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Characterization of Polymer Waste Containing Nano-fillers Prior its End-of-Life Treatment

Dinh Trinh Tran^{1,2} · Aurélie Joubert¹ · Danielle Venditti³ · Sylvain Durecu³ · Thierry Meunier⁴ · Olivier Le Bihan² · Emmanuel Fiani⁵ · Laurence Le Coq¹

Abstract This study aimed to characterize a polymer waste, originating from polyorganosiloxane polymerization processes, prior its end-of-life treatment in order to identify and quantify the possibly contained nano-fillers. The polymer waste was first characterized in terms of its physical–chemical properties by combining different approaches and analytic techniques such as standard ultimate and elemental analysis or techniques like infrared spectroscopy or thermogravimetric analysis coupled with gas chromatography and mass spectroscopy to define the polymer waste molecular structure. The second step was devoted to identify and characterize the nano-fillers contained in the polymer waste, if any, in terms of particle size distribution, morphology and composition. Due to the thermal degradability of the polymer waste above 50 °C, the cryo-ultramicrotomy and the transmission electron microscopy techniques were used. Polydimethylsiloxane was identified as the core polymer unit, and the presence of the suspected SiO₂ nano-fillers was confirmed, with three different morphologies detected: elongated and hexagonal,

both found in the particle size range of 100–500 nm in diameter; and spherical, present in the population of particles ≤100 nm in diameter. In particular, a relatively large amount of K (2.81 wt%) was also identified in the waste. The mass content of SiO₂ nano-fillers in the polymer waste was estimated to 24.4 wt%.

Keywords Waste characterization · Nanowaste · Polydimethylsiloxane · Nano-fillers · Nano-silica · End-of-life treatment

Introduction

In recent years, nanotechnologies have developed in a large variety of industrial sectors, like automobiles, electronics, computers and medicine. To document the marketing and distribution of nanoproducts into the commercial marketplace, the Woodrow Wilson International Center for Scholars and the Project on Emerging Nanotechnologies created the Nanotechnology Consumer Products Inventory (CPI) in 2005 [1]. 1814 consumer products containing nanomaterial were inventoried in 2014 from 622 companies in 32 countries. Silver was the most frequently used nanomaterial (24%) but 49% of the products (889) included in the CPI did not provide the composition of the incorporated nanomaterials. Although this inventory does not address comprehensive list of nanoproducts present in the marketplace, it illustrates the worldwide development of nanotechnologies. There has been an impressive global investment in the market for products incorporating nanotechnology, rising from about \$254 billion in 2009 and expected to reach \$3 trillion by 2020 [2].

Beside the advantages offered by nanotechnologies, numerous uncertainties also arise regarding their potential

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impact on the environment and human health, due to their exceptional properties and size-dependent functions such as zeta potential, surface charge, surface coating, magnetic and electrical properties and shape [3–5]. For example, the study of nanoparticle toxicity revealed that the nano-size characteristic of a particle may be determinant in its potential toxicity whatever the chemical composition, in other words, nanoparticles may be toxic even if larger particles constituted with the same elements are not [6]. In the perspective of sustainable innovation, the development of nanotechnologies requires a deep insight into nanosafety during the whole life cycle of products containing nanomaterials, from production to recycling and final destruction. For example, the European GUIDEnano research project, started in 2013, is developing a web-based guidance tool, which will help the nanoproduct users to design and apply of the most appropriate risk assessment and mitigation strategy for a specific product. In complement to the existing regulations in different frameworks, the tool will be used by industry to evaluate and efficiently mitigate possible health risks for workers, consumers and the environment associated to the use of nanotechnologies. In particular, the GUIDEnano project should propose suitable strategies to handle nano-enabled products at all the stages of their life cycle in order to minimize the potential for occupational or environmental exposure.

To date, there is no specific approved procedure for the waste management of nanoproducts and nanomaterials at their end of life, which can be called nanowaste. The organization for economic co-operation and development (OECD) published in 2016 current knowledge (non-exhaustive state-of-the-art) on the fate and possible impacts of nanomaterials in specific waste treatment processes, including recycling, incineration, landfilling and wastewater treatment processes [7]. Whatever the waste treatment process, the characterization of the nanomaterials, in terms of chemical composition and other characteristics including shape, size and structure, is required to understand the fate and behavior of nanomaterials in the process or their potential pathways of release to the environment. The lack of standard method makes it difficult for the nanomaterial or nanoproduct characterization for waste management industry. One further research recommended by the OECD [7], based on the importance of the topic and the absence of sufficient knowledge in the literature, is the identification and quantification of the nanomaterials entering waste treatment processes.

This study aims to characterize the physical–chemical properties of a polymer waste of unknown composition and in particular to identify, describe and quantify the nanofillers integrated into the polymer. Such characterization of polymer waste suspected to be a nanowaste may guide decision making about waste management.

Materials and Methods

Selected Polymer Waste

An industrial polymer waste in bulk-solid form was selected, sampled and provided by TREDI-Séché Environnement, a French specialist of hazardous waste treatment, as likely to contain nano-fillers. The polymer waste was originated from polyorganosiloxane polymerization processes. The selection of the polymer waste for the study was motivated by the large production of silicon dioxide (SiO₂) nanomaterials in the world, with average quantities of 5500 tons/year [8], widely extended to several industrial fields like chemical separation, car tires, printing inks, pharmaceuticals, cosmetics, and even animal feed [8].

Physical and Chemical Analysis of the Polymer Waste

Proximate Analysis

The polymer waste was analyzed to determine the moisture and the volatile organic compound (VOC) contents. The moisture of a waste sample is generally determined according to standard method, e.g. in NF EN 14346:2007 at 105 ± 3 °C until constant mass in a ventilated oven. Nevertheless, preliminary thermogravimetric analysis showed a degradation of polymer waste samples above 50 °C. Therefore, to quantify the exact proportion of water in the polymer waste, the Karl Fischer titration method was used, as recommended in the standard NF EN 14346:2007 when volatile compounds are encountered. Experiments were performed at 50 °C using a Karl Fischer apparatus (870KF-Titrino-plus and 860KF-Thermoprep) with 120 mg of polymer waste samples to determine the moisture and VOC contents.

The ash content was determined by heating 1 g of dried polymer waste sample in an oven at 815 ± 10 °C until constant mass, according to ISO 1171:2010. As for all other physical–chemical parameters, the tests were conducted in three replicates and the samples were previously dried at 50 °C until constant mass.

Loss on Ignition

The loss on ignition is the change in mass resulting from the heating of a sample under specified conditions. The amount of organic compounds (polycyclic aromatic hydrocarbons, organochlorine pesticides and poly chlorinated biphenyls) in the polymer waste was determined according to NF EN 15169:2007. A 1 g aliquot of the dried sample was heated in a ventilated oven at 550 ± 25 °C

under atmospheric conditions for 5 h. The organic content is approximately equal to the weight loss due to volatilization of the dry sample at 550 °C: organic matter is efficiently removed by combustion at 550 °C, whereas only carbonate minerals begin to decompose thermally at such a temperature.

Gross Calorific Value

The calorific value is an important parameter for end-of-life thermal treatment because it permits to estimate the ability of a waste to burn without adding supporting fuel. The gross calorific value, i.e. the total amount of heat released when the waste is burned, was measured by calorimetric bomb method (Calorimeter-Parr-6200) with certified benzoic acid as a reference to measure the thermal capacity of the bomb calorimeter, according to ISO 1928:2009. The dried polymer waste samples of 500 mg were pelletized for ignition in the assembled combustion bomb.

Ultimate Analysis (Percent of CHNS)

The percents of carbon, hydrogen, nitrogen and sulphur in the polymer waste were quantified with a Thermo-Scientific-FlashEA[®]1112 elemental analyzer, operating by dynamic flash combustion of the sample at 950 °C. 1 mg of dried polymer waste samples were analyzed (with 1 µg readability) in tin containers.

Elemental Analysis

Polymer waste samples were subjected to inductively-coupled plasma (ICP) to estimate their elementary chemical composition. Two physical analysis techniques by spectrometry were performed: the ions created by ICP were separated by mass spectrometry according to their charge and mass with a signal proportional to the number of ions (ICP-MS), and the photons created by ICP were counted by atomic emission (ICP-AES).

Such techniques require mineralization by dissolution (acidification and oxidation) of the waste samples. Dried polymer waste samples of 10 mg were dissolved according to NF EN 13657:2003: samples dissolved in aqua regia (HNO₃/HCl = 1/3, v/v) were heated at 200 °C in Teflon reactors, in a microwave oven (Ethos TC, Milestone). To enhance the solubilization of Si contained in silica, the alkali-fusion decomposition method with LiBO₂-Li₂B₄O₇ was also applied to the samples, because of the well-known recalcitrance of such mineral phases to digestion with hot aqua regia.

Finally, 12 elements (Al, Ca, Cr, Cu, Fe, K, Mg, Na, Sb, Si, Ti, Zn) were quantified in the polymer waste samples.

Molecular Structure

In addition to ultimate and elemental analysis, Fourier transform infrared spectroscopy (FTIR) measurements were performed to identify the chemical compounds and functional groups in the polymer waste. The measurements were performed with a Thermo-Nicolet-Nexus-670 using a SiC source, and TDGS detector. IR spectra were scanned between 4000 and 400 cm⁻¹ with a resolution of 4 cm⁻¹, and saved by attenuated total reflection in monoreflexion on a crystal of germanium or diamond. The dried samples were previously ground to obtain fine powders. The measurements were carried out with the KBr disk method.

To complete the analysis of the molecular structure of the polymer waste, the compounds formed by the thermal decomposition of samples were analyzed by thermogravimetric analysis combined with gas chromatography and mass spectrometry (TGA-GC/MS). The thermal decomposition of dried polymer waste samples of 1–1.5 mg was performed by a TGA/AT instrument-Q50. An air flow rate of 45 mL/min was applied to purge the sample area in a quartz furnace, and a helium flow rate of 5 mL/min was set as the purge gas for the microbalance. Two cycles of heating were applied: from 19 to 105 °C (5 °C/min) and from 105 to 850 °C (5 °C/min). For the two cycles, the compounds formed in the gas phase were fixed in an absorbent cartridge (Tenax or Chromosorb106) for later analysis with a Markes-Unity thermal desorber coupled with a GC-MS (Agilent-6890/5973 N). The column was a DB-VRX, 30 m in length, 0.25 mm in diameter, and 1.4 µm in thickness.

Characterization of the Nano-fillers in the Polymer Waste

The size and morphology of nano-fillers incorporated into the polymer were characterized by transmission electron microscopy (TEM), and the elemental composition of the nano-fillers was determined using energy dispersive X-ray spectrometers (EDX) integrated into the TEM system. This analytical technique was combined with preliminary preparation of the polymer waste samples by slicing them into small sections by ultramicrotomy. The Leica ultramicrotome (EM-UC7) with glass blades was used to slice samples into sections of 100 nm in thickness. Due to the degradability of the polymer waste at moderate temperature, the samples were frozen at -160 °C in liquid nitrogen and the freezing temperature was maintained during cryo-sectioning. The slices were collected on TEM copper grids coated with holey carbon film. They were observed by a TEM (Hitachi-HF-2000) at -180 °C with liquid nitrogen.

Results and Discussion

Physical–Chemical Characterization of Nanowaste

Combustible Quality

The combustible quality of the polymer waste was determined to address the incineration as end-of-life waste management option. When the waste was heated in the presence of air, the primary loss of material (92.7 ± 1.5 wt%, average value \pm standard deviation with $N = 3$) was observed below 525 °C, including the loss of VOCs (4.9 ± 0.6 wt%) and H_2O (25.0 ± 0.8 wt%) at 50 °C, and the loss of the main organic fraction (62.8 ± 0.1 wt%) from 50 to 525 °C. A small amount of material (1.0 ± 0.6 wt%) was lost between 525 and 815 °C (including the residual organic fraction, the structural water and the carbonates), and the ash content (residual inorganic fraction) was 5.9 ± 0.8 wt% at 815 °C.

Such determinations of loss on ignition values were completed by thermogravimetric analysis (Fig. 1). The results showed three degradation steps of the polymer waste in presence of air. The first degradation leads to a weight loss of 10% at 90 °C (45 – 130 °C for the beginning and the end of the peak); it is probably associated with the evaporation of VOCs and the initial degradation of the polymer chain. Note that the 10% weight loss is coherent with the 4.9% of VOCs loss at 50 °C from Karl Fisher experiments. The second degradation is maximal at 178 °C with a weight loss of 50% and partially overlaps the third step, whose significant mass change (20%) is maximal at 225 °C. The residual mass of the sample after the third degradation peak (300 °C) remained almost unchanged at around 10% until 850 °C at around 10%, meaning 90% of overall weight loss. This result is coherent with the loss on ignition values, i.e. around 93% of total weight loss after 5 h at 525 °C. After the 10 min of thermogravimetric analysis, the ash content at 850 °C represented 9.8% of the initial mass, which is coherent with the value of 5.9 wt% obtained for a much longer period (5 h) at 815 °C.

The calorimetric analysis showed a large amount of heat per unit weight of waste produced by complete combustion, with a gross calorific value up to 27.63 kJ/g (6.6 kcal/g). The value suggests a fairly good heating ability for the polymer waste compared to a typical combustible like coal, whose heat of combustion is commonly in the range 6.3 – 8.7 kcal/g [9].

Elemental Chemical Composition

The results of the ultimate and elemental analysis are presented in Table 1. The polymer waste contains two

Table 1 Major, minor and trace contents (mg/kg dw)

Organic elements (N = 3), average value \pm standard deviation					
C	H	N	S		
$207,800 \pm 1400$	$54,600 \pm 340$	<500	<500		
Inorganic and metalloid elements (N = 2), average value					
Si ^b	K ^a	Na ^a	Fe ^a	Al ^a	Ca ^a
39,100	28,100	523	228	<5	38
Cu ^a	Sb ^a	Zn ^a	Cr ^a	Mg ^a	Ti ^a
<5	<20	7.4	<5	10	<5

Sample digestion by ^a aqua regia ^b alkali-fusion

main elements, C and H, whereas the presence of N and S is negligible. The average proportions of C and H, expressed in total dry weight percent (dwt%), are 20.78 and 5.46 dwt%, respectively, with relatively small standard deviations ($<10\%$ of average values); mean recovery rates for C, H, N, and S in reference materials are very high with 97, 98, 98, 97%, respectively. The polymer waste contains significant proportions of Si and K, which account for 3.91 and 2.81 dwt%, respectively. The presence of other elements is either below trace levels (Al, Ca, Cr, Cu, Mg, Sb, Ti, Zn), or in small quantities <0.10 dwt% (Fe, Na). The average recovery rates of reference materials of these metals solubilized by aqua regia are higher than 90%, except for Si, which presents a recovery rate of less than 50%.

The degree of rigidity of the macromolecule network increases with the amount of silica incorporated and dispersed in the elastomer. The fire retardant properties of silicone elastomers are known to be intrinsically linked to the release of silica residues when exposed to elevated temperature. The released silica serves as an “insulating blanket”, which acts as a mass transport barrier delaying the volatilization of decomposition products. Therefore, it reduces the amount of volatiles compounds available for burning in the gas phase and the heat that feeds back to the polymer surface [10].

Identification of Molecular Structure

The FTIR spectrum for the polymer waste is shown in Fig. 2. Three characteristic bands at 798.9, 1018.8 and 1088.8 cm^{-1} are assigned to Si–O–Si vibrations [11–14]. The first one corresponds to the symmetric Si–O–Si stretch, while the others are affected by the asymmetric Si–O–Si stretch [12, 15]. Note that the Si–O–Si bonds may be

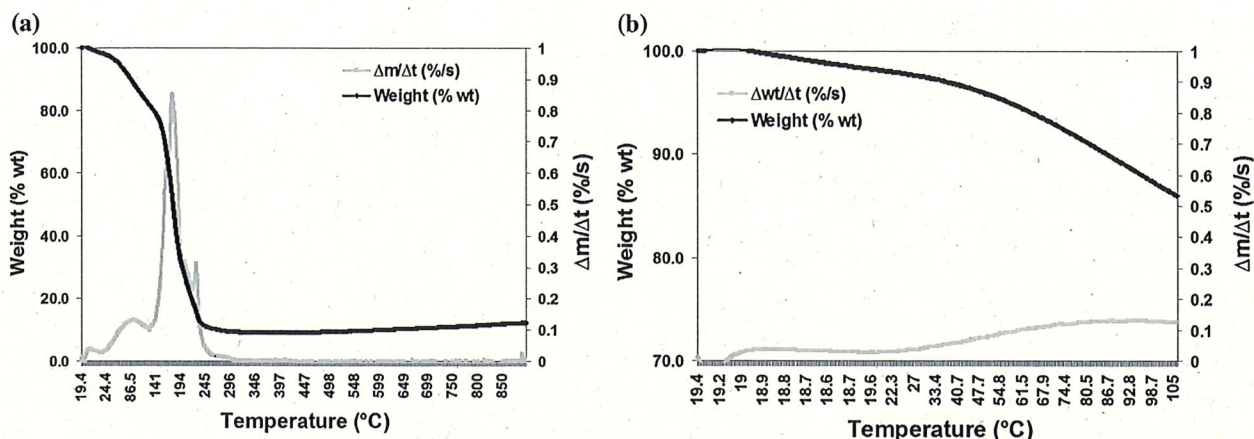


Fig. 1 TGA-analysis from 19 to 850 °C (a) and zoom on the 19–105 °C range (b)

present either in the polymer structure or in the nano-fillers (nano-SiO₂).

The band at 798.9 cm⁻¹ is associated with vibrations of Si-CH₃ stretching and CH₃- rocking [13]. The relatively weak absorption peak at 863.4 cm⁻¹ belongs to blocks of dimethyl D units [16]. The absorption peaks at 2963 and 2905.5 cm⁻¹ are affected by stretching vibrations of CH and CH₃ in the side-chain of the polymer [11], while the band at 1260.3 cm⁻¹ is assigned to CH₃ symmetric deformation of Si-CH₃ [13]. The infrared band at 1398.6 cm⁻¹ can be linked to symmetric CH₃ bending vibrations. Additional characteristic bands observed at 3346.4 and 1647.4 cm⁻¹ are affected by vibrations of OH stretching and OH bending of hydroxyl groups, respectively, adsorbed on the surface of either the polymer or the SiO₂ nano-fillers [15, 17].

These results from FTIR analysis indicate that the polymer waste contains principally polydimethylsiloxane (PDMS) [-Si(CH₃)₂-O]_n, SiO₂ present either in the polymer structure or in the nano-fillers, and water adsorbed on the polymer and/or SiO₂ surfaces.

Formation of Silicon Compounds from the Combustion of Polymer Waste Containing Nano-fillers

The identification by GC/MS of the compounds formed by thermogravimetric analysis of the polymer waste permitted to complete the determination of its molecular structure. The thermal oxidative degradation of the polymer waste were described from 25 to 105 °C, and from 105 to 850 °C in oxidative conditions (air). The main products formed in both steps are shown in Table 2. The principal fragments formed during the two thermal steps are cyclic oligomers, hexamethylcyclotrisiloxane being the smallest cyclic product, confirming the previous FTIR results suggesting that the polymer waste is PDMS-based. A number of smaller compounds present in minor or trace contents (<3%) were also detected, but not identified in the spectrum libraries of common molecules. The products formed during the second step (at higher temperature) of the oxidative degradation of the polymer waste contain unidentified and smaller compounds than during the first step. In addition, the comparison of relative surface densities of the products

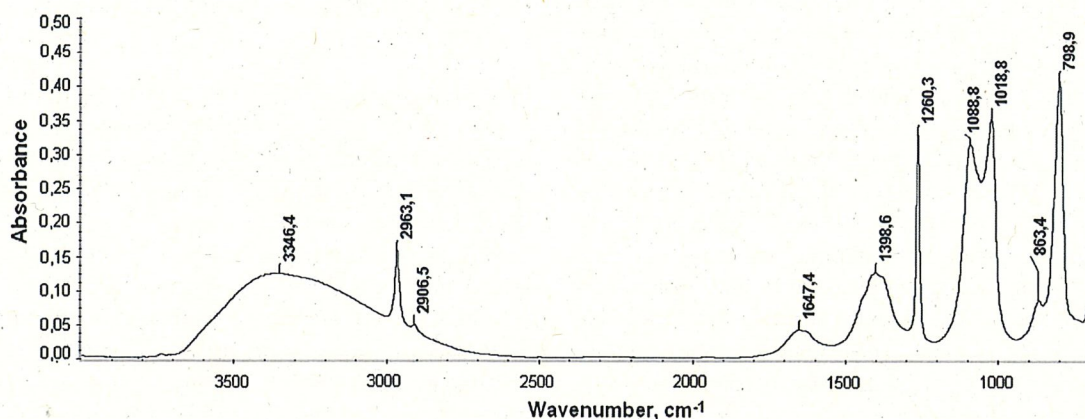


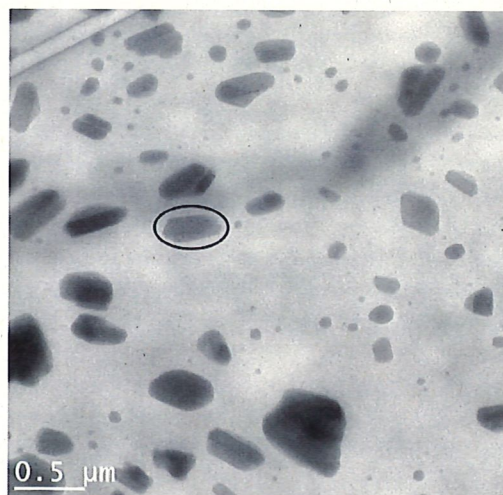
Fig. 2 FTIR spectrum in ambient conditions

Table 2 Thermal oxidative degradation products from GC-MS

	Retention time (s)	Surface intensity (relative value compared to tetramer, %)
25–105 °C		
Cyclotetrasiloxane, octamethyl	17.09	100.00
Cyclopentasiloxane, decamethyl	21.986	83.82
Cyclohexasiloxane, dodecamethyl	26.402	52.78
Cycloheptasiloxane, tetradecamethyl	30.197	17.07
105–850 °C		
Cyclotetrasiloxane, octamethyl	17.056	100.00
Cyclotrisiloxane, hexamethyl	6.697	87.26
Cycloheptasiloxane, tetradecamethyl	30.278	57.12
Cyclohexasiloxane, dodecamethyl	26.564	52.83
Cyclopentasiloxane, decamethyl	21.997	46.08
Silane, [[4-[1,2-bis(trimethylsilyloxy)ethyl]-1,2-phenylene]bis(oxy)]bis(trimethyl]	33.752	27.62
Cyclononasiloxane, octadecamethyl	36.73	14.83
Cyclodecasiloxane, eicosamethyl	39.378	6.49

formed during both steps reveals that about 35% of cyclic oligomers were formed in the first step through depolymerization in the temperature range of 50–105 °C. This may be attributed to the presence of water and impurities such as Na, Fe, Ca, Al, and particularly K which was found in significant proportion in the polymer waste (2.81 dwt%) from elemental analysis. The significant amount of K in the sample could be attributed to the use of KOH as a catalyst for ring-opening polymerization or polycondensation [10]. The presence of these elements and water may thus result in an accelerated decomposition of polymer, leading to a decrease in the temperature of depolymerization by an externally catalyzed mechanism [10].

Regarding the first step, tetramers and pentamers are the most abundant among the cyclic oligomers formed, with a ratio of pentamers/tetramers equivalent to 83.8%. This observation is quite different from studies in the literature [18] which report that, according to a normal distribution rule, trimers and tetramers should be the most abundant. However, most previous studies were performed at high temperature, up to 400 °C and higher [10, 18, 19], whereas during the present study, the polymer waste sample was only heated up to 105 °C in the first step, probably explaining the absence of trimers as major products. In this low temperature range, on the one hand, the supplied energy is not high enough to break down higher oligomers into smaller ones (trimers) with improved thermodynamic stability and, on the other hand, the condensation of fragments forming higher oligomers may become significant. Regarding the second step, as expected, the trimers and tetramers are the most abundant products with a tetramer/

**Fig. 3** Morphology of nano-fillers by TEM (4.9 k magnification)

trimer ratio equivalent to 87.3%, while higher cyclic oligomers, such as pentamers, hexamers, and heptamers, present comparable amounts close to 30%. Moreover, during this step, more compounds were observed in the gas phase including unidentified ones. These results are in accordance with Camino et al. [18], in which PDMS was heated in air to 800 °C at a heating rate of 80 °C/min. Finally, it should be noticed that the heating rate, the nature of PDMS (functional, end-groups), the fillers, additives, and impurities may result in different combustion mechanisms of this polymer, hence forming different kinds of compounds [10, 18, 19].

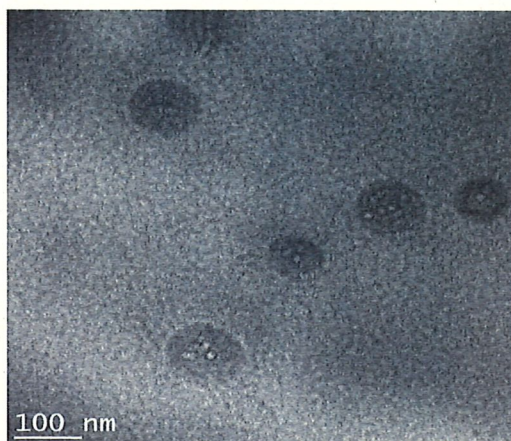


Fig. 4 Morphology of the smallest population of nano-fillers (spherical shape) by TEM (25 k magnification)

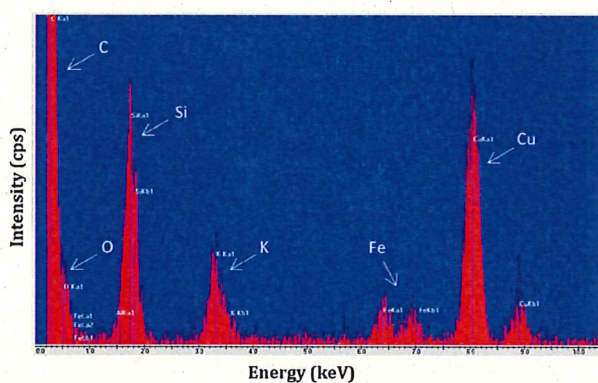


Fig. 5 EDX analysis of elongated and hexagonal particles

Nano-fillers Identification

Polymer waste samples were first observed by TEM to identify the possibly contained nano-fillers, revealing that the fillers in the polymer matrix contain only submicron particles (Fig. 3): three morphological shapes can be identified (1) elongated and (2) hexagonal, both found in the particle size range of 100–500 nm in diameter with elongated particles being somewhat smaller than hexagonal ones; and (3) spherical, present in the population of particles ≤ 100 nm in diameter (Fig. 4). These particle populations are well dispersed in the polymer matrix, and no significant aggregation is observed.

Regarding the chemical composition of particles, the results obtained by EDX indicated similar compositions in both hexagonal and elongated populations. Example of EDX spectrum of analyzed particles is presented Fig. 5 (spectrum corresponding to the particle encircled in Fig. 3). They contain mainly two elements, Si and K, in

decreasing orders of magnitude, and a small amount of Fe, suggesting either Fe impurity or the use of additives such as FeO, Fe₂O₃, or mica KAl₂(Si₃Al)O₁₀(OH)₂ [10] in the polymer waste. The latter assumption, however, can be excluded because, according to the elemental and EDX analysis, the proportion of Al is significantly lower than that of Fe, K, and Si. For particles smaller than 100 nm, they are primarily constituted of Si, O, and a small amount of Fe, suggesting the presence of nano-SiO₂. In comparison with Cendrowski et al. [20], who studied the upstream product (synthesized nanomaterial), the present polymer waste (downstream product) should contain nanospherical SiO₂. The presence of Fe can be associated with nano-fillers containing both Fe and Si, such as nano-Fe₃O₄ coated with SiO₂ reported in Ahangaran et al. [15]. However, our FTIR analysis of the polymer waste did not allow to identify typical Si–O–Fe vibration band at 578 cm⁻¹ and, according to the elemental analysis (Table 1) the Fe content is negligible compared to the Si one. Fe is therefore rather attributed to impurities, and its presence in the EDX spectra can be assigned to Fe in the matrix located close to the nano-fillers.

Estimation of Percentage of SiO₂ Nano-fillers

Silica is the most common filler incorporated into PDMS because of its reinforcing effect induced by hydrogen bonds between the oxygen atoms of Si–O in the PDMS chain and the hydrogen atoms of silanol groups on the surface of silica [10]. The percentage of SiO₂ nano-fillers integrated into the polymer (PDMS-based) waste was estimated from mass balance.

In the first step, the quantity of Si and O elements present in polymer chains was calculated from the PDMS formula [–Si(CH₃)₂–O]_n based on the C content revealed by the ultimate analysis (CHNS). Neglecting the end-groups of PDMS in the sample, the Si/C mass ratio is 28/24, and the C/O mass ratio is 24/16. Considering a measured average percentage of elemental carbon of 20.8 dwt%, Si and O contents in PDMS are 24.3 and 13.9 dwt%, respectively, assuming that C is mainly present in PDMS. Interestingly, Schnyder et al. [21] reported atomic concentrations of C, Si, and O measured in common PDMS close to theoretical values.

The nano-SiO₂ fillers were therefore calculated by subtracting C (20.8 dwt%), Si in PDMS (24.3 dwt%), O in PDMS (13.9 dwt%), H contents in the polymer (5.5 dwt%) and total major and minor element contents in the polymer apart from Si (3.0 dwt% for N, S, K, Na, Fe, Al, Ca, Cu, Sb, Zn, Cr, Mg, Ti) from the initial dry mass of the sample. In this way, the nano-SiO₂ percentage was estimated to 32.5 dwt% or 24.4 wt% (considering 25% of water

content). This concentration of nano-SiO₂ is commonly introduced into PDMS as a filler to improve its mechanical properties and enhance its optical clarity [10].

It should be noted that, according to this calculation, the total proportion of Si in the polymer waste will be 39.5 dwt% (24.3 dwt% in the PDMS and 15.2 dwt% in nano-SiO₂), whereas this value is 3.9 dwt% according to the analysis of total Si content performed by ICP-MS using alkali-fusion technique (Table 1). This technique is normally used as the standard method for Si recovery from silicate minerals [22]. The difference between the calculated and measured Si contents can be attributed to the fact that the PDMS contains a large amount of Si in its chains and, in our study, an open crucible was used for the sample digestion, which may result in the loss of volatile Si compounds, for example through the formation of cyclic oligomers (trimers, tetramers, pentamers). The concentration of Si obtained by ICP-MS measurement is probably strongly associated with the SiO₂ nano-fillers.

Conclusions

The polymer waste, originating from polymerization processes of polysiloxane, was shown to be primarily constituted of polydimethylsiloxane, SiO₂ nano-fillers, and K, probably used as a catalyst (KOH) for ring-opening polymerization and/or polycondensation. The polymer waste was also shown to be thermally degradable from low temperature of around 50 °C. The presence of nano-fillers was confirmed with three morphological shapes identified in the polymer waste samples studied: (1) elongated and (2) hexagonal, both found in the particle size range of 100–500 nm, and (3) spherical, present in the population of particles of diameter less than 100 nm. The percentage of SiO₂ nano-fillers probably incorporated in the polymer to reinforce its mechanical and optical properties, was estimated to 24.4 wt%. The combination of different techniques used in this study could be applied to characterize other nanowaste in solid form.

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References

1. Vance, M.E., Kuiken, T., Vejerano, E.P., McGinnis, S.P., Hochella Jr., M.F., Rejeski, D., Hull, M.S.: Nanotechnology in the real world: redeveloping the nanomaterial consumer products inventory. *Beilstein J. Nanotechnol.* **6**, 1769–1780 (2015)
2. Roco, M.C., Mirkin, C.A., Hersam, M.C.: Nanotechnology research directions for societal needs in 2020: summary of international study. *J. Nanopart. Res.* **13**, 897–919 (2011)
3. Borm, P.J.-A., Robbins, D., Haubold, S., Kuhlbusch, T., Fissan, H., Donaldson, K., Schins, R., Stone, V., Kreyling, W., Lademann, J., Krutmann, J., Warheit, D., Oberdorster, E.: The potential risks of nanomaterials: a review carried out for ECE-TOC. Part: *Fibre Toxicol.* **3**, 11 (2006)
4. Som, C., Wick, P., Krug, H., Nowack, B.: Environmental and health effects of nanomaterials in nanotextiles and façade coatings. *Environ. Int.* **37**, 1131–1142 (2011)
5. Bondarenko, O., Juganson, K., Ivask, A., Kasemets, K., Mortimer, M., Kahru, A.: Toxicity of Ag, CuO and ZnO nanoparticles to selected environmentally relevant test organisms and mammalian cells in vitro: a critical review. *Arch. Toxicol.* **87**, 1181–1200 (2013)
6. Fratoddi, I., Venditti, I., Cametti, C., Russo, M.V.: How toxic are gold nanoparticles? the state-of-the-art. *Nano Res.* doi:10.1007/s12274-014-0697-3 (2014)
7. OECD: Nanomaterials in Waste Streams: Current Knowledge on Risks and Impacts, OECD Publishing, Paris. doi:10.1787/9789264249752-en (2016)
8. Piccinno, F., Gottschalk, F., Seeger, S., Nowack, B.: Industrial production quantities and uses of ten engineered nanomaterials in Europe and the world. *J. Nanopart. Res.* **14**(9), 1–11 (2012)
9. Griepink, B., Wilkinson, H.C., Scholz, A.: The certification of the ash content and of the gross calorific value of three coals. Report, EUR 11000 (1987)
10. Hamdani, S., Longuet, C., Perrin, D., Lopez-Cuesta, J.M., Ganachaud, F.: Flame retardancy of silicone-based materials. *Polym. Degrad. Stab.* **94**, 465–495 (2009)
11. Huang, W., Yibei, F., Chaoyang, W., Yunshu, X., Zhishang, B.: A study on radiation resistance of siloxane foam containing phenyl. *Radiat. Phys. Chem.* **64**, 229–233 (2002)
12. Kim, D.S., Park, H.B., Rhim, J.W., Lee, Y.M.: Preparation and characterization of crosslinked PVA/SiO₂ hybrid membranes containing sulfonic acid groups for direct methanol fuel cell applications. *J. Membr. Sci.* **240**, 37–48 (2004)
13. Labouriau, A., Cox, J.D., Schoonover, J.R., Patterson, B.M., Havrilla, G.J., Stephens, T., Taylor, D.: Mössbauer, NMR and ATR-FTIR spectroscopic investigation of degradation in RTV siloxane foams. *Polym. Degrad. Stab.* **92**, 414–424 (2007)
14. Kim, S., Lee, C.-Y., Jin, M.H.-C.: Fourier-transform infrared spectroscopic studies of pristine polysilanes as precursor molecules for the solution deposition of amorphous silicon thin-films. *Sol. Energy Mater. Sol. Cells* **100**, 61–64 (2012)
15. Ahangaran, F., Hassanzadeh, A., Nouri, S.: Surface modification of Fe₃O₄@SiO₂ microsphere by silane coupling agent. *Int. Nano Lett.* **3**, 23 (2013)
16. Launer, P.J.: Infrared analysis of organosilicon compounds: spectra-structure correlations. In: Anderson, R., Arkles, B., Larson, G.L. (eds.) *Silicon Compounds: Register and Review*, 4th edn, pp. 100–103. Petrarch Systems, Bristol, PA (1987)
17. Deka, B.K., Maji, T.K.: Effect of SiO₂ and nanoclay on the properties of wood. *Polym. Bull.* **70**, 403–417 (2012)
18. Camino, G., Lomakin, S.M., Lazzari, M.: Thermal polydimethylsiloxane degradation. Part 2. The degradation mechanisms. *Polymer* **43**, 2011–2015 (2002)
19. Camino, G., Lomakin, S.M., Lazzari, M.: Polydimethylsiloxane thermal degradation Part 1. Kinetic aspects. *Polymer* **42**, 2395–2402 (2001).
20. Cendrowski, K., Chen, X., Zielinska, B., Kalenczuk, R.J., Rümeli, M.H., Büchner, B., Klingeler, R., Borowiak-Pale, E.: Synthesis, characterization, and photocatalytic properties of core/shell mesoporous silica nanospheres supporting nanocrystalline titania. *J. Nanopart. Res.* **13**, 5899–5908 (2011)

21. Schnyder, B., Lippert, T., Kötzt, R., Wokaun, A., Graubner, V.M.: Nuyken, O: UV-irradiation induced modification of PDMS films investigated by XPS and spectroscopic ellipsometry. *Surf. Sci.* **532**, 1067–1071 (2003)

22. ASTM C1463-00, Standard Practices for Dissolving Glass Containing Radioactive and Mixed Waste for Chemical and Radiochemical Analysis, ASTM International, West Conshohocken, www.astm.org (2007)