Available online at www.sciencedirect.com

SciVerse ScienceDirect

Procedia Environmental Sciences 16 (2012) 167 – 175

Procedia Environmental Sciences

The 7th International Conference on Waste Management and Technology

Recycling and disposal methods for polyurethane foam wastes

Wenqing Yang[a,*], Qingyin Dong[b], Shili Liu[a], Henghua Xie[a], Lili Liu[b], Jinhui Li[b]

[a] *Dongjiang Environmental Protection Co., Ltd., Shenzhen, 518104, China*
[b] *School of Environment, Tsinghua University, Beijing, 100084, China*

Abstract

With the wide application of polyurethane foam materials, a large number of polyurethane foam wastes need to be disposed. There are mainly three types of disposal technology, landfill, incineration and recycling in the world. In this paper, through comprehensive comparison, recycling is the most desirable way. Physical recycling method, due to the simple operation and relatively active application, in the short term is an effective means. Chemical recycling method, due to its higher technical difficulty, is difficult to realize large-scale industrialized production in the short term. And in the future, recovery utilization is the ultimate method.

Keywords: polyurethane; foam wastes; physical recycling; chemical recycling

1. Introduction

According to the statistics of China Polyurethane Industry Association, China polyurethane products yield grows rapidly, in 2000 the annual output was 1 million tons, about 3.5 million tons in 2007, but in 2011 it reached 7.5 million tons. Production and consumption scale ranks first in the world. Among them, the polyurethane foam is the largest polyurethane synthetic material varieties, and the total output accounts for about 60% of the polyurethane materials in China [1].

* Corresponding author. Tel.: +86-755-2726-4217; fax: +86-755-2726-4217.
E-mail address: yangwq@dongjiang.com.cn

doi:10.1016/j.proenv.2012.10.023

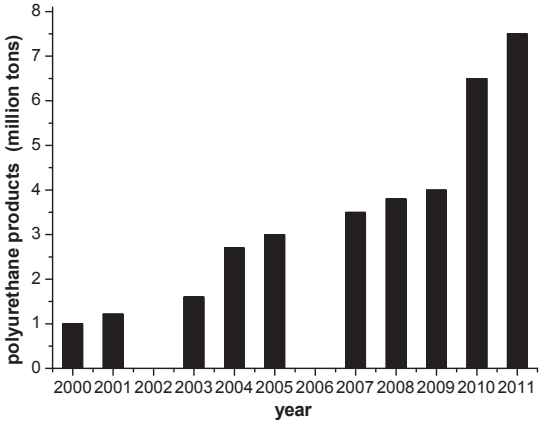

Fig. 1 Domestic polyurethane production in recent years

Polyurethane foam materials are used widely, inevitably leading to a large number of polyurethane foam wastes production. Polyurethane foam wastes mainly come from the production process of leftover materials and product scraps. Polyurethane soft foam products, because the production from different ways, produce wastes have bigger difference. During the process of rigid polyurethane foam products, 15 % of wastes will be totally generated [2]. In 2011 polyurethane output reached 7.5 million tons, and polyurethane foam accounted for 60%, while about 675,000 tons of polyurethane foam was abandoned. In addition, polyurethane foam products more than use fixed number of year, because of the performance will be decimated and scrap, with home appliance, furniture and other consumer goods in the most obvious scrap. For example, according to the present economic level and traditional habit in our country, every year there will be 14.66 million refrigerators of scrap. The average weight of polyurethane foam per refrigerator containing about 6.36 kg, about 93,200 tons of polyurethane foam wastes was produced each year [3]. In the 21st century, China has entered into the stage of peak of the refrigerator scrap [4]. In the near future, a large number of polyurethane foam wastes will emerge.

Polyurethane foam wastes belong to the white pollution, and affect the living environment. At the same time, because polyurethane foam plastics pile-up density is small, about 30 kg/m^3, stockpiling will take up a lot of area. Because of its difficult to degradation of ecological environment will cause adverse effect. Therefore, polyurethane foam wastes recycling will become China's urgent need to resolve major issues. Now there are quite a number of technologies, choose an environment friendly processing technology is very necessary.

2. Disposal technology

The disposal technology for polyurethane foam wastes is major consisted of three types, landfill, incineration and recycling [5-33]. There are two ways, physical recycling and chemical recycling, for recycling polyurethane foam wastes.

2.1. 2.1 Landfill

At first, people directly dealing with polyurethane wastes is landfill or burning. Because of small polyurethane foam plastic pile-up density, landfill will be serious waste of land resources. At the same time polyurethane wastes are very difficult to decomposition in the natural conditions, and in some

European countries, such as the Netherlands, Sweden, Denmark, Switzerland, they have promulgated rules prohibiting the use of land disposal. Australia and Germany, respectively in 2004 and 2005, issued the same provisions. New on the introduction of the EU regulations also banned in high carbon content material is land landfill [5-6].Therefore, landfill treatment is not wise.

2.2. 2.2 Incineration

Incineration is one way through the burning waste polyurethane materials for heat recovery. 1 kg polyurethane burning can produce calorific value of about 7000 kcal/kg, which can provide heat equivalent to the same weight of coal provides energy [7]. Through burning, it can make the wastes volume reduced by 99 %. Polyurethane foam wastes can shattered into grain, as fuel alternative coal, oil and natural gas recovery energy, and applied to cement or power. The American polyurethane industry federation conducted a series of experiments, and pointed out that in municipal solid wastes adding waste polyurethane elastomer and other components of solid plastic wastes (the most proportion 20%), can obviously improve its fuel calorific value [7]. Heejoon Kim [8] developed a novel and environmentally friendly disposal method for PU waste by mixing it with coal to produce a new composite fuel called Eco-fuel.

Incineration as a way in the recycling of polyurethane wastes occupies an important position [9], especially for those who can't use other methods of recycling wastes, burning can be a kind of good method. But if the Incineration process is incomplete combustion, it will produce poisonous gas which seriously polluted the atmospheric. Therefor the method is being phased out gradually.

2.3. 2.3 Recycling

Along with the environmental protection consciousness unceasing enhancement, especially in a sustainable development society today, people more and more realize the reasonable use of resources has been mentioned at a more important strategic height. Polyurethane foam wastes must be effectively disposed and recycled, which not only is the requirement of preventing pollution and environment protection, but also is the need of the production cost reduction and material utilization improvement. Due to its low density and high volume, polyurethane foam waste is difficult to treat and dispose of in landfill. And incineration will produce poisonous gas. There are two ways, physical recycling and chemical recycling, for recycling polyurethane foam wastes [10-14].

Table 1 Advantages and disadvantages of disposal process

Disposal treatment		Key technology	Advantages	Disadvantages
Landfill		Leachate guide line system, anti-seepage	1)simple operation 2)less input	1)difficult decomposition 2)waste of land resources
Incineration		high temperature burning	1)recovery energy 2)relatively mature technology 3)type of polyurethane wastes with not high demand	1)produce poisonous gas 2)serious air pollution and public hazard
Recycling	Physical	only change the physical form, as raw materials or	1)simple operation 2)less pollutant producing	1)certain requirements for wastes 2)product performance, reduced the

		packing to reuse	3)high production efficiency 4)relatively less equipment investment	market use limited range 3)low economic benefit
	Chemical	degradation reaction	1)get the pure raw material monomer/small molecule organic matter 2)product can be used as raw material for the preparation of new products	1)high temperature or high pressure 2)the safety performance of the high demand on the equipment 3)product need purification 4)by-products difficult to control

Landfill will be serious waste of land resources. At the same time polyurethane wastes are very difficult to decomposition in the natural conditions. Incineration will produce poisonous gas, and cause serious air pollution and public hazard. Landfill and incineration will not be recommended except in special circumstances. We can compare the advantages and disadvantages of them from the table 1. So, recycling is the most effective treatment method in the future.

3. Recycling

There are two ways, physical recycling and chemical recycling, for recycling polyurethane foam wastes [10-14]. Physical recycling is directly reusing polyurethane wastes without chemical treatment. Chemical recycling is following the degradation principle. Polyurethane wastes will gradually depolymerize for original reactant or other oligomer and even small molecule organic compound.

3.1. 3.1 Physical recycling

Physical recycling method is crushing polyurethane foam wastes, only changing physical form. The smashing solid particles have no reactive activity, but directly make new polyurethane products as recovery processing of raw materials. Through mixed with adhesives, they can make all kinds of mold products by the compression molding method. This is currently the most widely used method. The usage of waste polyurethane powder can be as high as 90%.

Physical recycling method is simple and convenient, with low cost, but there are still certain technical limitations at various physical recycling method processing. Performance of recovery products is poor, which only apply to some of the cheap products, and limit the market.

3.1.1 Bonding process

This method is the most common physical recycling method. The key points are: first the polyurethane foam wastes are shattered into fine flake, coating with adhesive, which is commonly MDI or PAPI, about 5%-10%. Direct access to water vapor of high temperature, make polyurethane adhesive melting or dissolved. And then press solidified into a certain shape of foam.

Jiang [15] regenerated a kind of waste rigid polyurethane foam plastic and produced insulation board. The present invention had simple process, low cost and environmentally friendly. But the largest defect is that performance of regenerated foam product was declining, which only applied to furniture, car lining and cheap components.

3.1.2 Hot press molding process

This method makes polyurethane softening, self-bonding under heat and pressure, without adhesive. Almost all kinds of polyurethane, due to its contain soft segment which has thermoplastic in the 150-220

℃ range, when heated to such temperature and pressure, can make to mutual bonding. Different polyurethane foam wastes and reworked material final products have different conditions of molding. For some low degree of crosslinking thermosetting polyurethane wastes, there is certain between thermal softening plasticity in the 100-220 ℃. Wastes can directly bond together in the range of temperature. The product is suitable for the low elongation and the poor surface performance requirements, such as damping tablet, fender, etc. Because of the limitation of processing temperature, this kind of method applies only to component known cases [11].

The polyurethane foam composite waste produced in the automotive roof lining production was press-formed into artificial board. The influence of the pressing parameter on the properties of the board was studied. The test results showed that the board formed under the temperature of above 150 ℃ had flexural strength of 15-28 MPa, water absorptivity of 0-2 % and density of 1.0-1.2 g/cm^3. The flexural strength is similar to that of the fiber board with medium density. The density is higher and the water absorptivity is much lower than that of the fiber board. The board with this feature could be used for the application situations which need resistance to water and high density such as furnishings in park and acoustics area [16].

3.1.3 Usage for filler

Polyurethane wastes, shattered into fritter or powder, can be used as filler to join a new polyurethane product, dosage of which can reach 20%. Within the scope of certainty and not affecting the product properties [10], it can be applied to make elastomer, energy absorption foam and sound insulation foam as the main products. Lin [17] shattered rigid polyurethane foam plastics into powder, removed impurities, mixed with polyether polyol and isocyanate, and made product.

In the construction industry, the rigid polyurethane foam powder can be directly added to concrete, in order to improve concrete adiabatic effects. The polyurethane wastes should be grinded to a certain particle size as construction materials of packing, such as roof heat insulating layer. The cement, sand, water and waste rigid polyurethane foam were mixed in the shop roof. As a result, the thermal insulation performance is good, with light quality, and still can ingot nail advantages. In Japan, it has been already used for mortar of light aggregate [12].

Toyota [13] made mudguard by addition10% powder RIM as packing in polyhydric alcohol. It can reduce 4 % -5 % cost. Amor [7] studied the reduction of concrete density and increased pore by addition of the rigid polyurethane foam plastics. In the same volume, adding polyurethane foam wastes can make concrete weight by 29 % -36 % reductions.

3.1.4 Extrusion and injection molding process

Through the thermodynamic function, extrusion can change the molecular chain into medium length, and hard polyurethane material becomes thermoplastic material, which is suitable for high strength, high hardness, but elongated undemanding plastic [11]. For soft microporous polyurethane foam wastes, they can be shattered into powder mixing to thermoplastic polyurethane making soles products [14].

Recycling process of waste thermosetting polyurethane was proposed based on mechanical and physical method. Wu [18] assumed that the plastics had a three-dimensional reticular cross-linkage body structure. The experimental results showed that carbonated group would break at C-O bonding when the device speed exceeded 1500 r/min and the experimental time exceeded 40 min. It meant that cross-linked structure was destroyed and the material resumed a thermoplastic behavior.

3.2. 3.2 Chemical recycling

The polyurethane polymerization is reversible. Function groups such as carbamic acid ester base, ester bond and ether bond will gradually depolymerize for original reactant or other oligomer and even small molecule organic compound under the condition of chemical reagents, catalysts and heating [19-20]. Through the distillation equipment, pure raw material monomer polyol and isocyanate, amine can be obtained [21-34]. Chemical recycling is following the degradation principle. High molecular weight polyurethane depolymerized for a reaction activity of low molecular weight oligomers at different degradation reagents. Oligomers and other compound reacted to prepare new polyurethane products. According to the different degradation reagents, the physicochemical properties and function of degradation products are different. This paper mainly introduces alcoholysis, hydrolysis, and amine solution and phosphate ester method.

3.2.1 Alcoholysis

Under the action of catalyst and low molecular weight alcohol, polyurethane degraded to low molecular weight liquid at a certain temperature. Choosing the right reagent and degradation condition can get high quality polyol, not only with low reaction temperature and short reaction time, but also with higher degradation efficiency. The most important detail is products without complex subsequent handling. It can be used directly as the raw material to preparation of polyurethane products [27]. At present, people generally accepted the reaction mechanism that carbonates was ruptured, replaced with short of alcohol chain, and releasing the long chain polyol and aromatic compounds.

Moreover, the glycolysis of rigid polyurethane foam with potassium acetate as catalyst, triethylene glycol as the agent was investigated. Polyurethane foam was used as raw material to produce preformed polymer. The effect of the amount of the alcohlysis product in the preformed polymer on the physical and mechanical properties of polyurethane waterproof coating was also discussed. The results showed that excellent performance sample was obtained when the recycled polyol content in a component was 20wt%, using potassium acetate as catalyst and the content was 2.0 wt% [28].

Polyurethane foam wastes were recycled by alcoholysis with 1, 2-propanediol. Polyol and amine compound were gained. Polyol compound was analyzed by infrared spectrum. Polyurethane prepolymer was prepared by polyol compound and TDI as A component (OH component), and the ethyl acetate solution of TDI (-NCO component) was prepared as B component (hardener) respectively. Then two-component polyurethane adhesive was gained. The effects of the ratio of the two components and the content of other additives on the properties of the adhesive were also studied [29].

Thermoplastic polyurethane was degraded by glycol and ethanolamine at 170 ℃. The degradation reaction was conducted under nitrogen atmosphere and accelerated by catalysts such as lithium acetate, which was evidenced by lowering the degradation temperature as well as the amounts of degradation reagent. The decomposition products were completely separated into two layers. The upper liquid layer

was a polyether polyol. The present glycolysis procedure allows a simple recycling of the hydroxyl terminated polyol in pure form [30].

3.2.2 Hydrolysis

Hydrolysis method is the use of alkali metal hydroxide as catalyst. Under the action of water vapor in 250-340℃, polyurethane hydrolysis degraded into diamine, polyol and CO_2 in high pressure. The diamine using distillation and extraction methods can be recycled, and polyol was got from hydrolysis residue. In the hydrolysis reaction process, improving the temperature and pressure or solvent existence condition can speed up the reaction rate [10].

Dai [31] compared with the TDA and NaOH as catalyst effect. Adding an appropriate amount of TDA effectively reduced the foam reaction activation energy, reduced reaction temperature, and improved the TDA's recovery. Due to the severe reaction conditions (high temperature and high pressure), equipment requirement and conditions are higher. The products of diamine cannot be directly used in the production of isocyanate. And polyol is also not easily purified, thus making the degradation cost greatly improved, limiting the utilization of this method in real application.

3.2.3 Amine method

Polyurethane foam is easy decomposed and formed the condition of containing hydroxyl and amino compounds in the primary amine, secondary amine compound. Decomposition mechanism is similar to ester exchange reaction. The amino group is active and the reaction can happen under low temperature. Carbamate base, biuret base, urea base formic acid ester and urea group fracture, generated a series of new multiple amine, polyol and aromatic compounds.

Xue [32] degraded the rigid polyurethane foams with fatty amine (such as diethylenetriamine, triethylenetetramine, four ethylidene five amine). The main reaction included the fracture of carbamate base, urea base, biuret base and urea base formic acid ester base, and the generation of polyol, multiple amine and aromatic compounds in the degradation process.

3.2.4 Phosphate ester method

Phosphate ester method is studied by Troev K. [33], putting forward a new method of polyurethane materials degradation. Degradation reaction can happen in 142 ℃ without catalyst. Troev K. speculated that alkylation reaction, free radical reaction and ester exchange reaction happened between polyurethane and phosphate. The final degradation products can soluble in chloroform, tetrahydrofuran, methylene chloride, dimethyl formamide and dimethyl sulfoxide, etc. They also compared with phosphoric acid ethyl ester, triethyl phosphate, chlorine ethyl triethyl phosphate, which degraded the microporous polyurethane elastomer in 180 ℃, the degradation product was liquid, containing phosphorus element or phosphorus and chlorine element oligomer [34]. These products can be used as a non-reactive additive to improve the flame retardant performance. Through the addition of hydroxyl compounds, amine or metal salt processing, they can be used to composite flame retardant polyurethane or flame retardant PVC materials.

Phosphate ester method can be utilized in some relatively mild conditions, but the product is mainly used as packing, and the usage is very limited, so the actual use is also less, which still needs further study.

Table 2 Comparison of different chemical recycling methods

	Degradation reagents	Reaction condition	Products	Application	Recommendation Rate
Alcoholysis	Low molecular	Low temperature	the long chain polyol	high quality polyol, as the	***

	alcohol		aromatic compounds	raw material to preparation of polyurethane products	
Hydrolysis	water vapor	high temperature and high pressure	diamine, polyol, CO_2	polyol can be used as polyurethane raw materials diamine can be translated into isocyanate	*
Amine method	primary amine or secondary amine	Low temperature	multiple amine, polyol, aromatic compounds	polyol can be used as polyurethane raw materials	*
Phosphate ester method	Phosphate ester	Low temperature	phosphorus element or phosphorus, chlorine element oligomer	flame retardant polyurethane or flame retardant PVC materials	*

4. Conclusion

Polyurethane foam wastes can be recycled in various ways, and all kinds of methods all have their advantages and disadvantages. However, recycling is a more desirable way. Physical recycling method, due to the simple operation and relatively active application, in the short term, will be an effective mean. Chemical recycling method, due to its higher technical difficulty, is difficult to achieve large-scale industrialized production in the short term, but in the long run, it will be for the ultimate and effective recycling method. Alcoholysis is effective recycling way, due to mild reaction condition and the good performance of product, and it has widespread attention.

Acknowledgements

The work is financially supported by the Environmental Protection Public Welfare Project (grant number 201109035).

References

[1] Geng J, Feng F, Wang DT. Application of Polyurethane Foams in the Environmental Field and Reuse of the Materials. Materials Review, 2012, 26(2): 78-83.

[2] Xu PL, Zhang SQ. Polyurethane materials manual. BeiJing: Chemical Industry Press; 2002.

[3] Lv SM. Environmental Protection Treatment and Pollution Prevention on Waste Refrigerators. China Environmental Protection Idustry, 2009, 7: 51-57.

[4] Fang Y, Zhao X, Hu JQ, et al. Study on recycling technology of polyurethane from disused refrigerator. Electrical Appliances, 2008, 11: 53-56.

[5] Li X. Comparative study on pyrolysis character of waste plastic between hard and soft polyurethanes. Harbin Institute of Technology, 2006.

[6] Wang W. Study on Recycling and Reuse Technology of WRPUF. North University of China, 2011.

[7] Liu JP, Wang YF, Zheng XX, et al. The reuse of polyurethane wastes. New Chemical Materials, 2010, 38(12): 21-23.

[8] Heejoon Kim, Wataru Minami, Tianji Li. Combustion Characteristics and Pollutant Control by Eco-fuel from Polyurethane Foam. Energy & Fuels,2006, 20: 575-578.

[9] Fukaya T, Watando H, Fujieda S, et al. Reheating decomposition process as chemical recycling for rigid polyurethane foam. Polym Degrad Stab, 2006, 91: 2549.

[10] Wang JR, Chen DJ. The chemical and physical recycling methods for polyurethane wastes. China Elastomerics, 2003, 13(6): 61-65.
[11] Ge ZQ, Xu HX, Li ZY, et al. Treatment and Recovery Methods for Polyurethane Wastes. Chemical Propellants & Polymeric Materials, 2008, 6(1): 65-68.
[12] Cao MG, Cao XR. Recycling and Disposing Methods for Rigid Polyurethane Foamed Plastic Wastes. Plastics, 2005, 34(14): 14-18.
[13] Xu WC, Song WS, Zhu CC, et al. The recycle and reuse of the polyurethane. China Elastomerics, 2008, 18(2): 65-68.
[14] Zhang YX. Recycling Technology of Used Thermosetting Plastics. China Plastics, 1997, 11(3): 56-64.
[15] Jiang BX, Xue HW, Xu B, et al. Waste rigid polyurethane foam plastics recycling regenerative production insulation board. CN1631631, 2005. 06. 29.
[16] Zhong SY, Li DF, Wang GS, et al. Recycling of Polyurethane Foam Composite Waste as Boards. China Plastics, 2011, 15(11): 67-70.
[17] Lin YF. Waste rigid polyurethane foam plastics recycling method. CN101096426, 2008.01.02.
[18] Wu ZW, Liu GF, Liu ZF, et al. Numerical simulation and experimental study on recycle of waste thermosetting polyurethane. China Plastics, 2012, 26(3): 92-98.
[19] Lu GF, Ding YB, Zhao CS, et al. Research development of chemical method recovery waste polyurethane at home and aboard. Chemical Engineer, 2004, 109(10): 45-51.
[20] Al-Salem S M, Lrttieri P, Baeyens J. Recycling and recovery routes of plastic solid waste (PSW): A review. Waste Manag, 2009, 29: 2625.
[21] Datta J, Pniewska K. Syntheses and properties of polyurethanes got glycolysis products obtained from waste polyurethane foams. Polimery, 2008, 53(1): 27.
[22] Zia K M, Bhatti H N, Bhatti I A. Methods for polyurethane and polyurethane composites, recycling and recovery: A review. React Funct Polym, 2007, 67(8): 675.
[23] Borda J, Pasztor G, Zsuga M. Glycolysis of polyurethane foams and elastomers. Polym Degrad Stab, 2000, 68(3): 419.
[24] Lee S H, Ohkita T, Teramoto Y. polyol recovery from biomass-based polyurethane foam by glycolysis. J Appl Polym Sci, 2005, 95(4): 975.
[25] Buggy M, Odriscoll B W. Recovery of polyol from flexible polyurethane foam wastes. Key Eng Mater, 1994, 99: 65.
[26] You K K, Durocher D T, Kierkus P C, et al. Chemical recycling of polyurethane and applications for the recyclates. J Cell Plast, 1998, 34(3): 261
[27] Hu CH, Wang XM, Xu YL. Research Progress of Glycolysis Waste Polyurethanes and Recovery Polyol. Polyurethane Industry, 2008, 23(4): 9-11.
[28] Fu XJ, Xu YJ, Liu SB. Preparation of Polyurethane Water proof Coating Using the Recycled Materials by the Alcoholysis of Rigid Polyurethane Foam. China Plastics Industry, 2011, 39(8): 85-94.
[29] Feng SH, Zuo JD, Liu ZJ. Alcoholysis and application of waste polyurethane. Modern Plastics Processing and Applications, 2004, 16(1): 15-17.
[30] Wang XK, Chen HB, Chen CG, et al. Chemical Degradation of Thermoplastic Polyurethane for Recycling Polyether Polyol. Fibers and Polymers, 2011, 12(7): 857-863.
[31] Dai ZY, BunPei Hatano, Jun-ichi Kadokawa, et al. Effect of diaminotoluene on the decomposition of Polyurethane foam waste in superheated water. Polymer Degradation and Stability, 2002, 76(2): 179-184.
[32] Xue SC, Mitsuru Omoto, Takao Hidai, et al. Preparation of epoxy hardeners from waste rigid polyurethane foam and their application. Journal of Applied Polymer Science, 1995, 56(2): 127-134.
[33] Troev K., Atanasov VI., Tsevi R., et al. Chemical degradation of polyurethanes I: Degradation of microporous polyurethane elastomer by dimethyl phosphonate. Polymer Degradation and Stability, 2000, 67: 159-165.
[34] Troev K., Tsekova A, Tsevi R. Chemical degradation of polyurethanes II: degradation of microporous polyurethane elastomer by phosphpric acid esters. Journal Applied Polymer Science, 2000, 76: 886-893.