

Nylon 66 수지의 압출 작업시 발생하는 휘발성유기화합물에 대한 노출평가

박승현

한국산업안전보건공단 산업안전보건연구원

Exposure Assessment for Volatile Organic Compounds Generated through Extruding Work with Nylon 66 Resin

Seung-Hyun Park

Occupational Safety & Health Research Institute, Korea Occupational Safety & Health Agency

ABSTRACT

Objectives: The purpose of this study was to identify the major volatile organic compounds generated during extrusion work with nylon 66 resin and evaluate causes of discomfort among extrusion workers.

Methods: A thermal decomposition experiment using nylon 66 resin collected at a worksite was conducted in the laboratory. Based on hazards identified through the thermal decomposition experiment, the exposure levels of the workers were evaluated.

Results: The major decomposition products were formaldehyde, acetaldehyde, aniline, cyclopentanone and diphenyl amine. These materials were identical to those sampled in the extrusion booth. The sources of the annoying smells, about which the workers had complained, were formaldehyde, aniline, diphenyl amine, and other hazards in the vapor and fine particles produced by the extrusion work. Formaldehyde, acetaldehyde, and aniline were detected from air samples among workers involved in extrusion work. However, the concentration levels were much lower than Korean occupational exposure limits. The average concentration levels of formaldehyde, acetaldehyde, and aniline were 0.0120 ppm, 0.0036 ppm and 0.0006 ppm, respectively.

Conclusions: The extrusion process at around 300°C thermally decomposes the nylon 66 resin, emitting formaldehyde, aniline, and other hazards, which might have made workers uncomfortable due to their smells. The workers exposure levels to volatile organic compounds were far lower than Korean occupational exposure limits. However, since formaldehyde is a human carcinogen and acetaldehyde and aniline are also confirmed animal carcinogens, it is recommended that exposure levels should be maintained at a minimum level.

Key words : decomposition products, extrusion, nylon 66, volatile organic compounds

I. Introduction

The author of this paper conducted an health hazard evaluation at a worksite, which extrudes Nylon 66 resin to coat break sensors at the request of its health manager. Extrusion of Nylon 66 resin, the last phase of the manufacturing process for break sensors, aims to protect the sensors by coating the surfaces with the resin. First

of all, around 10 sensors are placed on a frame with a pipe, which extrudes melted Nylon 66 resin at 300°C to coat the sensors. This process was carried out at a ventilated booth. However, it still seemed possible for the workers to be exposed to thermal decomposition products from the booth while opening the door to insert a sensor and then take out after coating. Indeed, they had made complaints about uncomfortable smells. To

*Corresponding author: Seung-Hyun Park, Tel: 052-7030-905, E-mail: sh903@kosha.net
Work Environment Research Department, Occupational Safety and Health Research Institute, 400 Jongga-ro, Jung-gu, Ulsan 681-230
Received: September 2, 2014, Revised: September 20, 2014, Accepted: September 18, 2014

This is an Open-Access article distributed under the terms of the Creative Commons Attribution Non-Commercial License(<http://creativecommons.org/licenses/by-nc/3.0>) which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

address the issue, the employer asked the author's institute to deliver an assessment on the hazards, which were produced by the Nylon 66 resin extrusion.

Nylon 66 is polymers composed of organic acids called adipic acid and amine compound called hexamethylene diamine, as shown in Figure 1(Source: Smith et al., 2012; Wikipedia). The molecular structure of Nylon 66 is composed of functional groups like an amide(O=C-NH) group, an amine(NH₂) group, and a ketone(C=O) group. Therefore, when the material is thermally decomposed, diverse compounds such as amide, amine and ketone compounds can be produced. According to an material safety data sheet(MSDS) on the monofilament produced from Nylon 66 and nylon 6 resin, it has carbon monoxide, ammonia, aliphatic amines, amides, and ketone compounds as its thermal decomposition products(Jarden applied material, 2008). Another MSDS illustrates that hazardous gasses or vapors can be released including ammonia, carbon monoxide, cyclopentanone, hydrogen cyanide, and nitrogen oxide as its decomposition products(Ensinger, 2010). The decomposition products vary depending on which bonds are broken and reconnected. It has been known that thermal decomposition of Nylon 66 produces byproducts such as amine compounds(-NH₂), isocyanate compounds(-NCO), nitrile compounds(-CN) due to breakage of N-C or C-C bonds(Lee & Kim, 2014). According to the research article of Puglisi et al.(2002), when nylon 66 was heated at 315°C for 60 min its intrinsic viscosity dropped noticeably and amino groups and cyclopentanone chain ends were generated in the heating process. Ballistreri et al.(1988) have proved that Nylon

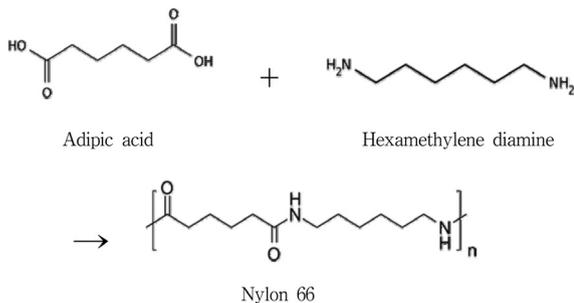


Figure 1. Structure of Nylon 66

66 creates cyclopentanone and amine compounds as thermal decomposition products. Smith et al.(2012) reported that acetone, ammonia, cyclopentanone, methylethylketone(MEK), 2-pentanone, and pyridine can be produced as thermal-oxidation degradation products of nylon 66.

The purpose of this study was to identify the major volatile organic compounds generated during extrusion work of Nylon 66 resin and evaluate causes which might have made extrusion workers uncomfortable.

II. Materials and Methods

1. Method to thermally decompose Nylon 66

About 10g of the bulk sample of Nylon 66 resin, which had been collected for a preliminary survey at the worksite, was heated in an erlenmeyer flask by a hot plate at 300°C. By using a personal air sampler and different types of absorption tubes, thermally decomposed products were collected. Although the temperature of the hot plate was kept at 300°C, the surface of the erlenmeyer flask hovered around 220°C~240°C. The melting point of Nylon 66 is about 260°C(KOSHA website), while the worksite melted Nylon 66 at 300°C. Therefore, the lab could not reach the melting point. However, vapor and other thermally decomposed materials were witnessed. The bulk samples had been collected from the resins produced by the manufacturers *D* and *B*. The worksite was using the *D* product, but it was considering turing to *B*. For sampling, a charcoal tube, a silica gel tube, and a 2,4-DNPH(2,4-Dinitrophenyl hydrazine) coated silica gel tube were used. The charcoal tube was utilized to collect general VOCs produced by heat while the silica gel tube was for aliphatic and aromatic amine. And, the 2,4-DNPH coated tube was to get formaldehyde and acetaldehyde. For quantitative and qualitative analyses on formaldehyde and acetaldehyde, the HPLC-UV(360 nm) system(Alliance System, Waters, USA) was introduced. And, in order to qualitatively assess the samples collected by the

charcoal and silica gel tubes, the GC-MS(Saturn 2000, Varian, USA) was used, while the GC-FID(5890, HP, USA) was harnessed for the quantitative analysis. Since only aniline and diphenyl amine have the exposure limits, their ingredients were analyzed at the lab. In terms of other materials, the ingredients were assumed according to the database(Wiley 6 & NIST 98) presented by the GC-MS.

2. Methods to assess the work environment

Acetaldehyde, formaldehyde, aniline, and diphenyl amine among the thermal decomposition products were the materials with occupational exposure limits. Therefore, the author evaluated the concentration of these hazardous chemicals exposed to the workers, who extruded Nylon 66. Moreover, the air velocity through the booth door was estimated to understand how well the space was being ventilated.

2-1. Sampling and analysis

1) Aldehyde compounds

In order to collect and analyze formaldehyde and acetaldehyde, the methods presented by EPA (Environmental Protection Agency) TO 11A and NIOSH(National Institute for Occupational Safety and Health) 2016 were taken into consideration. The samples were collected by a personal air sampler at the flow rate of 0.2 L/min with a silica gel tube coated with 2,4-DNPH. The collected samples were desorbed by acetonitrile. Then, they were analyzed by the HPLC-UV(360nm) system(Alliance System, Waters, USA). The HPLC column for the sample analysis was Nova Pak-C18(length × diameter: 150mm × 3.9mm, Waters, USA)

2) Aniline

In order to collect and analyze aniline, the method presented by NIOSH 2002 were referred. The samples were collected by a personal air sampler at the flow rate of 0.2 L/min with a silica gel tube. The collected samples were desorbed by ethanol. Then, they were

analyzed by the GC-FID system(5890, HP, USA). The GC column for the sample analysis was HP-5(length × diameter: 30m × 0.32mm, HP, USA).

3) Diphenyl amine

In order to collect and analyze diphenyl amine, the method presented by OSHA 78 was referred. The samples were collected by a personal air sampler at the flow rate of 1.0 L/min through a glass fiber filter treated sulfuric acid. The collected samples were desorbed by methanol. Then, they were analyzed by the HPLC-UV(285 nm) system(Alliance System, Waters, USA). The HPLC column for the sample analysis was Nova Pak-C18(length × diameter: 150mm × 3.9mm, Waters, USA)

4) Qualitative analysis for the samples collected in the extrusion booth

The thermal decomposition experiment discovered that a variety of chemicals including aldehyde, amine, amide, and ketone compounds were created by thermal decomposition of Nylon 66. However, the conditions at the lab were not identical to those at the worksite. Therefore, the author collected the vapor in the extrusion booth, where the workers would be at risk of high exposure. The collected samples were analyzed by using GC-MS(Saturn 2000, Varian, USA) for qualitative analysis. Database for library search was wiley 6 & NIST 98. In this way, the hazards would be qualitatively assessed accurately. The GC column was HP-5(length × diameter: 30m × 0.32mm, HP, USA).

2-2. Ventilation status of Nylon 66 extrusion booth

The extrusion process of Nylon 66 can be categorized into the two parts—inserting break sensors with the door open and extruding Nylon 66 with the door closed. The booth at the worksite was not completely sealed, because every corner of the booth had around 5 cm gap even with the door closed. To assess the ventilation status, the air velocity was measured with the door both closed and opened by using anemometer(8575, ALNOR, USA).

III. Results and Discussion

1. Results of Nylon 66 thermal decomposition

By heating Nylon 66 at 220 - 240°C, thermal decomposition products were gained including aldehyde, amine, and ketone compounds. The aldehyde compounds were qualitatively analyzed by HPLC, while other materials were assessed by GC-MS.

1) Thermal decomposition products of Nylon 66 manufactured by *D*

Table 1 presents the results of the GC-MS qualitative analysis on thermal decomposition products of Nylon 66 manufactured by *D*. It shows the decomposition products collected through a silica gel and a charcoal tube respectively. Considering the molecular structure of Nylon 66 and the analysis results, aniline was produced in the process of Hexamethylene diamine(HMDA) of the Nylon 66 structure turning to an aromatic ring due to thermal decomposition. Cyclopentanone also took the form of the ring structure from adipic acid(AA), an ingredient of Nylon 66. Diphenylamine was also created by linking the aromatic rings of HMDA and AA. Therefore, it can be understood that aniline, cyclopentanone, and diphenyl amine came from the Nylon 66 structure in the process of thermal decomposition. The silica gel tube collected a larger volume of aromatic amine compounds than the charcoal tube. The NIOSH method has already recognized its characteristic to seize the compounds better than other tubes.

Table 1. Major decomposition products collected from Nylon 66 of company D

Components collected by silica gel tube	Components collected by charcoal tube
Cyclopentanone	Cyclopentanone
Diphenyl amine	Diphenyl amine
Aniline	Others
Others	

2) Thermal decomposition products of Nylon 66 manufactured by *B*

Table 2 presents the GC-MS analysis on decomposition products of Nylon 66 manufactured by *B*. It shows the compounds collected by a silica gel tube and a charcoal tube respectively. The analysis results on *B* can be explained in the similar context of *D*. However, *B* shows a higher proportion of aromatic amine compounds compared to *D*.

Since *B* and *D* have different manufacturing technologies, the proportion of aromatic amine compounds in *B* was higher, which is well illustrated by Figure 2(*Product D*) and 3(*Product B*). They present Nylon 66 on the flasks,

Table 2. Major decomposition products collected from Nylon 66 of company B

Components collected by silica gel tube	Components collected by charcoal tube
Diphenyl amine	Diphenyl amine
p-Isopropyl diphenyl amine	p-Isopropyl diphenyl amine
Cyclopentanone	Others
Aniline	
Others	



Figure 2. Nylon 66 clots on the flask(*Product D*)



Figure 3. Nylon 66 clots on the flasks(*Product B*)

which had been heated by the hot plate. Both of the samples were melted and clotted. Although *Product D* was melted at some degree, it maintained the previous bead form. However, *Product B* was mostly melted. And, when it was cooled, the flask had some cracks due to contraction. The products were melted in the same conditions including the temperature. It was witnessed that *Product B* was melted at a higher speed, creating a significant amount of vapor and fine particles. In other words, the thermal decomposition processes were different between *B* and *D*. Since the degree of cohesion varied, *Product B* had a more active reaction of forming an aromatic ring on the HMDA part(The amine group). Although *Product B* was melted more easily, emitting more vapor, the proportion of aniline, which has an exposure limit, was higher in *Product D*. Therefore, it is difficult to determine which product is safer. In this context, it is necessary to secure adequate information on the products from the manufacturers when the worksite seeks to select its supplier of the Nylon 66 resin for extrusion.

2. Results of exposure assessment at the workplace

1) Concentration of hazards in the extrusion booth

The author conducted quantitative and qualitative analyses on the vapor in the extrusion booth, where the workers were at the risk of high exposure, while the system was being purged. The results were compared to those of the lab analysis(Thermal decomposition experiment) to obtain accurate assessments on the hazards which had actually affected workers. In the vapor, formaldehyde, acetaldehyde, aniline, cyclopentanone, and diphenyl amine were detected. Table 3 shows that the concentrations of these materials with occupational exposure limits except cyclopentanone.

Table 4. Exposure concentration of extrusion workers

Decomposition product	No. of samples	Exposure concentration (average ± standard deviation)	Occupational exposure limit
Formaldehyde	3	0.0120 ± 0.0009 ppm	0.5 ppm
Acetaldehyde	3	0.0036 ± 0.0011 ppm	50 ppm
Aniline	3	0.0006 ± 0.0001 ppm	2 ppm

Table 3. Concentrations of decomposition products in the extrusion booth

Decomposition product	Concentration
Formaldehyde	0.017 ppm
Acetaldehyde	0.038 ppm
Aniline	0.914 ppm
Diphenyl amine	0.671 mg/m ³

The decomposition products in the extrusion booth were identical to those in the lab tests. The concentrations of formaldehyde, acetaldehyde, aniline, and diphenyl amine were 0.017 ppm, 0.038 ppm, 0.914 ppm, and 0.671 mg/m³ respectively. It needs to be taken note that at the lab analyses, several aromatic amine compounds were detected, while other materials did not appear in the analysis on the booth sample except formaldehyde, acetaldehyde, aniline, cyclopentanone, and diphenyl amine.

2) Workers exposure concentration

The author carried out analyses on workers exposure concentrations of the material with occupational exposure limits including formaldehyde, acetaldehyde, aniline, and diphenyl amine, which were proven to be emitted during the lab analysis on thermal decomposition products. As presented in Table 4, diphenyl amine, which appeared in the analysis on the extrusion booth, was not found.

The concentration levels were found to be far lower than Korean occupational exposure limits(OELs). For example, the average exposure level of formaldehyde was 0.0120 ppm, 2.4% of the OEL(0.5 ppm). Acetaldehyde also showed a very low concentration level(0.0036 ppm) while its OEL is 50 ppm. The concentration of aniline

was a mere 0.0006 ppm(the OEL is 2 ppm). In addition, although formaldehyde and acetaldehyde were found, the concentrations levels were similar to those around the area about 10 meters away from the extrusion process, which were 0.0093 ppm and 0.0022 ppm respectively.

3) Evaluation on the ventilation of the Nylon 66 extrusion booth

The booth door opened frequently. In addition, since it was not completely sealed, the booth corners were always open. When the door was opened, the air velocity was 0.15 - 0.3 m/s. And, when it was closed, the air velocity was 0.2 - 0.5 m/s. It was observed that when the door was closed, the air current in the lower part of the gate was dispersed. It is assumed that the air current in the lower part, which is relatively slow, was disturbed by the current at the worksite. In addition, some workers were using electronic fans, making the ventilation difficult. Therefore, the ventilation system's efficiency should be improved through the inspection, although the concentration of the hazards was much lower than the occupational exposure limits since the workers made complaints about the uncomfortable smells.

3. Health hazards and smells of the thermal decomposition products

Considering the complaints about the irritating smells of the vapor and fine particles produced during the extrusion, the author referred to MSDS and ACGIH 2010 documentation to obtain the information on the health hazards and smells of the hazards, which were proven to appear by the thermal decomposition analyses and the

assessment on the work environment. As Table 5 shows, the materials have their unique irritating smells, some of which stimulate the body.

IV. Conclusions

The workers involved in the extrusion of Nylon 66 had made complaints about the irritating smells of the vapor and fine particles. Against this backdrop, the author conducted the evaluation on health hazards, which would be caused by the extrusion work. The results of the evaluation are as follows.

The Nylon 66 resin was heated and thermally decomposed at 220 - 240°C. The major decomposition products were formaldehyde, acetaldehyde, aniline, cyclopentanone and diphenyl amine. These materials were identical to those sampled in the extrusion booth.

The sources of the annoying smells, about which the workers complained, were formaldehyde, aniline, diphenyl amine, and other hazards in the vapor and fine particles produced by the extrusion work. Formaldehyde is a carcinogen with an irritating odor. Aniline is an animal carcinogen, which causes oxygen deficiency with fish-like smell. Diphenyl amine also stimulates the body with an irritating odor.

Formaldehyde, acetaldehyde, and aniline were detected from air samples of workers involved in the extrusion work. However, the concentration levels were much lower than Korea's occupational exposure limits. The average concentration levels of formaldehyde, acetaldehyde, and aniline were 0.0120 ppm, 0.0036 ppm and 0.0006 ppm respectively.

In the same test conditions, the Nylon 66 resins of

Table 5. Health hazards and smells of the Nylon 66 thermal decomposition products

Decomposition products	Health hazards	Carcinogenicity	Smell
Formaldehyde	Irritation, cancer	1A	Pungent, irritating odor
Acetaldehyde	Irritation	2	Fruity or pungent odor
Aniline	Increase in methemoglobin	2	Fish-like
Cyclopentanone	Irritation	-	Mint
Diphenyl amine	Liver, kidney or blood dyscrasia, irritation	-	Flower, irritating odor

both *B* and *D* created decomposition products, albeit some differences in the proportions. *Product B* was melted at a higher speed, emitting more fine particles and aromatic amine compounds. Meanwhile, *Product D* had a higher proportion of aniline compared to *B*. Therefore, it is necessary to secure adequate information on the products from the manufacturers when the worksite seeks to select its supplier of the Nylon 66 resin for extrusion.

In conclusion, the extrusion process at around 300°C thermally decomposes the Nylon 66 resin, emitting formaldehyde, aniline, and other hazards, which might have made workers uncomfortable due to their smells. However, since the exposure concentrations in the work conditions were far lower than Korean occupational exposure limits, it is assumed that the health of the workers would not be affected unless they are highly sensitive. But, since formaldehyde is a human carcinogen and acetaldehyde and aniline are also confirmed animal carcinogens, it is recommended that the exposure level should be maintained at a minimum level.

References

- American Conference of Governmental Industrial Hygienists (ACGIH). Documentations of the Threshold Limit Values and Biological Exposure Indices. ACGIH, 2010
- American Conference of Governmental Industrial Hygienists (ACGIH). Threshold Limit Values(TLVs) for Chemical Substances and Physical Agents and Biological Exposure Indices(BEIs). ACGIH, 2014
- Ballistreri A, Garozzo D, Giuffrida M, Impallomeni G, Montaudo G. Primary thermal decomposition processes in aliphatic polyamides. *Polym Degrad Stab* 1988;23:25-41
- Edinburg plastics, Inc. Material safety data sheet: Nylon-66 thermoplastic resin. 2007
- Ensinger. Material safety data sheet: TECAMID Nylon 6/6 & TECAMID HS Nylon 6/6. 2010
- Environmental Protection Agency(EPA). Compendium of methods for the determination of toxic organic compounds in ambient air(Compendium method TO-11A): Determination of formaldehyde in ambient air using adsorbent cartridge followed by high performance liquid chromatography(HPLC). EPA, Cincinnati(OH); 1999
- Korea Occupational Safety and Health Agency(KOSHA). KOSHA Chemical Information Center, MSDS/GHS. [cited 2014 Aug 4]; Available from <http://www.kosha.or.kr>
- Lee BY, Kim YC. Study on the physical properties of nylon66/glass fiber composites as a function of extrusion number. *J Korea Acad Industr Coop Soc* 2014;15(6):3990-3996
- National Institute for Occupational Safety and Health (NIOSH): NIOSH Manual of Analytical Method (NMAM) 2002, 4th Ed., 1994
- National Institute for Occupational Safety and Health (NIOSH): NIOSH Manual of Analytical Method (NMAM) 2016, 4th Ed., 1994
- Occupational Safety and Health Administration(OSHA). Sampling and Analytical Methods No. 78: Diphenylamine/n-Isopropylaniline, 1989
- Puglisi C, Samperi F, Giorgi SD, Montaudo G. MALDI-TOF characterisation of thermally generated gel from Nylon 66. *Polym Degrad Stab* 2002;78:369-378
- The Ministry of Employment and Labor of Korea. Occupational Exposure Limits on Chemical Substances and Physical Agents. Notification of the Ministry of Employment and Labor of Korea, No. 2013-38, 2013
- Smith JN, White GV, White MI, Bernstein R, Hochrein JM. Characterization of volatile nylon 6.6 thermal-oxidative degradation products by selective isotopic labeling and cryo-GC/MS. *J Am Soc Mass Spectrom* 2012;23:1579-1592
- Wikipedia. Nylon 6-6. [cited 2014 Aug 4]; Available from http://en.wikipedia.org/wiki/Nylon_6-6