



# Principles for Evaluations of Healthiness of New Materials

# 9

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## Abstract

During the twentieth century, many new human-made materials have been developed, often leading to only subsequent understanding of the damaging

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effects these have on human and environmental health. This chapter traces the key patterns in historical and recent recognitions of harmfulness of human-made substances used in building materials. It uses the history of the past recognition to propose a need for insisting on an improvement in the way human and environmental health are considered when developing new materials including ecomaterials.

During the twentieth century, many new human-made materials have been developed, often leading to only subsequent understanding of the damaging effects these have on human and environmental health. This chapter traces the key patterns in historical and recent recognitions of harmfulness of human-made substances used in building materials. It uses the history of the past recognition to propose a need for insisting on an improvement in the way human and environmental health are considered when developing new materials including ecomaterials.

By systematically reviewing past and current examples, it is possible to demonstrate that the existing processes do little to prevent the introduction of harmful substances into manufacture. Consequently any development of new materials should actively include consideration of the impacts of human and environmental health in early stages of the design of materials.

To illustrate this, the chapter uses a range of examples from well-recognized problems with lead and asbestos to currently poorly recognized risks of nanotechnology, biopolymers, and ongoing use of substances with mild but suspected adverse health impacts. The overall conclusion is that so far human society has been slow to recognize the health risks, and even when these were reasonably known, the new chemicals entered prolific productions without adequate effort to consider or eliminate such risks.

The existing patterns of slow recognition of health risks should be broken by calling for earlier and more comprehensive investigations of totality of likely impacts new materials present for the human environment and health.

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## Introduction

In recent years, there has been an increased need to develop new ecomaterials capable to alleviate some of the environmental problems generated by the previous generation of materials. However, the questions about the possible adverse impacts of any new materials on human health still remain open and should be actively addressed as part of development of any new ecomaterials. Using the example of building materials, this chapter explains the inherited trends of issues with the new materials, problems with slow responses, and elimination of even the well-known problem chemicals and reviews some families of newer materials for their potential to contribute to a continuation of the existing trend.

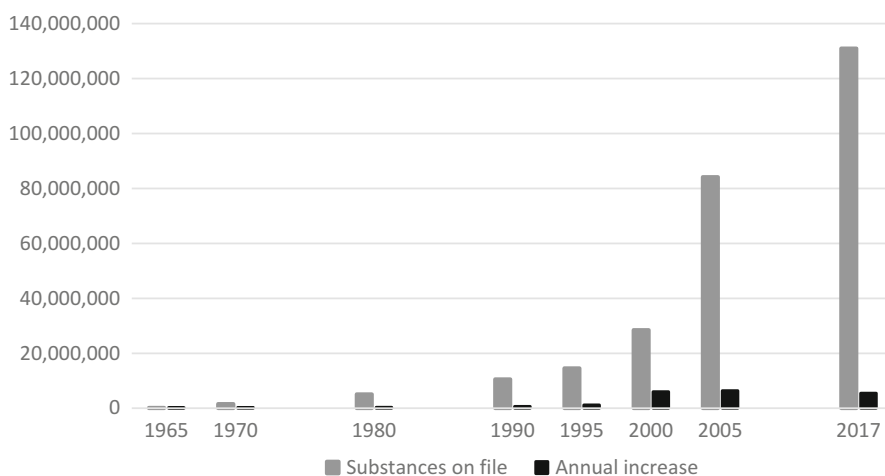
This chapter uses history of past recognition to propose a systematic framework for evaluating the present and anticipating future health issues. It evaluates the past and current practices with regulation of the problem substances as a social and historical construct and analyzes patterns in existing responses to health concerns. In most cases, this is a story of delayed action. As a result, humans have been

exposed to many highly harmful substances, and many of these have been released into the natural environment. Breaking this pattern should be one of the priority tasks when developing new materials.

## Rise of Human-Made Chemicals

Since the second half of the nineteenth century, and especially since the World War II, a large number of new human-made, synthetic chemicals have been developed, and this is still an accelerating trend. Chart 1 shows the exponential increase in registered new human-made substances between 1965 and 2017. It is important to observe that while in 1965 there were already 211,934 substances registered, in Chart 1 this number is dwarfed in comparison with the increases which have followed since. Yet, many of the commonly used chemicals were developed by this time. It was between the mid-1920s and immediate post-World War II period that a real acceleration of innovation with polymers can be observed. Poly(vinyl chloride) (PVC), polyethylene (PE), poly(ethylene terephthalate) (PET), polystyrene, poly(styrene-butadiene) (SBR), poly(styrene-co-acrylonitrile) (SAN), poly(acrylonitrile-co-butadiene-co-styrene) (ABS), polycarbonate, polyurethane (PU), nylons, aramids, and polyamides were all invented and entered manufacture during this period [40].

Only decades after the start of this accelerated development of new human-made substances it was recognized that these were starting to impact many aspects of human life and the natural environment. In 1962, Rachel Carson wrote one of the early critiques of this development for its potential of devastating impact on the environmental health [7]. By the late 1970s, concerns had been raised about the lack



**Chart 1** Showing increase in number of known chemicals in the world and annual increase (Based on combination of data from [5, 8])

of information about toxicity of many of the newly developed chemicals. In 1984, the US National Academy of Sciences/National Research Council reported that the minimal data was available for only 22% of the US high production volume (HPV) chemicals [5]. The HPV chemicals are the most commonly used chemicals nowadays defined as those used in amounts higher than 1 million tons per year. These amounts are counted separately for economically large regions, with the USA and the EU both counting separately their own HPV chemicals. Worldwide, there are about 30,000 substances in the groups of HPV chemicals. By the closing of the twentieth century, it was estimated that in the EU only about 14% of HPV chemicals had made publicly available the most basic data, and for 21% no data existed at all, while in the USA only 7% of HPV chemicals had full toxicity data, and for 43% no information on toxicity was available [5]. In 2007, the EU set a new policy on Registration, Evaluation, and Assessment of Chemicals (REACH) aimed at filling the gaps in data for the HPV chemicals. Since then, the European Agency of Chemical Substances (ECHA) has been creating a central database, and a number of chemicals have had thorough assessments. Currently, this database is more likely to list a specific chemical as a problem than similar US and other sources. Although, human-made chemicals are not the only substances that can present hazards to human and environmental health, this exponential increase in such chemicals and incompleteness of health assessments for many of them send very disturbing signs.

### **Lifestyle Changes Which Increased the Importance of the Impact from Building Materials**

This rise of synthetic chemicals corresponds with another important and unrelated development, which increases importance of what is in the common materials: the increase in the proportion of time people spend indoors. In recent years, it has been reported that most people spend between 80% and 93% of their time indoors [29]. While countries and regions with strong agriculture might show somewhat milder overall trends, many urban dwellers have been found to spend as little as 30–75 min per day outdoors [11]. These proportions signal that nowadays indoor air quality is of much greater importance for people's health than it was in pre-industrialized societies. Yet, some of the key materials influencing the indoor air quality are poorly studied for their impact on health. For example, insufficient information exists for health assessments of 95% of chemicals used in construction products [36].

In fact, problems with poor health outcomes and indoor air quality were observed and grouped under a term "sick building syndrome" by the early 1980s. This problem reflected the introduction of a number of new synthetic chemicals into buildings and the fact that the buildings became increasingly airtight in response to the energy crisis of the 1970s [2]. Although building and furnishing materials played an important role in this problem, these were not unique in their negative contribution to indoor air quality and people's health, rather all materials found indoors contributed. In the decades that followed, the problem was often seen as closely

related to the air exchange rate, and the expected artificial ventilation rates were gradually increased [56]. However, more recent studies indicate that indoor air quality in homes is generally poorer than in offices and other public buildings, due to the lack of instance on artificial ventilation [34]. Thus, the opportunities for poorer health outcomes due to new, insufficiently tested materials used indoors are still very much present.

This trend of indoor concentrations of human-made chemicals opens another important issue: What happens when we are exposed to the multiplicity of harmful chemicals at the same time or if these chemically interact within a relatively constricted space? This is an area of study which has seen an exponential increase in research in some of the key publications in this area [57]. Yet, despite this, additive and synergistic effects of combinations of chemicals is an area of significant lack of information and research ([3], p. 61). The sheer numbers and level of lack of knowledge can be blamed for this. One estimate considered how long would it take to evaluate 1,000 chemicals in combinations of only three chemicals interacting, at 15,000 tests per year, and concluded that it would take 11,000 years to complete. When they looked into combinations of 11 chemicals, the result was even more out of our reach as it would take millions of times longer than the universe has existed ([3], p. 61). While it is true that testing abilities and overall knowledge are constantly increasing, this clearly suggests a need for different approach to this lack of very much needed knowledge. The need for an alternative approach is especially clear when we consider the continuing exponential increase in development of new chemicals.

## Precautionary Principle

At the same time, there are serious problems with developing sufficient scientific knowledge to explain fully the health mechanisms underlying human health reactions to exposure to many toxicants which points toward an alternative position some authors suggest “prudent avoidance” or the precautionary principle [51]. The precautionary principle was established as Principle 15 of the 1992 Rio Declaration on Environment and Development and states “where there are threats of serious or irreversible damage, lack of full scientific certainty shall not be used as a reason for postponing cost-effective measures to prevent environmental degradation” [41]. Applied to indoor air, the precautionary principle implies avoidance of building and furnishing materials suspected to be harmful to human health without waiting for proof of their harmfulness.

In many ways, the healthiest approach would be to use only substances that are proven to be harmless. This approach would echo well with the definition of health adopted by the WHO in 1946: “[h]ealth is state of complete physical, mental and social well-being and not merely the absence of disease or infirmity” [59]. The most important application of such principles is avoiding introduction of new materials which contain substances already somewhat recognized as able to adversely impact health.

## Historical Patterns

In order to understand the existing patterns in recognition and action against the new human-made substances which might present a problem for human and environmental health, it is useful to evaluate historical patterns in such recognition. The key questions for this analysis are: How much improvements can be observed over time? Is the human civilization showing signs of accelerating the recognition of problems and ideally even acting on the problem before the new chemicals enter production?

In order to answer these questions, a simple system of three stages is helpful, looking into early recognitions as Stage 1, efforts to regulate use as Stage 2, and finally activities surrounding complete ban of a substance as Stage 3. Although for specific substances some of these stages could overlap and progress at different speeds, the three stages of progression with recognition of risks posed by certain substances organize available information into a system supporting clarity of interpretation and illustrating the key patterns in the development and assimilation of new scientific knowledge.

The following three sections are organized by the three stages but, in a reverse order, starting with the most recognized health hazards in building materials.

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## The Most Recognized Risks from Stage 3 Substances: Lead and Asbestos

Stage 3 substances have been clearly recognized as health hazards and are especially relevant for this discussion because only they can help in evaluating the effectiveness of their elimination and how long the whole process took. These can help answer questions such as: How successful was the elimination of the most known hazards? At what speed did it occur? What were the key observable obstacles?

### Issues with Banning of Lead (Pb)

Lead (Pb) has been used by human society for at least 4,000–5,000 years [6]. Lead is a naturally occurring metal which has been used historically for a number of applications because of its low melting point and easy pliability. During the twentieth century, it was extensively used as stabilizer for lead-based paints and in leaded petrol. Lead can negatively affect almost every organ, system, and process in the human body, including the cardiovascular, gastrointestinal, hemolymphatic, urinary, immune, nervous, and reproductive systems, and can cause tumors in laboratory animals. This is possible because lead can be misinterpreted by the body as beneficial element calcium and thus can take over functional roles of calcium [50]. For the same reason, lead is readily stored in bones, hair, and teeth, where it can stay for decades.

As early as 370 BC, Hippocrates made some of the earliest recorded observations of health issues related to lead and other heavy metals ([41], Chap. 6). Some sources

have proposed that lead poisoning influenced the fall of the Roman Empire. Better understanding of the risks eventually led to the passing of the first Food and Drugs Act by the British Parliament in 1875, but despite this cast lead solders and other lead toys were fairly common until the late 1940s and early 1950s ([41], Chap. 6). Therefore, it is possible to observe that lead was already in the Stage 1 of recognition of health risks before the start of the twentieth century but that the real action against it, indicative of transition to the second stage, did not start until much later.

During the 1970s, systematic actions against lead exposure started in many parts of the world. In this period the main focus was leaded petrol and lead-based paints. Recognition of the health risks associated with lead in petrol increased during the 1970s leading to removal of leaded petrol in many countries during the 1980s and 1990s [6] and banning of lead-based paints [31]. Therefore, for many developed countries during the 1970s, lead has gone through the second stage of recognition of risk, leading to bans from the 1970s.

Unfortunately, it is still impossible to talk about complete global ban on the use of lead. In part this is because the existing regulations against lead are not global; rather, these are common in more developed countries, and many less developed countries still do not have such regulations in place. As recently as 2011, lead was found in high levels in new paints in 20 countries from five continents [17]. Some specific uses of lead also continued for much longer, for example, lead-containing batteries are still on the market of most countries worldwide. Even more disturbing recent progress with removal of lead is from the use as stabilizer for polyvinyl chloride (PVC). The deadline for voluntary removal of lead stabilizers from PVC in Europe was 2015, preceded in 2005 by the voluntary removal of lead in PVC piping for water supply [15].

The efforts to ban the most wide-scale use of lead during the 1970s provide an important anchor in the history of removal of lead, however, lead is still globally present as a problem, and early in the twenty-first century, its global consumption is on the rise, with China contributing to about half of its production and consumption [53]. The situation is similar with other heavy metals, such as mercury and cadmium. Importantly, only during these recent years, more research has appeared in the developed countries on impacts of lower exposure to lead [24], and the full understanding of the adverse health impacts of low-level exposures to lead is still developing.

Therefore, while it is possible to talk about an almost complete ban of lead in many developed countries since the late 1970s, this example can hardly be seen as a positive or reflective of an effective removal of a well-known hazardous substance from industrial use. It is evident that some of the industry was late with the removal of lead and that this removal is globally uneven, leading to the global increase in the production and consumption of lead in recent years, and some of the knowledge needed for more complete action has only recently started to become available as the average exposure to lead fell among the populations of the developed countries.

It should also be mentioned that because of its very long half-life, the historical use of lead has already released much lead into the environment, where for most life-forms it also acts as a toxicant. Even in the areas where it has been banned, lead

continues to present environmental risks in soil and dust, especially close to significant roads [6]. Newer research is observing that lead exposure seems to fluctuate in relation to seasons and that different plant varieties absorb more lead from soil or might help reduce lead toxicity within the body. Environmental persistence of substances hazardous both for humans and other life-forms is only starting to receive greater research consideration.

## Issues with Banning of Asbestos

Similarly as with lead, the use of asbestos began 4,500 years ago. Asbestos is a commercial name for a group of naturally occurring mineral silicate fibers of the serpentine and amphibole series [37]. The main shared feature these mineral silicate fibers have is that they easily break into long thin fibers [13]. The ease of break, the mineral composition which gives it properties against fire, and the ability of the asbestos fiber to reinforce a surrounding material, such as cement, have given rise to a number of uses of asbestos in roof tiles, in wall cladding, in vinyl flooring, in fire protection, and in friction products (such as car breaks). Unfortunately, the same features that gave asbestos fiber its applicability are the foundation of the health problems it causes. Asbestos exposure can lead to a series of different lung diseases, such as pulmonary fibrosis (asbestosis), pleural abnormalities (effusion and plaques), and malignancies (bronchogenic carcinoma and mesothelioma) [13]. Although the precise molecular mechanism involved with asbestos within the human body is not yet fully understood [62], it seems that its long fibers create a series of processes that inhibit normal cell functioning and trigger the defensive mechanism, which becomes chronic due to cellular inability to expel pollution of the size and proportions of asbestos fibers [13].

In 1898, Adelaide Anderson, Principal Lady Inspector of Factories in the British Home Office, recognized that the “sharp edge” of the asbestos dust leads to much illness and death from respiratory disease in those working with asbestos ([12], p. 38). With this, the recognition of the suspected health issues with the use of asbestos was in the Stage 1 by the start of the twentieth century. Early regulations in the use of asbestos commenced with the 1931 formation of the British Asbestos Industry Regulations ([12], p. 38), thus moving asbestos into the Stage 2 of early regulations against it. The concerns with asbestos were further confirmed in the early 1960s when the relationship between lung cancer and mesothelioma and asbestos exposure was also scientifically established ([12], p. 38). This discovery led to a number of improved regulative changes which started to trickle through during the 1970s, and this period can be seen as the later part of the Stage 2, still focusing on attempts to regulate the use of asbestos.

However, from the 1980s it is possible to observe more complete regulations and official bans on the use of asbestos taking the recognition into the final Stage 3, although complete bans were slow to appear. For example, a complete ban on the use of asbestos took place in Italy in 1992, in New Zealand in 2002, in Australia in 2003, and in Japan in 2005 [39]. By 2012, 52 countries had completely banned use



of any form of asbestos. Correspondingly, the global production and consumption of asbestos has fallen in recent years. The global demand for asbestos peaked around 1977, when about 25 countries produced a total of 4.8 metric tons per year, which were used in 85 countries [37]. By 2015 and 2016, global production of asbestos was still at about 2 metric tons per year, with Russia contributing over half of the global production, followed by China, Brazil, and Kazakhstan [55]. The fact that global consumption of asbestos is currently just under half of what it was at the time of its peak simply signals that to date ban of asbestos is not globally universal.

In common with lead, after the initial bans, the use of asbestos was allowed for specialist situations where asbestos was seen as being irreplaceable. In this case, fireproofing was allowed to continue for longer than other uses. Another similarity is that we are still learning about the consequences of lower exposure to asbestos, and those findings suggest that lower exposures are more harmful than previously recognized [35]. Finally, asbestos also presents an environmentally persistent toxin, with full implications of its historical releases still to become better known.

## Conclusion on Lead and Asbestos

Examples of lead and asbestos show that even those well-known and reasonably well-regulated against substances in Stage 3 of recognition are to date not fully eliminated from industrial use. Therefore, if anything these examples suggest that there are no examples as yet of full elimination of hazardous substances.

It is also relevant to observe that although these substances have been banned in many countries, new insights on their impacts on human and environmental health are still becoming available. That demonstrates that even now it is impossible to talk about a complete evidence necessary to make a fully informed decision about the use of these substances. Consequently, these examples strongly reinforce the need to act before the full scientific evidence can be available, as it can take many decades of concentrated research to arrive to full medical evidence.

However, the most disturbing lesson from the examples of lead and asbestos is that both of these substances have been recognized as hazardous from the start of the twentieth century, yet during this century, their use exponentially increased in all countries, before regulative efforts only from the 1970s to 1980s to significantly limit their use. It is hard to say with certainty if this was possible due to the trend of waiting for solid evidence to regulate against the use of a certain substances (which really did develop during the twentieth century) or because the twentieth century industry gave priority to convenience of the use over human health. However, it is clear that the fundamental paradigm of thinking about the materials has to change away from what was common during the twentieth century. This is especially the case as environmental health increases in importance, and environmentally persistent pollution, such as lead and asbestos, begins to be considered for their ongoing environmental impact, in addition to the human health impact.

## Progression with New Regulations Against Stage 2 Substances: Formaldehyde and Phthalates

Stage 2 substances provide good examples of the contradictions and difficulties associated with the process of starting to eliminate substances recognized as harmful. This stage could take long periods of time and include many substages. Although in terms of the allowable thresholds for exposure there is a significant qualitative difference between these substages, the differentiation between these substages tends to be blurred if developments are accelerated. This blurring is the reason these are clearer if discussed as one stage. Good examples for Stage 2 are formaldehyde and phthalate plasticizers. In order to provide background for Stage 2, these examples are discussed within the context of other VOCs and general issues associated with indoor air quality. The key question posed while conducting the review of Stage 2 substances is: Can an acceleration of the progression from early regulations to complete ban be observed in recent years?

Stage 2 examples also start to explain some of the difficulties facing elimination of organic chemicals. In contrast to very persistent substances such as lead and asbestos which can be measured, many of the human-made organic chemicals are more reactive, fast to change their form, while also having some similarities with the chemicals commonly produced within the human body. These characteristics make measuring and limiting of the accepted levels challenging.

### Formaldehyde

Formaldehyde (HCHO) is a naturally occurring organic chemical which is a product of one-carbon metabolism. Worldwide production of formaldehyde is over 21 million tons, for resins and adhesives for a range of products from composite wood materials, insulation, textiles, biocide, paper, and even in cosmetics as preservative [48]. At room temperature, formaldehyde is a colorless, flammable gas with pungent odor, in higher concentrations likely to cause a burning sensation to the eyes, nose, and lungs [4]. Formaldehyde is most problematic for its carcinogenicity [20], and this is especially relevant because of its high volume of use. It is estimated that around 2000, almost one million workers were exposed to formaldehyde above background levels just in the EU [21]. Although formaldehyde is a naturally occurring chemical, the extent of its industrial use of newly synthesized formaldehyde makes it one of the human-made chemicals.

Scientifically, formaldehyde was first described in 1855, and by 1867 a German chemist achieved its synthesis through dehydration of methanol [49]. The early twentieth century saw much development in applications of formaldehyde. In 1907, the combination of phenol and formaldehyde became available to industry under the name “Bakelite.” In 1931, the first glue based on the combination of urea and formaldehyde entered the market, and the first commercial particle board was produced during World War II in Bremen, Germany and since 1950 has become a common alternative to solid wood [49]. Such products tend to release formaldehyde

due to chemical reactions between indoor air and the resins, specifically, due the hydrolysis of urea-formaldehyde resins. Formaldehyde is still mainly used for resins and glues, and about 70% of its total production is used in alternatives to solid wood [22].

At normal room temperature, formaldehyde readily evaporates [58]. Chemicals with this ease of evaporation on normal room temperatures are normally grouped into the volatile organic compounds (VOC) [16], and formaldehyde is one of the better known VOCs. In contrast to lead and asbestos, which are naturally occurring substances unrelated to the natural processes of living organisms, formaldehyde is part of the natural chemistry and metabolism of many living organisms, and, therefore, it is much harder to talk about complete elimination of formaldehyde. Its reactivity and quick absorption in humans make it additionally difficult to evaluate. Formaldehyde is found in most human and other living cells in varying concentrations as a normal product of the metabolism of serine, glycine, methionine, and chlorine [9]. In ambient air, the half-life of formaldehyde is about 1 h, because it either is transformed into carbon dioxide through the process of photooxidation or reacts with hydroxyl radicals to give formic acid [58].

Formaldehyde can enter the human body through inhalation, ingestion, or dermal absorption [26]. In addition to formaldehyde emissions in air, it has been used in many cleaning and cosmetic products and even as a food preservative for some Italian cheeses, dried foods, and fish [26]. Once absorbed, the high solubility of formaldehyde in water causes possible rapid absorption in almost every tissue in the body [26]. The biological half-life of formaldehyde is extremely short at about 1 min.

Quick reactivity of formaldehyde is also to blame for health issues it can cause; however, these were only observed as the problems became notable following the popular use of formaldehyde-containing building products. In 1962, indoor air pollution from release of formaldehyde from installed particle board was first observed [49]. During the 1960s and 1970s, some very high indoor concentrations of formaldehyde were observed, and since then great efforts have been made to reduce its release into indoor air. In 1977 in Germany, an early guideline on formaldehyde specified a value of 0.1 ppm for human exposure in dwellings. By 1981, early regulations of formaldehyde emissions from wood-based materials were established in Germany and Denmark, followed by the USA in the mid-1980s [49].

Since 1981 the International Agency for Research on Cancer (IARC) has evaluated formaldehyde every few years and, in 2004, reclassified it from group 2B “possibly carcinogenic to humans” to group 1 “carcinogenic to humans” [20, 63], with additional adjustments to this classification in 2012 [21]. In a similar move, in 2014, the European Commission has classified formaldehyde as a 1B carcinogen and mutagen 2 [48]. It is considered that genotoxicity and cytotoxicity of formaldehyde play a role in its carcinogenesis [58]. However, formaldehyde is also considered to be a “threshold carcinogen” which means that under a certain threshold, the risk is negligible [48]. Such treatment of formaldehyde reflects well the fact that it is naturally found in human tissue and food, and any combustion process leads to some release of formaldehyde into the outdoor air [58]. These two features of formaldehyde have been vividly

discussed in recent literature, some suggesting “no observable adverse effect level” (NOAEL) approach [33] and others giving great attention to relationship between indoor and outdoor formaldehyde concentrations [48].

This analysis suggests that by the early 1980s, formaldehyde was already in the Stage 2 with some early regulations against it in place. Considering that many of its industrial applications only became known around the World War II, this suggests a very short Stage 1 of early recognition that some action against formaldehyde could be needed. However, even since the formal recognition of carcinogenesis of formaldehyde, it is far from being eliminated from production. The US efforts have been slower than expected, with delays in implementation of the standards for formaldehyde emissions from composite wood products [16] and only three policies for other applications adopted by now in two of the US states [47]. Recent progressive voluntary schemes aimed at eliminating problem chemicals in buildings, list formaldehyde as a problem [23]. However, when probed in detail, it seems that even the most accomplished built solutions based on these systems have been granted an exception to use added formaldehyde [28]. Therefore, while clearly in Stage 2 of recognition for decades, currently formaldehyde is not nearing Stage 3 and complete ban.

## Phthalate Plasticizers in Polyvinyl Chloride (PVC)/Vinyl

Phthalates are a group of aromatic chemicals containing a phenyl ring with two attached and extended acetate groups. They are added to polyvinyl chloride (PVC) and other plastics to increase their flexibility and transparency and are used in proportions as varied as 10–60% of final products [30]. Phthalates are also produced in fairly high volume of over 213,000 metric tons per year (EPA 2012), while their main consumer, the world production of PVC, is at around 40 million tons and second largest plastic by volume. In plasticized form, PVC is commonly used for vinyl flooring and upholstery, shower curtains, wallpaper, wiring, food containers, cling wraps, toothbrushes, toys, tools, car parts, adhesives, and sealers [4, 30]. Although there are some real human and environmental health issues associated with PVC itself, this discussion focuses on the example of recent regulative efforts to limit the use of phthalate plasticizers because this is where more of regulative effort has occurred to date.

Because plasticizers are not part of the chain of polymers that make plastics, they can be gradually released from these products [4, 30]. Phthalate plasticizers belong to the group of semivolatile organic compounds (SVOCs), which is a subgroup of the VOCs which are less volatile because they need higher temperature than common indoors to transfer into gas form [60]. Nevertheless, some SVOCs tend to be released over time.

Since 2008, the ECHA has included eight phthalates in their list of substances of very high concern [14]. This is a list of substances which under the REACH program require authorization before use and currently contains 43 substances (phthalates make one fifth of the total list). The following phthalates are listed: di(2-ethylhexyl) phthalate (DEHP) in 2008, dibutyl phthalate (DBP) in 2008, benzyl butyl phthalate

(BBP) in 2008, diisobutyl phthalate (DIBP) in 2009, bis(2-methoxyethyl) phthalate in 2011, n-pentyl-isopentyl phthalate in 2012, diisopentylphthalate (DIPP) in 2012, and diethyl phthalate (DPP) in 2013. The reason for inclusion of all of these chemicals is their toxicity for reproduction, with specific reasons ranging from impairing fertility, causing harm to the unborn child, and being an endocrine disruptor [14]. Some have also been noted as dangerous for the environment and toxic for aquatic organisms. The majority of these phthalates are colorless or lightly colored liquids, which have little or no smell, which would make it practically very difficult to observe any exposure to phthalates, especially when these are released from finished plastic products.

When releases of phthalates from plasticized PVC in interiors were evaluated, it was established that because of saturation and sorption processes and because these establish an equilibrium over a long period of time, a very small amount of plasticized PVC emits almost as many phthalates as a larger area and that this did not change with increased ventilation rates [1]. Therefore, Afshari et al. [1] concluded that “if there is any surface material in an interior that contains plasticizers, it is impossible to avoid the phthalates in indoor air.” Similar difficulties were observed by others [60]. Once emitted into the indoor air, phthalates find their way into household dust [18].

Historically, different phthalates have received prolific use in different periods. Di (2-ethylhexyl)phthalate (DEHP) is a short-chain phthalate frequently found in older PVC products. In 1999, the European Union regulated against its use in toys, and this was followed by regulations for other products [19]. Since then, longer-chain phthalates such as di-iso-nonyl phthalate (DINP) have been used more, and there is hope that the 2005 European Union ban of use of all phthalates in toys that can be put in a baby’s mouth will have the same positive effect and that the development of non-phthalate plasticizers could follow [19]. Because of this historical background, DEHP is better researched than other phthalates, and existing regulations might treat different phthalates as presenting varying levels of health risk.

There is still limited epidemiological evidence related to phthalates, and decisions to classify these chemicals as being of very high concern are mainly based on animal studies. Studies of the health impact of DEHP on rats have established that it is an endocrine disruptor with antiandrogenic activity, and it suppresses testosterone-related processes [32]. Once DEHP is absorbed in the lining of the gut, it metabolizes into mono-2-ethylhexyl phthalate (MEHP), which has antiandrogenic activity ten times greater than DEHP [32]. However, current studies confirm that during the second half of the twentieth century, vinyl flooring contained DEHP in combination with other phthalates [18], and the impact of exposure to these cocktails of phthalates is still to be better understood.

As with lead and asbestos, early animal studies have so far tended not to quantify the impact of lower doses and complex combinations of factors have on human health. Consequently, research findings such as those now available for older phthalates should be considered as moving from earlier substages of Stage 2 of recognition to more developed later substages, where the dose effect is evaluated. From that perspective, it is good that changes have started to be implemented even

without conclusive epidemiological evidence for human exposures. However, the fact that the ECHA has classified a number of phthalates as substances of very high risk is only part of the process, as it takes much longer for risk to be integrated into regulations worldwide. For example, over the same years, ECHA has been classifying an increasing number of phthalates as a problem; in the USA the US Agency for Toxic Substances and Disease Registry (ATSDR) has kept the list of the same four phthalates on their website: di(2-ethylhexyl)phthalate (DEHP), di-*n*-butyl phthalate, di-*n*-octylphthalate (DNOP), and diethyl phthalate [4]. These present a range of more and less problematic phthalates, and although for some regulation thresholds for exposure are mentioned, none of the ATSDR pages discuss active regulations against their use. In part, at least, this could be reflective of how up to date the information is because the ATSDR webpages on phthalates have not been updated since before 2008, presenting the information produced between 1995 and 2002 [4]. This clearly signals an internationally uneven treatment of phthalates, which is very symptomatic of the early Stage 2 of recognition.

## Conclusion on Formaldehyde and Phthalates

The examples of formaldehyde and phthalates suggest some potential acceleration with recognition of risks in recent decades. However, this acceleration is still modest, and both examples show that substances which are reasonably well recognized as risk continue being used in manufacture for decades. Although, some regulations against phthalates have been set in place before the complete scientific evidence is available, it should also be noted that these are still partial interventions. Both formaldehyde and phthalates are still in use, despite the fact that the existing recognitions of their harmfulness can be seen as a formal acknowledgment that there is sufficient evidence to completely avoid these in production.

The overwhelming conclusion from the evaluation of these chemicals is that it is difficult to observe a dramatic difference in the way these more recent examples have been treated compared to well-known examples of lead and asbestos. This suggests that while some changes are observable, the core values observed with Stage 3 substances might be still in operation. Consequently, it is possible to ask: Is this a sign of persisting trend of waiting for full scientific evidence, which is often impossible for decades? Or is lesser priority being given to health than industrial advantages even at the start of the twenty-first century?

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## Early Recognition of Risks from Stage 1 Substances: Replacement Substances and Nanomaterials

Following the review of issues with incomplete removal of the well-known hazards, gradual but still slow progression with current removals, it is relevant to also evaluate the processes and decisions which surround the introduction of new substances into extensive manufacture or Stage 1 substances. The question is: Are there

any observable trends of avoidance of the introduction of new chemicals into production when some concerns have been noted on the potential health impact of these? In contrast to removal which tends to have financially adverse implications, at the point of introduction, finances are invested into the application of the new substance, and selecting a substance which is less likely to need subsequent elimination could be seen as financially desirable. For many substances this is a very quiet phase. Nevertheless, this is where the change should start taking place for all new materials, with the careful consideration of the health implications before these are fully integrated into manufacture.

This section evaluates whether it is possible to observe indications of such activities becoming common. Good examples for this are substances introduced as a replacement from now eliminated hazards and completely new materials such as nanomaterials.

## Replacement Substances

One important area of new development is substances that replace those phased out as hazardous. Titanium dioxide ( $\text{TiO}_2$ ), or titanium white, is a common additive to acrylic and other paints, which adds whiteness and reflective properties and helps to stabilize these chemically. In many ways, titanium dioxide is a replacement for lead in paints. It is also found in many other products from food, medicine, and toothpastes to plastics, papers, and inks. In 1966 the USA and in 1969 the EU approved food-grade titanium dioxide as an inactive ingredient in human food and labeled it E171 [25, 43]. Between 1916 and 2011, an estimated total of 165 million metric tons of titanium dioxide was produced globally [25]. This prolific use of titanium dioxide, at both micro- and nanoparticle sizes (both are found in E171), has only recently inspired research on its impacts on human health. Pele et al. [38] demonstrated that a proportion of ingested titanium dioxide is absorbed into the bloodstream, while others have investigated the toxicity of such particles [27, 43]. Titanium dioxide appears to cause inflammation, pulmonary damage, fibrosis, and lung tumors. It also appears to be genotoxic and possibly carcinogenic to humans [63]. Currently reported health issues tend to focus more on nanoparticles than microparticles of titanium dioxide, leaving the assessments still incomplete. While titanium dioxide in paints is unlikely to be absorbed as directly as when added to food, the patterns of the poor recognition of the potential risks of this commonly used substance echo the patterns observed with lead. Titanium dioxide can be seen as making transition into Stage 2 of recognition with some regulative action likely to follow the recent increase in research in this area. Unfortunately, currently it is impossible to avoid products containing titanium dioxide, as for many alternatives do not exist.

Recently, replacements for phthalate plasticizers, and fire retardants have been developed. For phthalates and fire retardants, early observations show that regulations against one set of such chemicals produced an increase in the use of other chemicals from the same family. For phthalates the change was from



shorter-chain phthalates (such as DEHP) to longer-chain phthalates (such as DINP) [19] and to a number of non-phthalate plasticizers. For fire retardants the change was from a polybrominated diphenyl ether (PBDE) fire-retardant mixture pendaBDE to more prolific use of tris(1,3-dichloroisopropyl) phosphate (TDCPP), a suspected human carcinogen [52]. Unfortunately, in both cases the replacement chemicals are simply less researched and less well understood for their health effects [19, 52]. The issue here is the interpretation of the wording: “suspected of adverse health effects.” If using the precautionary principle, “suspected” could be seen as meaning “probably” if not “likely,” while the manufacturers seem to be interpreting it as “ready to use.” This is especially the case with TDCPP which is at least in the early Stage 2 of recognition. This poor use of precautionary principles when new substances are introduced as replacements, despite the tangible concerns that these are in the entry stages of recognition as risks, is very problematic. It suggests an almost cyclic process where less known but suspected hazards are introduced to replace better established hazards, clearly triggering the same process again.

Similarly, although many formaldehyde-free products are increasingly available, currently there are only a very small number of studies on their health impact, indicating replacements are introduced without much evaluation of their health effect. However, there are some exceptions. For example, one study explored the health impact of the change from a phenol-formaldehyde bonding agent in fiberglass insulation to a carbohydrate-carboxylic acid binder, observing that *in vitro* this binder did not impact the biosolubility of glass wool insulation but also noted that droplet sizes had an impact [42]. Droplet size of the bonding agent, which greatly varied in the samples studied, seems controllable by careful manufacturing. This indicates that sophisticated research is needed in these early stages of development of new materials, if they are to be reliably safe.

## Nanomaterials

One area of recent development is materials that use nanoparticles. With the technology that enables design at scales unprecedented in the past, a range of completely new material characteristics is becoming available for the first time. Unfortunately, there are already warnings about nanoparticles. Researchers have remarked that nanoparticles are likely to impact the human body similarly to microparticles, the best known of these being the asbestos family [13]. If learning from the experiences with asbestos, the problem would seem to be the shape and size of particles and their biopersistence within the human body. For asbestos it was the long, thin shape and very long biopersistence that produced inflammation and subsequent onset of disease after a long latency. Because this knowledge is available, it seems reasonable to use it when developing new materials with similar features. However, texts that deal with design and the exciting opportunities nanotechnology offers fail to mention risks associated with such particles [61], indicating the same mistakes could be repeated.



## Conclusion on Replacement Materials and Nanomaterials

This review shows that there are no real indications of processes or method set in place to support avoidance of future problems. As the example of titanium dioxide as replacement for lead shows, potential problems were clear from the introduction of this replacement substance. Recent changes in which chemicals are extensively used also show only signs of avoidance of more recognized risks, while still relying on chemicals which are suggested to be possible problem but less researched at the time.

However, nanomaterials are probably the most disturbing example, as there is a growing body of research showing not only theoretical but also practical issues with nanoparticles, yet this is far too frequently put aside when promoting the excitement with the new technology and options that it presents. Clearly, there is potential for many nanomaterials to be harmless for human and environmental health; however, the disregard of active consideration of such implications is very concerning and sends very worrying signs that the changes achieved over the last century might not have been as significant as needed in terms of paradigm change.

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## Could Biopolymers Present a Positive Example?

Although currently, as much as 95% of all synthetic substances are manufactured from fossil resources [45], in recent years there has been an increase in the development of biopolymers. This section evaluates biopolymers as potentially a positive example, searching for qualitative insight on how much improvement these materials bring.

There is more than one approach to developed of biopolymers. For example, because of the great similarities in organic chemicals extracted from crude oil or from grown materials, some efforts have focused on developing systems for extracting the same seven key hydrocarbon building blocks used in majority of common petroleum-based polymers. Hydrocarbons consist entirely of hydrogen and one to eight carbon atoms as their building blocks: syngas (C1), ethylene (C2), propylene (C3), C4 olefins or butadiene (C4), benzene (C6), toluene (C7), and xylene (C8) [40]. In principle at least, the same key chemicals can be derived from grown bioresources using: ethanol  $C_2H_5OH$ , glycerol  $C_3H_8O_3$ , xylose  $C_5H_{10}O_5$ , fructose  $C_6H_{12}O_6$ , and glucose  $C_6H_{12}O_6$  [10]. One of the great advantages of this way of developing hydrocarbons is that instead of energy intensive steam cracking of fossil fuels, grown carbohydrates can be transformed into simple sugars and fermented into ethanol and glycerol, and from these ethylene and butadiene can be produced [10]. This approach could lead to the production of the same polymers that are already in use but sourced from bioresources.

Other research efforts are seeking to find ways to develop new polymers which are better suited to the chemistry of bioresources. Specific alternative technologies include the production of olefins using bio-ethanol dehydration, methanol to olefins, catalytic fast pyrolysis of lignocellulosic biomass, and bio-oil upgrading [44].

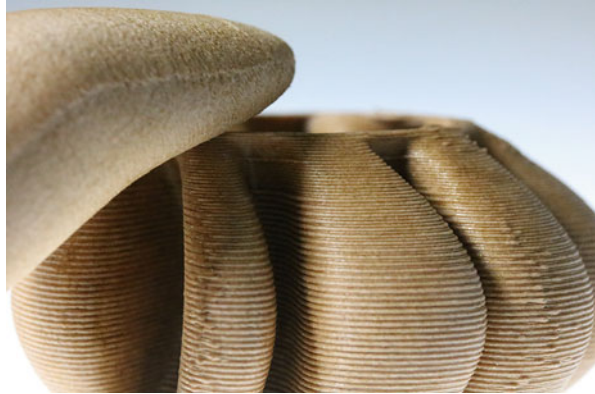
Unfortunately, to date manufacturing polymers using these processes has not arrived to the point of financial viability [44], which is understandable, given that research focusing on the development of these chemicals has only begun reasonably recently. Ethanol is one chemical that can be readily obtained from biomass by fermentation, and in recent years, its production has been increasing [45].

One innovative approach uses fluid catalyst cracking of hydrodeoxygenated vegetable oils derived from Norwegian spruce pulping [44]. The intention of the initial research was to examine if similar processes commonly used to derive hydrocarbons from fossil fuel could be effective for breaking down naturally occurring oils into hydrocarbons. The resulting chemicals were closely comparable to those in steam cracking of naphtha and were especially successful in deriving ethane and propene [44]. All approaches to develop hydrocarbons from bioresources are still in the innovation phase, when it is still hard to anticipate which of the solutions will prove to be most useful.

Using bioresources, which are presumably renewable, to develop petrochemicals already in use would be an improvement to relying on finite fossil fuel resources. However, as soon as hydrocarbons are used in any production process, it is important to emphasize that majority of other issues associated with polymer production are brought into focus. All hydrocarbons pose significant risks both for human health and the natural environment [40]. In fact, apart from the syngas, all of the other hydrocarbons are already recognized as toxic and should at least be seen as in Stage 2 of recognition as health risks. In addition, all of these chemicals are flammable, some require pressurized storage, and many are VOCs [40]. It is unfortunate that their use for manufacture of conventional polymers has not been banned as yet, and from that perspective, it would be good to avoid introducing additional use of such components. Therefore, it is questionable if any biopolymers manufactured using hydrocarbon chemistry can be even fully seen as ecomaterials.

Another approach to the development of new polymers is to develop new chemistry based around the chemicals commonly found in bioresources without mimicking the existing petrochemical industry by using hydrocarbon chemistry. One such material is poly(lactic acid) (PLA) which has entered the market as an alternative to poly(ethylene terephthalate) (PET) and polystyrene. PLA is a thermoplastic, which makes it very recyclable, but it is also considered to be biodegradable and compostable alternative for many packaging and more durable plastics [10]. In PLA, the monomer, lactic acid, is produced by bacterial fermentation of corn starch or sugar [10]. However, the disadvantage of PLA is that like many other polymers, it requires very specific conditions for biodegradation, and to date municipal collection of PLA for recycling does not exist in many places. Wood dust can be added to PLA as a natural stabilizer and filler, without any reduction to recyclability and biodegradability of the biopolymer. PLA with wood dust has been shown to capture some of the benefits of both conventional plastics and wood-based products. For example, as conventional polymers it can be used for 3D printing, while similarly with other wood-based products, the finished product can be surface treated. Figures 1, 2, and 3 illustrate the expressive potential of such applications.

**Fig. 1** Hannah Tilsley, waxed 3D-printed model, PLA and wood flour filament, design project in the first-year course Digital Creation, coordinated by Bernard Guy at Victoria University of Wellington, 2017



**Fig. 2** Anita Neupert, stained and waxed 3D-printed model, PLA and wood flour filament, design project in the first-year course Digital Creation, coordinated by Bernard Guy at Victoria University of Wellington, 2017



While there is great promise and reason for excitement with the development of biopolymers, it should also be acknowledged that such practices are likely to create a competition between land to grow food crops and land to grow crops for the production of biopolymers. In fact, in late 2006, the price of tortilla flour in Mexico doubled, because of the rise of the US corn prices stimulated by the US interest in

**Fig. 3** Danielle Patterson, painted 3D-printed model, PLA and wood flour filament, design project in the first-year course Digital Creation, coordinated by Bernard Guy at Victoria University of Wellington, 2017



the manufacture of biofuels from corn [46]. This provoked a significant public outcry since about half of Mexico's population lives in poverty and relies on tortillas as a main food source [46]. This aspect of considering the benefits and disadvantages of using more biopolymers has to be carefully considered. In this example, the efforts to increase the production of biofuels in the developed world led to hunger of the less developed countries. Biopolymers could present similar costs.

Furthermore, in 2010 an analysis of biopolymers compared to conventional fossil fuel polymers on adherence to green design principles and life-cycle environmental impacts observed that while the biopolymers clearly scored higher on the adherence to green design principles and a reduction of the environmental impacts of production, their total life-cycle environmental impacts were higher than those of some of the conventional polymers [54]. To a large extent, this was because this comparison measured the total impacts of growing biomaterials used to generate biopolymers, and these processes are currently less efficient than what conventional petrochemical industry has achieved. However, it was conclusive that when it comes to health and environmental pollution side of impact, biopolymers were much better [54].

Therefore, although more development in biopolymer industry is still needed, there are some significant positive suggestions that materials focused on using bioresources might provide a solid basis for the next generation of ecomaterials. The most important insight from this analysis is that no aspect of biopolymer production should be considered in itself as certainly better, rather, each should be probed and carefully evaluated, as there is much potential for great aspirations to fall short in actual execution. Nevertheless, such efforts should be encouraged to stimulate innovation and development in this new area.

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## Conclusion

This chapter shows that the society has been slow to recognize the health risks associated with building materials. Even when health risks were reasonably well-known, problem substances, such as lead and asbestos, entered prolific production

without adequate effort to consider or eliminate health risks. Some acceleration in the process of the recognition of problems and regulative efforts to eliminate these can be noticed with formaldehyde and phthalates, now in processes of elimination. However, this is still a modest acceleration which does not challenge the structure of slow response: extended periods of waiting for conclusive scientific information, and the resistance to voluntarily implementing change when some formal recognition is already available. The most concerning finding is the clear evidence that new replacement substances are introduced into manufacture even now without significant investigation of the possible health impacts. In fact, even examples which are highly likely to have adverse impacts, such as nanomaterials, are treated without active acknowledgment of this knowledge, highlighting that the paradigm of poor recognition of issues is still operating in many parts of human society.

While biopolymers suggest a possible positive example, there is still little evidence that the impact on health is specifically behind their intensive production. Rather, it seems very possible that the similarity between less altered natural chemistry used in these materials agrees better with human and environmental health. Similarly, there is little evidence to suggest that extensive studies of impact on health accompanied such developments.

This chapter shows a consistent continuation of the trend of slow recognition of health risks, failure to consider this aspect before introduction into substantial production, and slow responses to calls to make the change and avoid problem substances. This pattern should be broken by calling for earlier and more comprehensive investigations of the totality of likely impacts new materials present for the human and environmental health.

In a sustainable industry, when developing new materials, especially those aiming to be ecomaterials, the possible adverse impact on human and environmental health should be considered quite actively at the time of development of the new materials. This is especially important because there appears to be an absence of a positive model of a new paradigm of development of materials which actively considers human and environment health implications as a highly important aspect of industrial development. All ecomaterials should model this new paradigm.

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