DISCUSSION

Life cycle and nano-products: end-of-life assessment

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Abstract Understanding environmental impacts of nanomaterials necessitates analyzing the life cycle profile. The initial emphasis of nanomaterial life cycle studies has been on the environmental and health effects of nanoproducts during the production and usage stages. Analyzing the end-of-life (eol) stage of nanomaterials is also critical because significant impacts or benefits for the environment may arise at that particular stage. In this article, the Woodrow Wilson Center's Project on Emerging Nanotechnologies (PEN) Consumer Products Inventory (CPI) model was used, which contains a relatively large and complete nanoproduct list (1,014) as of 2010. The consumer products have wide range of applications, such as clothing, sports goods, personal care products, medicine, as well as contributing to faster cars and planes, more powerful computers and satellites, better micro and nanochips, and long-lasting batteries. In order to understand the eol cycle concept, we allocated 1,014 nanoproducts into the nine end-of-life categories (e.g., recyclability, ingestion, absorption by skin/ public sewer, public sewer, burning/landfill, landfill,

Electronic supplementary material The online version of this article (doi:10.1007/s11051-012-0720-0) contains supplementary material, which is available to authorized users.

E. Asmatulu · J. Twomey · M. Overcash (⊠) Department of Industrial and Manufacturing Engineering, Wichita State University, 1845 Fairmount, Wichita, KS 67260-0133, USA e-mail: mrovercash@earthlink.net air release, air release/public sewer, and other) based on probable final destinations of the nanoproducts. This article highlights the results of this preliminary assessment of end-of-life stage of nanoproducts. The largest potential eol fate was found to be recyclability, however little literature appears to have evolved around nanoproduct recycling. At lower frequency is dermal and ingestion human uptake and then landfill. Release to water and air are much lower potential eol fates for current nanoproducts. In addition, an analysis of nano-product categories with the largest number of products listed indicated that clothes, followed by dermal-related products and then sports equipment were the most represented in the PEN CPI (http://www.nanotechproject.org/inven tories/consumer/browse/categories/ 2010).

Keywords Nanoproducts · Life cycle end-of-life · Recycling · Environmental Impact · Life cycle analysis · Nanotechnology application

Introduction

The definition of end-of-life (eol) for a product is a specific point at which the product does not satisfy the initial purchaser or owner needs. At the eol, a product has a fate or destination which can range from disposal in the environment to reuse. This applies to all products, including nanotechnology products (nanoproducts or nanomaterials).Twenty-four countries in the world are estimated to currently use nanotechnology to produce different nano-products (PEN 2010). According to Senjen, there were 700 nano-products on the market by 2006, but most of these were not labeled or publicly known (Senjen 2010). The Woodrow Wilson Center's Project on Emerging Nanotechnologies (PEN) catalogued 1,014 nano-products in August 2009 (Consumer Products Inventory, CPI). The PEN CPI is a convenient catalogue attempting to document the magnitude and diversity of products referred to as nano-products, those apparently containing or using nano-materials as a part of the product. The PEN CPI also primarily contains consumer products, but also some industrial products. However, the criteria to be on the PEN CPI list may be imperfect (Berube et al. 2010), and might better be referred currently as a fuzzy image of the nanoproducts classification. A primary concern with the PEN CPI is that actual presence in the marketplace is not confirmed nor is the list updated frequently (Berube et al. 2010). Thus, nanoproducts are one class of products for which better understanding of the eol phase of the life cycle analysis can be used to improve the environmental impact.

The end-of-life flow of the large number of products from society provides a framework for the small number of products that are now labeled as nano. The eol is largely dictated by the infrastructure established by society to manage these products. Where recycling infrastructure has grown, this eol alternative is generally viable and can be looked upon to expand for similar products or materials. Infrastructures for treating discharges as wastewater are also in place. In addition, infrastructure for landfill and incineration operate to manage large potions of eol products. The assumption made here is that these infrastructures would be used in an analogous way for respective nanoproducts. The only difference might be that if nanomaterials are very expensive, there would be a greater incentive for recovery. However, this has yet to be identified on a wide-spread basis nor does this preliminary evaluation address enhanced technologies (separation, extraction, purification, etc.) to recover nanomaterials. However, nanoproducts may just be recycled without recognition of the nanocontent.

Analyzing the end-of-life stage of a product is critical because significant impacts or benefits for the environment may arise at that stage. Discarding used product to the landfill or mixing with wastes in the public sewer may not be the preferable end-of-life fate for the products. In general, environmental benefits accrue when products are recycled because of the reutilization of materials, thus preventing consumption of limited natural resources. Based on the end-of-life strategy of a product, product designers can produce recyclable, easy to remanufacture, and simple to disassemble products which will reduce the environmental effect and energy consumption of products. Material selection is also an important step in designing environmentally friendlier products. In addition, product recovery through recycling and remanufacturing minimizes the amount of waste transferred in landfills. Thus, the main benefits of analyzing nanoproduct eol are to produce ecologically acceptable products, expand techniques for product recovery, and enhance waste management skills (Gungor and Gupta 1998).

There is a relatively small literature on recycling nanoproducts. Recycling of nanoscale materials necessitates collecting used nanomaterials, separating the compounds, and recovering and reusing in the same or different products. Separation and recovery processes can be achieved using various physical, chemical, and physicochemical methods. Combustion is another nanowaste treatment method where nanoscale products, such as carbon in materials, polymers, and similar compounds can be burned to reduce the environmental effects or for energy production (heat) (Piotrowska et al. 2009).

Nanoscale metallic and ceramic materials can be melted to produce bulk materials where the bulk materials can be utilized in a different industry for various purposes, and also potential toxicity of nanoscale products can be minimized in this way. Melting temperatures of the nanoscale materials will deviate from the corresponding bulk materials (Olapiriyakul and Caudill 2009). Most of the time, the melting temperatures are considerably reduced at the nanoscale due to the high surface area, energy, and broken atomic bonds on the surfaces, which can significantly lower the emission and cost of recycling and treatment processes. The environmental impact of the nanoproducts discarded to the landfills will thus be drastically reduced.

Lloyd and Lave 2003, investigated economic and environmental impacts of nanocomposites in the automobile industry, and found that recyclability and reparability are important for this industry. Most of the metal parts ($\sim 80\%$) in the motor vehicle are recycled, while most of the plastics are shredded and dumped to the landfills. Polymeric (nylon) based clay (e.g., montmorillonite and kaolin) nanocomposites gained much attention for the industry and several research programs have been conducted in this field. Some of the clay-based nanocomposites have been used in the automobile industry because of the strength and high flame resistant of the new material. It was stated that these nanocomposites can be recycled without further changes on the materials and used in the same field (Lloyd and Lave 2003). Fiber reinforced composites have a very long service lifetime as long as the polymeric parts of these composites are protected from the environmental effects (e.g., UV light, moisture, oxygen and ozone, acids, and pigments). In general, polymeric coatings are used to protect the composite from the environmental effects. However, polymeric coatings experience physical, chemical, and physicochemical deterioration as the result of these aggressive conditions. Recently, the surfaces of composites are coated with carbon nanotubes (CNTs) associated polymeric coatings to protect the composites (Asmatulu et al. 2010). At the end of the composite life cycle, CNTs in the polymeric coating can be removed from the surface of the composites and acid digested to separate the CNTs from the coating in addition to combustion. The process during the acid digestion may reduce the length of CNTs, which is another concern to be considered.

The study described in this article had several objectives. At the broadest level an objective was to minimize the effect of products on the environment by bringing greater focus to the end-of-life (eol) stage. The second objective was to provide a preliminary assessment of eol for the specific class of products labeled as nano-products. These have been the focus of attention with regard to manufacturing and consumer effects, but a unified evaluation of nanoproduct end-of-life can help improve the overall life cycle characteristics of nano-products. The third objective was to develop a preliminary assessment of the potential for nano-product recycle/reuse since nanomaterials have higher material costs and may have high reuse life cycle credits and thus be important to the field of nano-products.

Methodology

This study is based on using the comprehensive PEN CPI list of 1,014 nano-products as documented on

February 18, (PEN 2010). The PEN list is the largest nanoproduct compilation currently available. The PEN CPI categorized nano-products into the eight different application areas, appliances, automotive, cross-cutting, electronics and computer, food and beverage, goods for children, health and fitness, and home and garden. Each category has subcategories, for example, the health and fitness category has clothing, cosmetics, filtration, personal care, sporting goods, and sunscreen. The eol study did not use this concept of product application categories for analysis, but instead used an end-of-life framework, described below.

The critical distinction made in this research is that products and specifically nanoproducts have the potential or expected likelihood of a certain end-oflife category. These potentials are assigned with a general set of assumption related to nano and closely related non-nano products. These categories reflect that after the use phase, a product or components of a product are in three general physical states, (a) gas or volatile liquid, (b) liquid to be managed as wastewater, and (c) a product or solid material. There three states were expanded into nine categories used elsewhere for environmental fate (FRS 2011; Allen and Rosselot 1997; E-Frat 2011). These nine categories were used to assign each nanoproduct to an end-of-life category (as described in the results and discussion section). This is not a declaration that the product is neither completely in one category nor in the case of recycle that it is currently recycled. The preliminary categorization herein gives a broad distribution or framework from which more detailed research on actual products or the overall distribution would be done. The rubric for categorization is given in the results section.

The first step of our methodology was to group similar products into one category. This reduced the 1,014 nano-products to 294 nano-product categories. As an example for shampoo, there are different companies producing shampoos under the different brand names but all of these eventually contain nanomaterials and applications that are very similar, so we group these as one. Also, there are different companies producing the same products, such as clothes and selling under the different names and types. The PEN CPI nano-products list consists of 137 clothing products which include fabric, shirt, pants, dresses, socks etc. Eventually, most of the clothes eol destinations are the same (recycling); thus, instead of using 137 products we gathered all clothes elements under the one product entry. We can define clothes as a recyclable product due to the equivalency of non-nanoproduct clothing reuse (such as, donating to people who need clothing). After the reuse, clothes scrap may go to landfills. Furthermore, the PEN CPI counted 35 sun screen body lotions that consumers use only once because no matter what protection factor (SPF) or chemical composition, the common sun screen products end-of-life are same, which is absorbed by the skin or washed away. Thus, it is not necessary to count each sun screen body lotion individually.

The second step of our methodology was to categorize the end-of-life of the 294 nano- product groups. As a preliminary framework, each of the 294 product groups was assigned to one eol category. This binary approach reflects the preliminary stage of any analysis, since no previous attempts have been made to examine end-of-life for nanoproducts. Future studies might be able to do field surveys to subdivide into multiple eol categories, but those marketplace assessments for 1,000 + products are not currently available and so a preliminary, simpler categorization binary rule was adopted.

Results and discussion

The complete classification of the 294 nano-product groups was based on the estimated primary end-oflife. These are shown in the supplementary information for this article, so that a transparent list is available to the reader. The supplementary information has six information columns, including number of products (1-294), eol, product names, number of similar products combined, applications, and specific use in the products (usually where the nanoproduct is located). The PEN data do not consistently designate how the nanomaterials are included in each product and so we cannot decide the nanomaterials recycle potential because physical and chemical properties of nanomaterials can be changed, and so nanomaterials recyclability options may be reduced. The product can still be recycled as an actual entity.

Nine categories of end-of-life groups were first selected;

- (1) recycle,
- (2) ingestion,

- (3) absorbed by skin then public sewer or water body,
- (4) public sewer or water body,
- (5) burning then landfill,
- (6) landfill,
- (7) air release,
- (8) air release then public sewer or water body
- (9) others.

The criteria to assign an eol fate to each nano products are described below. These eol groups are so widely studied and written about that no references or descriptions of these technologies are needed. We recognize there may be multiple fates for any given nano-product, but have tried to assign each nanoproduct to just one primary fate category.

Recycling is a process of collecting used materials to produce new products so that potential value of eol products will not be lost (The League of Women Voters 1993), and thus recycling is one eol category which was used. Product recycling depends substantially on an infrastructure for collection, technology for recycle or reuse of a product or material in a product, and the economic value of products. With respect to nanoproducts, even with an imprecise catalogue (PEN CPI) it should be possible to begin analysis of eol of these products. Nano-products eol were assigned to recycling if similar non-nano-products are generally mentioned as recycled. Thus, non-nano batteries are recycled and so the nano-product battery eol was also categorized as recycle. This serves to identify the potential that eol batteries may offer as the ability to recycle the nano material in such batteries. As another example, nonnano lubricants are often recycled or reused as a fuel in transportation vehicles hence nanoproduct lubricant was assigned to this eol category. Cost-benefit analysis of whether recycling is viable was not done in this study. Besides the economical analysis, environmental benefits such as reducing resource use, waste minimization, and protecting human health play essential roles for the decision on material recyclability, but were not quantified herein. Resources such as earth911 and Department of Public Works Milwaukee were also used to help identify product recycling (Earth 2010; Department of Public Works Milwaukee 2010).

Ingestion is another category in which nano-products were assigned, if taken into the body by drinking or eating. Either these will dissolve and stay in the body or are excreted to the public sewer system. The information to separate retention versus excretion was not available and so all were listed as ingested.

A third category was for nano-products that are *absorbed by the skin* and in part washed away and delivered to *public sewers or body of water*. Some examples can be body lotion or sun screen products, some of which contain nanomaterials.

Direct discharge to the *public sewer* is the fourth category. Laundry detergent is an example nano product that at the end of the cleaning steps, mostly goes to the public sewer.

Burning/landfill was the fifth category as nano products (e.g., engine oil) can be burned in an incinerator and ashes can be sent to the landfill. The burning processes can be beneficial for the hazardous and clinical wastes that cannot be directly sent to the landfill. After the incineration process, the bottom and fly ash of hazard wastes can be typically landfilled. These nano-products tend to be disposable medicalrelated products.

Landfill is the sixth category and is based on the lack of any apparent alternative in the other eol categories.

The seventh category is nano-products that can be partially released to the *air*. As an example, odor eliminator spray or other gas or solvent products can be released to air.

The eighth category is a small subset of nanoproducts that can be lost to the *air* in use but also transferred by rain from the point of use to *public sewer or body of water*, such as surface coatings.

Other is the smallest category and reflects product eol that are difficult to put the product in one eol category. For instance, plant grow mixture is given to the plants, which can be mixed with surface water by runoff but that can also be consumed by human and animals. Thus, it is very difficult to define a sequence and eol.

The condensed grouping of 294 nano-products were thus examined individually and assigned to an eol category. These are shown in the supplementary information Table 1 for this article, so that a transparent list is available to the reader. While there may be alternative category choices for any one of these nano-products, the general results by category remain primarily the same. Where multiple similar products were grouped together this can be seen in the column entitled number of similar products combined, thus relating the 1,014 PEN CPI list to the recombined list of 294 nano-products. Figure 1 shows a distribution by number of the 1,014 products based on the end-of-life stage. In Fig. 2 we graphed the same eol destination utilizing the categorization (294 groups) of this research to reduce duplication. Figure 2 verified that the categorization did not distort the eol distribution, since Figs. 1 and 2 generally agree in the relative eol categories, except absorb by skin/public sewer and landfill are reversed. Also it must be noted that these distributions are only of product or product groups and do not reflect the actual magnitude of products in the market place and used by consumers. As is seen from the Figures, a majority of the used products have potential for recycle. The other categories are as shown.

As a further means of interpreting to current nanoproduct eol fate, Fig. 3 makes further refinements by combing the two categories, absorbed by skin and ingestion into one category called direct human uptake. Landfill and burning/landfill are similarly combined to one category, as are air release and air release/public sewer. In this form, we see that the potential for recycle is still the largest eol of the current nano-products (40%). The body uptake by human and partly by animals is the second largest (25%). Landfill is the third (20%) while discard to water, to air, and other as the smallest eol categories (8, 6, and 1%, respectively).

Interpreting these eol data it would appear that the potential to recycle post-consumer products including the nano-material content is reasonably high. This potential is based on the large percent of nano-products (40%) that are in products currently recycled for equivalent non-nano-products. However, at this time only few citations could be found to document any post-consumer nano-product recycling (Gungor and Gupta 1998; Piotrowska et al. 2009; Olapiriyakul and Caudill 2009; Asmatulu et al. 2010; Lloyd and Lave 2003).

This low number of citations may be related to the lack of development for recycling infrastructure technology or the cost. The recycling technology for nano-products might benefit by developing technology based on the distribution of nano-materials found in the PEN CPI (Berube et al. 2010), which primarily was 61% silver, 21% carbon, 7% gold, and 6% iron. The eol fate of direct uptake by human is characterized for about 25% of nano-products. Air and water exposures are together the lowest eol fate of nano-products.

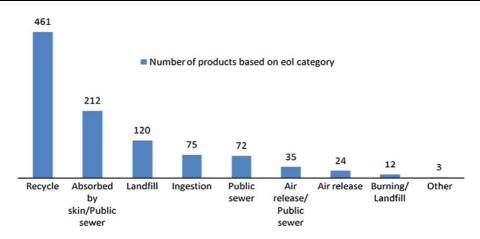


Fig. 1 Nano-product distribution based on the end-of-life, total PEN CPI list (1,014 products)

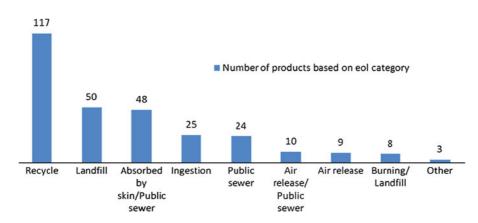


Fig. 2 Eol nano-product list distribution with consolidation of similar products (294 total)

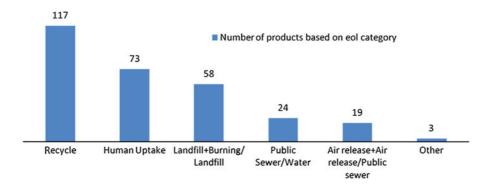


Fig. 3 The recombined nano product eol list distribution (294 total)

The large fraction of nanoproducts that are generally in the recycle eol category was unanticipated. This discovery may be considered unexpected by the nanoproduct research community because when searching for research and publications as a reflection of how the public, industry, or academics view recycling, there are relatively few citations. These citations are listed above and reviewed in the Introduction. In general, there are very few publications found in a literature search regarding nanoproduct recycle, thus reflecting the lack of understanding of the potential relative eol fate of this nanoproduct category. Additional implications or research that may be derived from these findings relate to the question of how nanoproducts differ from similar non-nanoproducts. Are the nano and non-nano products different in some undiscovered way with respect to recycling or reuse? Another issue from identifying the role of recycling as a non-nanoproduct eol is whether the nano materials add value to recycling since there materials are generally more costly or do nanomaterials impede recycling for other chemical or material reasons.

Analyzing these end-of-life results also identifies that less than 6% of these products fit into the human impact of product inhalation category (small particles) perceived as the primary concern for nanoproducts. This may have a research impact that differs from current research expectations for nanoproducts. That is, future research priority should account for the relative size or distribution of the actual marketed products and the eol categories from this study. In other words, do we understand adequately the end-oflife of the largest volume of nanoproducts in the market today?

An effort to reconcile future research to eol implications might need to develop more effort on dermal and direct ingestion implications of nanoproducts. In addition, more emphasis on whether nanoproducts have some distinctive behavior or fate in landfills (this study did not theorize such differences, but only connects the need for research to the distribution of eol alternatives for nanoproducts).

This eol analysis of nanoproducts, (supplementary information Table 1), also produces insights into the current nature of these products, as catalogued in the (PEN 2010). After consolidation of the 1,014 nanoproducts into distinct product groups (294) there is a range of listed products per distinct group or category. The average number of similar product per group was thus 3-4 with many having only one product. However, there are implications from examining those groups with more than ten products per group, Table 1. These more populated groups reflect a response to the market as new manufacturers use nanomaterials to create these products. The largest group by far is clothing. This is followed by dermalrelated products of sunscreen, moisturizer, and anti-aging products. The third largest group was interestingly hair irons. Bicycle and tennis equipment was another large group. All the other entries on Table 1 are in the 10–15 products per group range.

 Table 1 Major nanoproduct distribution derived from the (PEN 2010)

| Product category encompassing multiple nanoproducts found in the PEN CPI list | Number of products per category |
|---|---------------------------------------|
| Clothes | 137 |
| Sunscreen | 35 |
| Hair iron | 28 |
| Body lotion moisturizing | 22 |
| Bicycle products | 21 |
| Anti-aging cream | 17 |
| Tennis racket | 16 |
| Toothpaste | 14 |
| Health supplements | 13 |
| Computer processors | 13 |
| Beauty soap | 11 |
| OLED screen | 10 |
| Air purifier | 10 |
| Hair dryer | 10 |

The results shown in these Figures and Tables can be used as a benchmark for nano-products if a similar catalog for PEN CPI is made in 5 years (2015). Again, the authors caution that these results are for the fuzzy profile of nano-products given by the current PEN CPI, but do provide a general magnitude of eol understanding to stimulate further development of solutions for eol environmental improvement.

Limitations and future research

It is recognized that the numbers and category sizes shown in the research are approximate because of the limitation of any comprehensive catalogue for nanoproducts (Berube et al. 2010). This concern about actual presence in the marketplace is not a significant factor in this analysis as the products listed are still in some existence and do demonstrate the diversity if nanoproducts. In addition, we have required each given product to best fit into a single category. The recycling category is, at best, the potential for reuse since no economic analysis or infrastructure development were separately studied at this time. Instead, analogous non-nano-product recycling was used for this eol category. While the potential implications of nano-product recycle are noticeable, the actual effect of nanomaterials on recycling systems could not be inferred from these preliminary results. Future demand for recycling technology for nano-products may be stimulated by the actual market size of individual products or the potential value of these nanomaterials, but neither could be interpreted from this first stage study of end-of-life for nano-products. Finally, the actual market size of any given nanoproduct was not used to weigh the eol product computations.

Future research is intended to search for recycling firms in operation that have been actually recycling nano-products by virtue of the product recycled. Also remaining work should incorporate with the other life cycle stages of nano-products, such as cradle-to-gate and gate-to-gate that can provide an understanding of entire life cycle concept of environmental impacts. The information herein may improve the ability to do a broader nanoproduct risk analysis by those with expertise in that field. Another future research goal would be to look in-depth at the top recycling categories, Table 1, as to what technology exists or needs to be developed to recover nanomaterials by recycling as an enhancement over just product recycle. These new topics might also address whether the nanomaterials recovery is economically feasible or might entail risk.

Conclusions

Nanomaterials have outstanding properties (e.g., mechanical, electrical, optical, magnetic, and thermal) and are used for a number of different applications. Although nanomaterials research and development have been growing for over a decade, life cycle analysis of these materials has not yet been widely studied. In this study, we focus on the eol stage of life cycle analysis, as we categorized nano-products in different groups based on the final destination after use. Within the life cycle analysis framework, exploring eol of the nano-products offers benefits from considering environmental sustainability impacts, such as energy and material consumed. This study confirms that current nano-products appear to have high recycle potential which leads to use less natural resources, and also spends less energy to obtain high technology products again. The largest potential eol fate was found to be recyclability, however little literature appears to have evolved around nano-product recycling. At lower frequency is human uptake and then landfill. Release to water and air are much less likely eol fates for current nano-products. In conclusion, recycling and reuse of the nano-products open new possibilities for nanomaterials sustainability. Further research is needed to identify availability of recycling infrastructures and cost-benefit analysis of recycling nano-products.

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