4,463,154 (1984).
19. Disteldorf, J.; Hubel, W.; Schmitz, K. US. Pat. 4,912,210 (1990).
20. Gras, R. US. Pat. 6,916,897 (2004).
21. Laprand, A.; Boisson, F.; Delolme, F.; Méchin, F.; Pascault, J.-P. *Polym Degrad Stab* 2005, 90, 363.
22. Potter, T. A.; Slack, W. E. US. Pat. 5,124,427 (1992).
23. Bock, M.; Pedain, J.; Slawy, W.; Konig, K. US. Pat. 4,177,342 (1979).
24. Tazzia, C. L. US. Pat. 6,538,094 (2001).
25. Wicks, D. A.; Yeske, P. E. *Prog Org Coat* 1997, 30, 265.
26. Wagner, K.; Klinkmann, K. US. Pat. 4,051,165 1977.
27. Stagg, F. E. *Analyst* 1966, 71, 557.
28. Polish Committee for Standarization. *Paints and varnishes—Determination of film thickness*, PN-EN ISO 2808, Warsaw, Poland.
29. Polish Committee for Standarization. *Paints and varnishes—Determination of specular gloss of non-metallic paint films at 20°, 60° and 85°*, PN-EN ISO 2813, Warsaw, Poland.
30. Polish Committee for Standarization. *Paints and varnishes—Falling-weight test*, PN-EN ISO 6272, Warsaw, Poland.
31. Polish Committee for Standarization. *Paints and varnishes—Cross-cut test*, PN-EN ISO 2409, Warsaw, Poland.