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Quantitative Determination of PA6 and/or PA66 Content in Polyamide-Containing Wastes

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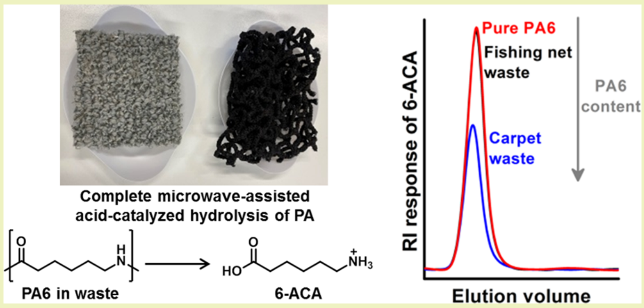

ABSTRACT: A fast, robust, and convenient method for quantitative determination of polyamide-6 (PA6) and polyamide-66 (PA66) in plastic wastes is presented. The method includes a straightforward procedure for complete hydrolysis of polyamides (PAs) into the constituent monomers and their quantitative determination in hydrolyzates by high-performance liquid chromatography on a mixed-mode column, from which the contents of a particular PA are determined. The method was developed on neat PA6 and PA66 as well as their mixture and was further utilized on PA-based composites and postconsumer wastes (carpet and fishing net wastes) containing PA in different amounts. The information on the content of a particular PA type in plastic wastes is important because it determines the maximum recovery of PA constituent monomer(s) by chemical recycling and consequently suitability of waste as a feedstock. Moreover, the proposed method allows for convenient differentiation between PA6 and PA66 in their mixtures, which is difficult to assess with precision by conventional characterization techniques.

KEYWORDS: *polymer waste, chemical recycling, microwave chemistry, polyamide content, liquid chromatography*

■ INTRODUCTION

Recent trends in plastic waste management are focused on improved plastic waste recycling because this could have a long-term impact on reduced greenhouse gas emissions, dependence on finite petroleum resources, and disposal of plastic wastes in the environment and will finally recover the economic value of plastic wastes.[1] Enhancement of plastic recycling beyond the current level includes among others improvements in chemical recycling within a circular economy, which is promoted by the industry as well. By chemical recycling, the polymer waste is converted to the feedstock for monomers, fuel production, or other value-added products and intermediates.[2−6] Furthermore, chemical recycling is a promising alternative to recycle composites, containing reinforcement additives, which are otherwise difficult to recycle by mechanical methods.[1,7] To accelerate chemical recycling, selective and efficient catalysts are being developed, which at the same time keep the depolymerization process economically viable.[1−4,8]

Polyamide-6 (PA6) and polyamide-66 (PA66) are versatile semicrystalline polymers with high chemical resistance and good thermal and mechanical properties.[9] They are produced from fossil resources, usually in the form of fibers or thermoplastics, for the use in a broad scope of applications (textile, automotive, electrical, electronic, construction, packaging, coatings, and other industries). Currently, both PA types are produced on an annual worldwide multimillion ton scale, and the production is estimated to be continuously growing, which is associated with increasing waste management issues of these nonbiodegradable polymers.[3,10] Furthermore, they are often used as PA blends or in combination with other polymers like polypropylene or polyethylene as well as composite and multicomponent materials such as carpets, which further complicate PA recycling processes.[7,9]

A primary goal of PA6 and PA66 depolymerization is to produce the constituent monomer(s), these are ε-caprolactam (cyclic monomer) or ε-aminocaproic acid (linear monomer), and hexamethylenediamine (HMDA) and adipic acid (AA), respectively, which can be further utilized in the synthesis of new PA or other polymers because the properties of recycled monomers resemble those of commercial raw materials. Several attempts to recycle PA66 and especially PA6 have been reported, including depolymerization by hydrolysis,[11−15] organocatalyzed ring-closing depolymerization in ionic liquids,[16−19] ammonolysis,[20] alcoholysis/glycolysis,[21−25] and thermal decomposition under pyrolytic conditions in sub-/supercritical fluids.[26−38] Depolymerization time of PA by acid-

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catalyzed hydrolysis has been significantly shortened by using microwaves as an energy source compared to the processes using conventional heating.[39,40] Depolymerization processes reported so far result either in incomplete depolymerization, where final reaction mixtures consist not only of monomer(s) but also of linear and cyclic PA oligomers, or other low-molecular-weight chemical compounds of different physicochemical properties and functionality from PA constituent monomers(s). Currently, PA6 and PA66 are chemically recycled on an industrial scale in the United States and Europe, where the high energy and decontamination costs are economically balanced by the high price of virgin PA, making the processes cost-efficient.[7] For chemical recycling of PA, the information on the content of a particular PA type in different waste materials is extremely useful because it determines the maximum monomer recovery from the waste and consequently the price and suitability of waste as a feedstock.

The overarching objective of this work was to develop a simple and efficient method for quantitative determination of PA6/PA66 in different waste types. It also enables convenient differentiation of PA6 from PA66 and other PA types in waste mixtures; the information which is difficult to assess with precision by conventional characterization techniques such as Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR), and differential scanning calorimetry. Prerequisite for such method development is a straightforward depolymerization of PAs into the constituent monomers. The depolymerization reaction has to be carried out until completion and in the absence of side reactions in a reasonable time frame so that the final reaction mixture does not contain any PA oligomers and side products. To this end, we have developed a microwave-assisted hydrolysis of PA catalyzed by hydrochloric acid (HCl), by which complete PA depolymerization to the constituent monomer(s) is achieved. The obtained depolymerization mixtures (hydrolyzates) were analyzed by high-performance liquid chromatography (HPLC), where we searched for a robust and simple method to quantitatively determine the content of PA constituent monomers in the hydrolyzates, from which the content of a particular PA in the waste material can be calculated. State-of-the-art methods comprise qualitative and semiquantitative evaluation of water-soluble PA degradation products by HPLC on C18 or C8 reversed phase columns by using evaporative light scattering (ELS), chemiluminescence, or mass-selective detectors.[41−46] RP-HPLC separates PA monomers as well as linear and cyclic PA oligomers. RP-HPLC was also reported as a tool for evaluation of migration of cyclic monomers and oligomers from PA food contact materials into food and food simulants.[43,44,47,48] However, currently available methods in terms of quantitative determination of PA constituent monomers in hydrolyzates suffer either from nonlinear detector response in a large concentration range or non-conventional detection. Furthermore, determination of the PA content in the case of incompletely depolymerized PA is hampered because the response factors are not known for all oligomers due to the unavailability of corresponding standards. For the determination of the content of a particular PA monomer in hydrolyzates, we have chosen isocratic HPLC on a mixed-mode column with refractive index (RI) detection, which does not require any monomer derivatization. The proposed method for quantitative determination of PA in waste materials was verified in terms of accuracy and precision by analyzing neat PA standards, while method selectivity for PA6 and PA66 was examined by analyzing their 1:1 mixture. Furthermore, the method was tested on PA composites and postconsumer waste samples such as carpet waste and a mixture of waste fishing nets.

■ EXPERIMENTAL SECTION

Chemicals and Materials. All chemicals used were of analytical grade. HCl (18.5 wt %), used for depolymerization of PA samples, was prepared by diluting 37 wt % HCl (Merck KGaA). Acetonitrile (ACN) from Honeywell, Riedel-de Haen, Chromasolv, HPLC gradient grade, ≥99.9%; trifluoroacetic acid (TFA) from Acros Organics, ≥99.5%; or formic acid (FA) from Honeywell, ≥99% were used as received for preparation of mobile phases. Water was purified using a Milli-Q reverse osmosis system to obtain MQ-water (MQ) with typically 18.2 MΩ cm resistivity and <4 ppb carbon (Millipore, Watford, UK). Monomer standards ε-aminocaproic acid (or 6-aminohexanoic acid, 6-ACA), HMDA, and AA of high purity (>99.9%) were purchased from Sigma-Aldrich, USA. Salts of amino acid (6-ACA·HCl) and diamine (HMDA·2HCl) were prepared by dissolving an appropriate monomer standard in excess amount of 18.5% HCl, then evaporating the solvent on a rotatory evaporator and drying the resulting residue at 50 °C in a vacuum chamber until constant weight. PA6 and PA66 polymer standards were purchased from Sigma-Aldrich. Glass-fiber reinforced PA66 (PA66-GF) (35 wt %) was obtained from Kordsa, Turkey, and glass-fiber reinforced PA6 (PA6-GF) (30 wt %) was purchased from Lanxess, Energizing Chemistry, Germany. Waste carpet and mixture of waste fishing nets as typical examples of postconsumer wastes were obtained from Aquafil, Slovenia.

Homogenization of Postconsumer Waste Samples. To prepare representative and homogeneous waste samples, about 5 g of the sample was homogenized by milling on a ball mill. For this purpose, ∼0.5 g of the waste sample was loaded into a 35 mL stainless steel vessel together with a 25 mm stainless steel ball (Tehtnica Millmix 20, Domel, Slovenia). The vessel was hermetically closed and cooled in liquid nitrogen at −196 °C for 10 min. Then, the sample was ground for 2 min with a frequency of 30 Hz. After milling, the vessel was warmed up to ambient temperature to prevent the sample from absorbing the moisture. Thus-ground sample (5 g) was homogenized and used for further degradation experiments.

Monitoring the Course of PA Hydrolysis Reaction. *Microwave-Assisted Hydrolysis of PA.* PA6 or PA66 standard sample (∼4 g) in the form of pellets was accurately weighed into a borosilicate glass vial, suitable for a microwave oven Monowave 300 equipped with the camera as well as temperature and pressure sensors (Anton Paar GmbH, Austria). A magnetic stirring bar and 8 mL of 5.56 M HCl were added to the sample. After sealing, the reaction vessel was placed in a microwave oven, where it was heated to a predetermined temperature of 170 or 190 °C (power of the magnetron automatically varied in the range of 0−850 W). Because of the microwave reactor design, it was not possible to take aliquots from the reaction mixture during the course of the reaction. Therefore, the degree of depolymerization was followed by performing identical experiments with different times. The reaction vessel was then cooled to 55 °C by a stream of compressed air. The solvent was removed from the reaction mixtures by rotary evaporation and further drying in a vacuum oven at 50 °C until constant weight. The resulting dry solid residues of PA66 were further homogenized by grinding in a mortar. Thus-obtained dry PA hydrolyzates were analyzed by ^{1}H NMR and HPLC.

^{1}H NMR Spectroscopy. ^{1}H NMR spectra of dried and homogenized reaction mixtures of PA66 were recorded in DMSO-d_6 with added TFA and tetramethylsilane ($\delta = 0$) as an internal chemical-shift standard. ^{1}H NMR spectra of PA6 reaction mixtures were recorded directly by using C_6D_6 as an inset. Measurements were performed at room temperature (RT) on a Varian Unity Inova 300 MHz NMR spectrometer (Varian, Inc., USA) with both the relaxation delay and acquisition time of 5 s.

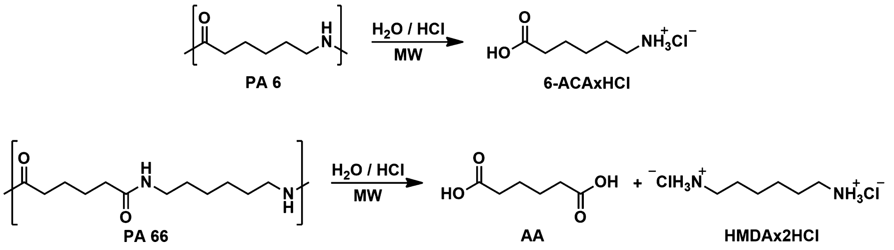

Figure 1. Reaction scheme of HCl-catalyzed hydrolysis of PA6 and PA66 into their constituent monomer(s).

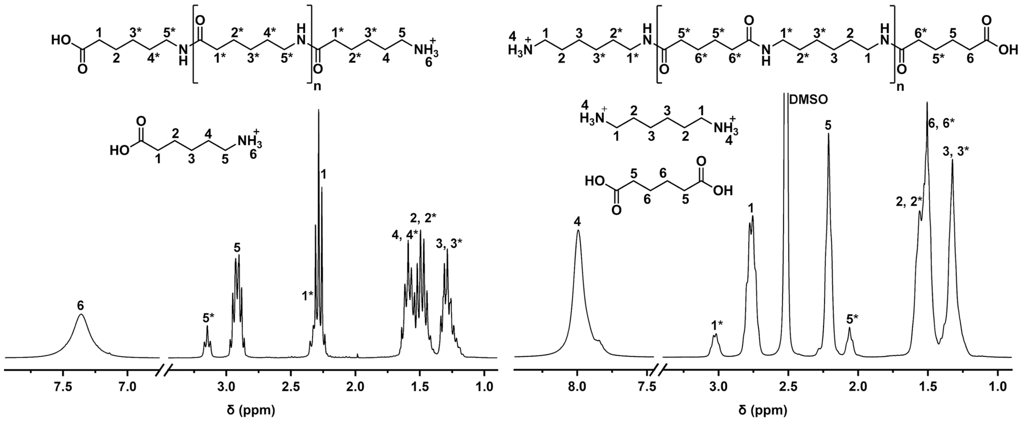

Figure 2. ^{1}H NMR spectra of reaction mixtures obtained after 5 min microwave-assisted, acid-catalyzed hydrolysis of PA6 (left) and PA66 (right) at 170 °C. ^{1}H NMR spectrum of the PA6 reaction mixture was recorded directly by using C_6D_6 as an inset. PA66 reaction mixture was dried and homogenized before ^{1}H NMR analysis in DMSO-d_6 with added TFA.

HPLC Chromatographic Conditions. Dry PA6 or PA66 hydrolyzate (~500 mg) was dissolved in 100 mL of the mobile phase of starting composition, that is, ACN/MQ water containing 1 vol % of ACN and 0.1 vol % of FA = 1/99 (v/v) during constant stirring for at least 2 h. Afterward, 0.5 mL aliquot was taken from the mixture and further diluted to 5 mL to obtain a solution concentration of 0.5 mg/mL. The presence of oligomers in PA hydrolyzates was assessed by a reversed-phase HPLC on an Agilent Zorbax Eclipse XDB C18 column (4.6 × 150 mm; 5 μm). A chromatographic system consisted of an Agilent 1100 Series binary pump (Agilent Technologies, Inc., USA) equipped with a model 7725i Rheodyne (Bensheim, Germany) manual injector and an ELS detector (ELSD) (Agilent Technologies, Inc., USA). The mobile phase used was a gradient of ACN as solvent A and MQ containing 1 vol % of ACN and 0.1 vol % of FA as solvent B. A linear gradient of the mobile phase composition ran from A/B 1/99 (v/v) to A/B 30/70 (v/v) in the first 20 min, then isocratic elution was held for 5 min, after which the gradient was restored back to A/B 1/99 (v/v). The mobile phase flow rate was 0.5 mL/min, and the column temperature was 30 °C. ELSD was operated at evaporator and nebulizer temperature of 50 °C. The injection volume of thus prepared sample solutions onto the column was 20 μL.

Quantitative Determination of PA6 and/or PA66 Content.

Microwave-Assisted Hydrolysis of PA. A typical depolymerization procedure for quantitative determination of PA6 and/or PA66 in PA-based samples is the following: ~150 mg of the sample in the form of powder or pellets was accurately weighed into a borosilicate glass vial, suitable for a microwave oven Monowave 300. Then, a magnetic stirring bar and 6 mL of 5.56 M HCl were added to the sample. The reaction vessel was then sealed and placed into a microwave oven, where it was heated to a predetermined temperature of 170 °C. At that temperature, the sample was treated for 30 min, and then, the reaction vessel was cooled to 55 °C by a stream of compressed air. If necessary, the liquid phase was filtered through a glass filter with a pore size of 1.0 μm (CHROMAFIL Xtra GF-100/25, Sorbent Technologies, Inc., USA) to remove reinforcement additives (glass-fibers) and/or other insoluble sample constituents. The filtrate was then quantitatively transferred into a 100 mL flask. The solid residue was carefully washed with water, and thus-obtained solution was quantitatively transferred to the rest of the liquid phase. The solvent and HCl in the filtrate were then evaporated on a rotary evaporator, and the residue was dried in a vacuum chamber at 50 °C. Afterward, the dried solid was dissolved in an appropriate solvent and diluted to a final volume of 100 mL to perform HPLC measurements.

Quantitative contents of PA constituent monomers in hydrolyzates were determined by isocratic HPLC on a Primesep analytical 100 column (4.6 × 150 mm; 5 μm, SIELC Technologies, USA). The separations were performed on an Agilent Technologies chromatographic system equipped with the isocratic pump, column heater, and Agilent 1260 Infinity Series RI detector (Agilent Technologies, Inc., USA). The mobile phase consisted of a defined mixture of MQ, ACN, and TFA, which was supplied at a flow rate of 1 mL/min. Mobile phase composition consisting of MQ/ACN/TFA was 70/30/0.27 (v/v/v). The injection volume of sample solutions was 20 μL. The separations were carried out at 30 °C, while the temperature of the RI detector was set to 35 °C. The concentrations and contents of monomers in PA hydrolyzates were calculated from the calibration curves, plotted from the peak areas in HPLC chromatograms of the corresponding standards (6-ACA, 6-ACA·HCl or HMDA, and HMDA·2HCl) recorded at different but known solution concentrations (0.5, 1, 1.5, 2, and 2.5 mg/mL) by the same HPLC method. From the concentration and content of 6-ACA, 6-ACA·HCl or HMDA, and HMDA·2HCl in the hydrolyzate, the amount and the content of PA in the original sample were calculated, according to eqs 1 and 2

$$m = \frac{(A - b)}{a} \times V \times k \tag{1}$$

$$\%(\mathrm{PA}) = \frac{m}{m_0} \times 100 \tag{2}$$

where m is a determined mass of PA in the weighed sample, m_0 is a mass of the sample used for hydrolysis, A is a peak area of the PA constituent monomer in the chromatogram of PA hydrolyzate, a is a slope of the calibration curve, b is an intercept of the calibration curve

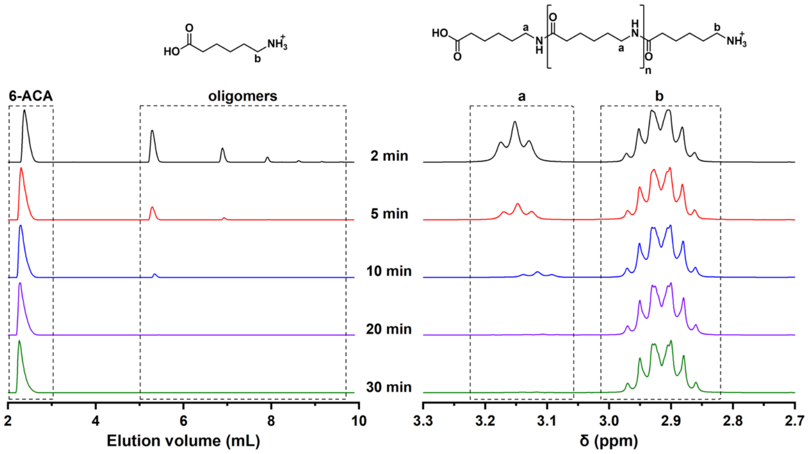

Figure 3. RP-HPLC (C18 column coupled to an ELSD) chromatograms (left) and enlarged ^1H NMR spectra typical for oligomers (right) of PA6 reaction mixtures hydrolyzed at 170 °C for different reaction times. HPLC chromatogram and ^1H NMR spectrum of the reaction mixture hydrolyzed at 170 °C for 30 min show complete PA6 hydrolysis because only 6-ACA was detected.

on y-axis, V is a volume of the measuring flask (100 mL), and k is a recalculation coefficient, taking into account a difference between the molecular weights of the PA6 or PA66 repeating unit and the monomer from which the calibration curve was constructed: M(PA6 repeat unit)/M(6-ACA) = 113.16/131.17 Da = 0.863; M(PA6 repeat unit)/M(6-ACA·HCl) = 113.16 Da/167.63 Da = 0.675 and M(PA66 repeat unit)/M(HMDA) = 226.35 Da/116.21 Da = 1.948; M(PA66 repeat unit)/M(HMDA·2HCl) = 226.35 Da/189.13 Da = 1.197.

■ RESULTS AND DISCUSSION

Complete Hydrolysis of PAs into the Constituent Monomers. For determination of the PA content in plastic waste, we developed a fast degradation method, whereby PA6 completely depolymerizes into 6-ACA and PA66 into AA and HMDA (Figure 1). Oligomers and side products in the final reaction mixtures of PA6 and PA66 were not detected by ^1H NMR (Figure S1). Depolymerization experiments were performed by microwave irradiation because direct heating of the reaction mixtures was shown to be more efficient and easier to control than indirect by conventional heating. HCl serves both as a catalyst in PA hydrolysis and is also consumed during the reaction by formation of hydrochloride salts of ACA and HMDA.

Degree of PA hydrolysis was studied as a function of reaction temperature, reaction time, and molar ratio between HCl and amide bonds. The extent of PA hydrolysis was followed by ^1H NMR and HPLC on a C18 reversed phase column in a gradient elution mode as both techniques detect the presence of water-soluble oligomers in reaction mixtures. ^1H NMR spectra of PA hydrolyzates irrespective of a degree of amide group conversion show absence of any foreign signals that would indicate the presence of side products, demonstrating straightforward hydrolysis of PA6 and PA66 into the corresponding oligomers and/or monomer(s) (Figure 2).

Degree of PA hydrolysis was assessed from ^1H NMR using eq 3

$$\text{PA degradation degree (\%)} = \frac{I[-\mathrm{C}\mathbf{H}_2\mathrm{COOH}]}{I[-\mathrm{C}\mathbf{H}_2\mathrm{COOH}] + I[-\mathrm{C}\mathbf{H}_2\mathrm{CONH}-]} \times 100 \qquad (3)$$

RP-HPLC was found to be superior over ^1H NMR for detection of trace amounts of oligomers (below 1%) in hydrolyzates because in ^1H NMR spectra both methylene signals near the amide group of PA oligomers partially overlap with the satellites of methylene signals near the carboxyl and amine groups of AA and HMDA. On the contrary, RP-HPLC coupled to an ELSD undoubtedly detects PA oligomers even when their content is extremely low. For both PA types, complete hydrolysis was achieved at a HCl/amide bond molar ratio of at least 1.25 in 30 and 10 min reaction time at the reaction temperatures of 170 and 190 °C, respectively, as indicated by the degree of PA degradation monitored by ^1H NMR and absence of oligomer peaks in HPLC chromatograms of hydrolyzates (Figure 3, Table S1). Furthermore, ^1H NMR and HPLC results show the absence of cyclic ε-caprolactam in the final PA6 degradation products because under the chosen experimental conditions it hydrolyzes into the linear 6-ACA, which is consistent with the literature data.[14] Complete PA hydrolysis was achieved also in the presence of reinforcement additives or other sample constituents. After depolymerization, the hydrolyzate of PA6 standard was a clear solution at RT and that of PA66 was a clear solution at reaction temperature, while AA partially precipitated from the solution during cooling to RT.

HPLC Method Development for Quantification of PA Constituent Monomers in Hydrolyzates. PA standards and composite samples were analyzed in the form of pellets as received, while postconsumer waste samples (i.e., carpet and fishing net wastes) were first homogenized by grinding larger sample amounts on the ball mill in order to analyze the representative samples. In further experiments, PA samples were depolymerized at 170 °C to keep the pressure as low as possible (4.6 bar at 170 °C vs 10 bar 190 °C) because a possible presence of additives, such as commonly used calcium carbonate in carpet waste, additionally contributes to the pressure increase due to carbon dioxide formation. In order to ensure full conversion of PAs into the monomers, the depolymerization was carried out for 30 min, while the sample load was reduced to perform experiments in high excess of HCl because acid can be consumed also for neutralization of basic additives present in waste materials (e.g., Al_2O_3 in carpet waste).

RP-HPLC is an indispensable tool to assess the type and relative share of water-soluble oligomers in PA hydrolyzates; however in combination with an ELSD, it suffers from a nonlinear detector response in a large concentration range.

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Furthermore, during cooling of PA66 hydrolyzates to RT, AA partially precipitates from the reaction mixture, while HMDA in the form of hydrochloric salt (HMDA·2HCl) is water soluble. Furthermore, postconsumer wastes can consist of water-insoluble constituents (inorganic reinforcement additives, PP, EVA, PVC, SBR latex, bitumen, etc.), hampering quantification of PA66 via the AA, therefore, we focused on quantitative determination of the HMDA·2HCl monomer in PA66 hydrolyzates. The HMDA·2HCl is difficult to analyze by HPLC because it interacts strongly with silica, while on the reverse-phase column it poorly retains. For direct quantitative determination of HMDA·2HCl and/or 6-ACA·HCl in PA66 and PA6 hydrolyzates, respectively, we developed an HPLC method that does not require monomer derivatization and allows measurements in an isocratic mode and thus the use of RI as a concentration detector. For this purpose, a mixed-mode HPLC column with a stationary phase consisting of hydrophobic alkyl chains with embedded acid residues (Primesep 100 HPLC column) was chosen.

Separation of compounds containing an amine group in the structure on the mixed-mode column is governed by hydrophobic and cation-exchange mechanisms.[49−52] The extent of electrostatic interactions of amine-containing compounds with the column packing material can be easily controlled by a mobile phase pH via the content of TFA, while the extent of hydrophobic interactions is controlled by the amount of ACN. Elution order of monomers from the mixed-phase column is AA, followed by 6-ACA, and finally HMDA, irrespective of the fact whether amine groups of 6-ACA and HMDA are initially in the form of amine salt (6-ACA·HCl, HMDA·2HCl) or not. Such an elution order is preserved even if the contents of TFA and ACN varied and is reversed to that observed on the C18 column (retention time: HMDA < ACA < AA), demonstrating a prevailing electrostatic interaction of 6-ACA and especially HMDA with the mixed-mode stationary phase.

Another prerequisite that has to be fulfilled when analyzing amines in the form of salts with a counter-ion different from that of the acidic component in the mobile phase is rapid and quantitative exchange of the monomer counter-ions (Cl^-) with the acid anions (CF_3COO^-) in the solvent to ensure retention of the amine-containing monomers solely in the form of trifluoroacetic salts. In this way, distortion of the peak of the amine-containing monomer in the chromatogram is avoided, while the specific RI increment (dn/dc) over the monomer peak is uniform, allowing for its quantification by the RI detector. Our results show that an appropriate peak shape of 6-ACA·HCl and HMDA·2HCl in the chromatograms is obtained when the content of TFA in the solvent used to dissolve the PA hydrolyzates is at least equimolar to the amine groups of the particular monomer. The most optimal mobile phase composition consisting of MQ/ACN/TFA is 70/30/0.15 and 60/40/0.27; v/v/v for 6-ACA·HCl and HMDA·2HCl respectively; however, the former mobile phase is not appropriate for the HMDA·2HCl because it elutes as a very broad unsymmetrical peak between 12.7 and 16 mL (too weak mobile phase; molar ratio between TFA and $-NH_2$ is less than 1), while the latter mobile phase composition is not appropriate for 6-ACA·HCl as it exits the column too early (at 2.75 min) to be reliably quantified (too strong mobile phase; Figure 4).

An appropriate mobile phase composition for simultaneous qualitative and quantitative determination of both constituent monomers of PA6 and PA66 in hydrolyzates is MQ/ACN/TFA of 70/30/0.27; v/v/v because both elute from the column in a narrow elution volume range with baseline separated peaks (Figure 4). In such a mobile phase composition, 6-ACA in the form of salt or not shows a narrow and symmetric peak in a wide concentration range, while somewhat broader peak was obtained for HMDA and HMDA·2HCl. Besides, it was noticed that HMDA as a difunctional amine shows an overloading effect at lower injected masses than 6-ACA monofunctional amine as expected but without affecting the linear response of the RI detector.[53]

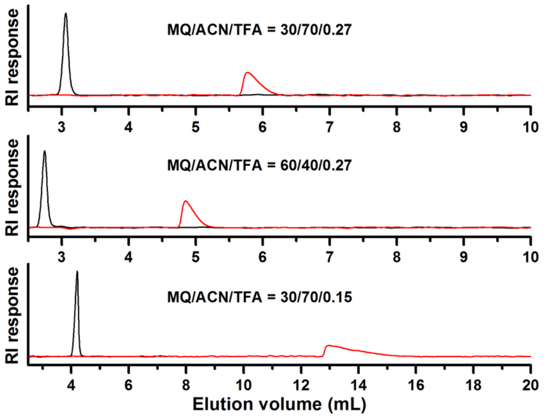

Figure 4. HPLC chromatograms obtained on a Primesep 100 mixed-mode column coupled to an RI detector for 6-ACA·HCl and HMDA·2HCl in different MQ/ACN/TFA; v/v/v mobile phase compositions; bottom: 70/30/0.15 optimal for 6-ACA·HCl; middle: 60/40/0.27 optimal for HMDA·2HCl, and top: 70/30/0.27 optimal for simultaneous quantification of both monomers.

At complete exchange of Cl^- ions of 6-ACA·HCl or HMDA·2HCl with CF_3COO^- of TFA, the determined monomer content in the hydrolyzate and consequently the PA content in the sample should be the same regardless of whether the calibration curve is constructed from the corresponding as-supplied monomers (6-ACA and HMDA) or their hydrochloric salt. To confirm this, the calibration curves were constructed from 6-ACA and HMDA as well as their hydrochloric salts. Monomers were dissolved in a suitable solvent to prepare stock solutions, from which lower sample concentrations were made by appropriate dilution. Calibration curves, representing the area under the monomers' peaks in HPLC chromatograms as a function of monomer concentrations, are linear for all four monomers with correlation coefficients (R) equal to or higher than 0.9997, indicating complete monomer mass recovery from the column and complete Cl^-/CF_3COO^- anion exchange as well (Figure S2). Correlation coefficients, approaching unity, together with low values of intercept of calibration curves thus suggest good linearity of the method.

Method Accuracy and Precision Evaluated on PA6 and PA66 Standards and Their Mixture. Accuracy of the method for quantitative PA determination was verified on PA standards and their 1:1 mixture. PA6, PA66, and their mixture were hydrolyzed according to the above-described procedure in three parallel weighed samples. For each sample weight, three HPLC measurements were performed to calculate relative standard deviations (RSD) of the peak area in HPLC chromatograms. The contents of PA6 and PA66 in PA standards and their mixture, calculated from the determined contents of the corresponding monomers in PA hydrolyzates based on the calibration curves constructed from 6-ACA and HMDA or their salts, are highly comparable, when the difference between the molecular weights of the PA repeating unit and the monomer used for the construction of the calibration curve was taken into account (eqs 1 and 2, Figure 5, Tables 1 and S2). Good accuracy of the method is indicated by the calculated values of sample mass recovery, while good precision is indicated by the calculated value of RSD between the parallel measurements. RSD of three measurements of the same sample is less than 1 wt % with high repeatability between the in parallel weighed samples (<1 wt %), while mass recoveries of PA6 and PA66 standards including their 1:1 mixture are very close to 100 and 50%, respectively, indicating suitability of the proposed method for quantitative determination of PA6 and PA66 contents even if both of them are the constituents of the same sample (Tables 1 and S2).

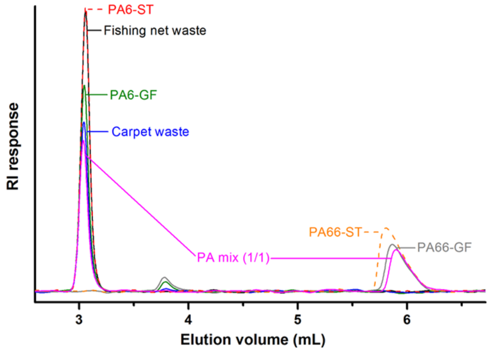

Figure 5. HPLC−RI chromatograms of hydrolyzates of PA6 and PA66 standards, their 1:1 mixture, PA6-GF and PA66-GF, waste carpet, and waste fishing nets, as obtained on the mixed-mode Primesep 100 column.

Determination of PA Content in Composite Samples and Postconsumer Wastes (Carpet Waste and a Mixture of Waste Fishing Nets). The samples were depolymerized according to the above-developed procedure. After reaction completion, the obtained hydrolyzates were filtered to remove glass-fibers and/or other insoluble sample constituents. The solid residues were carefully washed with water, and thus-obtained solutions were quantitatively transferred to the filtrates. The solvent and HCl in filtrates were then evaporated on a rotary evaporator, and the residues were dried in a vacuum chamber until constant weight. Afterward, the dried solids were dissolved in an appropriate solvent and diluted to a final volume to perform HPLC measurements.

According to the manufacturer's instruction, PA6-GF and PA66-GF contain 30 and 35 wt % glass-fibers, respectively, the values which were also confirmed by thermogravimetric analysis (TGA) (Figure S3). The determined contents of PA6 and PA66 in PA6-GF and PA66-GF samples are 68.9 and 62.9 wt %, respectively, which perfectly agree with samples' specifications when a content of additives (up to 1−2 wt %),

Table 1. Contents of PA6 and PA66 in PA Standards, as Determined by Microwave-Assisted, Acid-Catalyzed PA Hydrolysis and Further Determination of Monomer Contents in Hydrolyzates by HPLC Using a Primesep 100 Column and Calibration Curves from 6-ACA, 6-ACA·HCl and HMDA, HMDA·2HCl, Respectively (See Eqs 1 and 2)[a]

	1st parallel	2nd parallel	3rd parallel	1st parallel	2nd parallel	3rd parallel
		calibration curve from 6-ACA			calibration curve from HMDA	
weight	147.6	147.6	147.6	147.5	147.5	147.5
peak area	4000	3945	3963	2347	2330	2349
	3999	3940	3964	2340	2360	2341
	3991	3953	3960	2357	2347	2361
average	3997	3946	3962	2348	2346	2350
determined mass, mg	171.4	169.0	169.8	76.5	76.0	76.6
	171.3	168.8	169.8	76.3	77.0	76.4
	171.0	169.3	169.6	76.9	76.6	77.0
average, mg	171.2	169.0	169.7	76.6	76.5	76.7
mass recovery, wt %	100.2	98.8	99.2	101.1	100.4	101.2
	100.2	98.7	99.3	100.8	101.7	100.9
	100.0	99.0	99.2	101.5	101.1	101.7
average, wt %	100.1 ± 0.1	98.8 ± 0.2	99.2 ± 0.1	101.2 ± 0.4	101.1 ± 0.6	101.3 ± 0.4
average between parallel samples		99.4 ± 0.6 wt % of PA6			101.2 ± 0.1 wt % of PA66	
		calibration curve from 6-ACA·HCl			calibration curve from HMDA·2HCl	
determined mass, mg	220.8	217.8	218.8	122.8	121.9	122.9
	220.7	217.5	218.8	122.5	123.5	122.5
	220.3	218.2	218.6	123.3	122.8	123.6
average, mg	220.6	217.8	218.7	122.9	122.8	123.0
mass recovery, wt %	101.0	99.6	100.0	99.7	99.0	99.8
	100.9	99.4	100.0	99.3	100.2	99.4
	100.7	99.8	99.8	100.1	99.7	100.3
average, wt %	100.9 ± 0.1	99.6 ± 0.2	99.9 ± 0.1	99.7 ± 0.4	99.6 ± 0.6	99.8 ± 0.4
average between parallel samples		100.2 ± 0.6 wt % of PA6			99.7 ± 0.1 wt % of PA66	
RSD between parallel samples, %		0.6			0.1	

[a] MQ/ACN/TFA = 70/30/0.27; v/v/v was used as the solvent and mobile phase. The content of water, as determined by TGA, was subtracted from PA weights.

Table 2. Contents of PA6 and PA66 in Glass-Fiber Reinforced Composites and Postconsumer Waste Carpet and a Mixture of Waste Fishing Nets, as Determined from the Contents of Monomers in Hydrolyzates by HPLC Using a Primesep 100 Column and Calibration Curves from 6-ACA and HMDA·2HCl, Respectively (See Eqs 1 and 2)[a]

	1st parallel	2nd parallel	3rd parallel	1st parallel	2nd parallel	3rd parallel
		PA6-GF			PA66-GF	
mass recovery, wt %	69.2	68.6	69.1	62.9	62.9	62.9
	69.4	68.3	69.1	63.1	63.0	62.5
average of mass recovery, wt %	69.3 ± 0.2	68.4 ± 0.3	69.1 ± 0.02	63.0 ± 0.3	63.0 ± 0.1	62.7 ± 0.3
average between parallel samples		68.9			62.9	
RSD between parallel samples, %		0.7			0.2	
		waste fishing nets			waste carpet	
mass recovery, wt %	96.0	96.8	96.5	56.4	57.5	57.2
	96.5	96.6	96.4	56.7	57.1	57.1
average of mass recovery, wt %	96.3 ± 0.4	96.7 ± 0.2	96.5 ± 0.1	56.6 ± 0.4	57.3 ± 0.4	57.2 ± 0.1
average between parallel samples		96.5			57.0	
RSD between parallel samples, %		0.2			0.7	

[a] MQ/ACN/TFA = 70/30/0.27; v/v/v was used as the solvent and mobile phase. The content of water, as determined by TGA, was subtracted from sample weights.

observed also in HPLC chromatograms of composite hydrolyzates as the small intensity signals at 3.8 mL, is taken into account (Table 2, Figure 5). This signal most likely belongs to water-soluble degradation products of ester- or amide-based additive(s) commonly used in PA-based composites as processing auxiliaries and stabilizers. Waste fishing nets contain a high amount of PA6 (96.5 wt %, Table 2, Figure 5), while the rest of the sample consists mainly of bitumen as a hydrophobic coating present on the surface of fishing nets, as indicated by FTIR and ^{1}H NMR spectra of 2−3 wt % solid residues obtained after filtration of hydrolyzates (Figure S4). On the other hand, carpet waste contains only 57 wt % of PA6 (Table 2, Figure 5). The residue after carpet hydrolysis represents ∼13 wt % and consists mainly of styrene butadiene (SB) latex (Figure S5), which is commonly used a binder for fusing the face yarn to backing. Aluminum trihydroxide ($Al(OH)_3$) was added to polymer backing as a fire-retardant filler, as demonstrated by FTIR and TGA results of carpet (Figure S6). Because $Al(OH)_3$ reacted with HCl during PA hydrolysis forming a water-soluble product, its content was assessed from the residue after TGA analysis of carpet, which coincided with a mass loss because of decomposition of $Al(OH)_3$ into Al_2O_3 and water at 283 °C (Figure S6). Its amount in the carpet was estimated to be ∼29 wt % and is thus a significant contributor to the total carpet weight. In summary, the waste carpet consists of 57 wt % PA6, 13 wt % SB latex, and 29 wt % $Al(OH)_3$, a sum of which is close to 100 wt %, indicating robustness of the method despite the presence of various constituents and additives in complex waste samples.

CONCLUSIONS

We present a method for quantitative determination of PA6 and/or PA66 in waste materials, which allows us to accurately evaluate the maximum recovery of PA constituent monomers from the waste and consequently the waste price and its suitability as a feedstock. A typical procedure for quantitative PA determination includes straightforward microwave-assisted hydrolysis of PA using HCl as a catalyst under the conditions allowing for complete PA degradation into the constituent monomer(s). After hydrolysis, the reaction mixture is filtered if necessary, followed by evaporation of water and HCl from the hydrolyzate on a rotary evaporator and further drying the solid residue in a vacuum oven. Thus-obtained dry hydrolyzate is dissolved in a suitable solvent for HPLC analysis, which is performed in an isocratic mode on a mixed-mode HPLC column using RI as a concentration detector. The monomer content in the hydrolyzate is determined from a calibration curve constructed by plotting peak area as a function of concentration of a suitable monomer standard. The content of PA in the sample is then calculated from the monomer content in the hydrolyzate by taking into account the differences between the molecular weights of PA repeating units and the monomer used for the construction of the calibration curve. The developed analytical method is fast, robust, accurate (mass recoveries of PA6 and PA66 standards and their 1:1 mixture are close to 100 and 50%, respectively), and repeatable (RSD < ±1.0%) and was demonstrated to be applicable for PA-based composites and postconsumer PA-containing plastic wastes such as carpet and fishing net wastes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.0c04190.

> PA hydrolysis as a function of reaction time at 170 and 190 °C; quantification of PA6 and PA66 in their mixture; experimental conditions for FTIR and TGA measurements; TGA characterization of glass-fiber reinforced PA composites; FTIR and ^{1}H NMR spectra of residue obtained after microwave-assisted hydrolysis of waste fishing nets; and FTIR spectrum of carpet backing and TGA curve of waste carpet (PDF)

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