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Case Report

유리섬유강화 플라스틱을 이용한 적층공정 근로자들의 스티렌 노출 평가: 보건진단 사례

최상준[1] · 정연희[2]

[1]대구가톨릭대학교, [2]원진노동환경건강연구소

Exposure to Styrene in the Lamination Processes with Fiberglass-Reinforced Plastics: Health Diagnosis Case Report

Sangjun Choi[1] · Yeonhee Jeong[2]

[1]*Department of Occupational Health, Catholic University of Daegu*
[2]*Wonjin Institute for Occupational and Environmental Health*

ABSTRACT

연구목적: 이 연구는 노동부의 보건진단 명령에 의해 유리섬유 강화플라스틱(FRP)을 이용한 이중벽 탱크 제조 사업장의 적층 공정 근로자들을 대상으로 스티렌 노출 특성을 평가하기 위해 수행되었다.

연구방법: 스티렌의 주요발생원 파악을 위해 불포화 폴리에스테르 수지(UPR), 경화제, 조색제, 세척액 등의 원료 내 스티렌 함유량을 가스크로마토그래피 질량분석기(GC-MS)를 이용하여 분석하였다. FRP 적층 공정에 근무하는 작업자들을 대상으로 NIOSH 1501 공정시험법에 의해 공기 중 스티렌 노출 농도에 대한 개인노출 평가를 실시하였고, 생물학적 노출 지표로 뇨 중 만델릭산을 채취한 후 고성능액체크로마토그래피(HPLC)로 분석하였다. 또한 각 직무 특성과 단위작업 중심으로 스티렌에 대한 단시간 노출평가를 수행하였다.

연구결과: 스티렌의 함유량이 가장 많은 주요 원료는 중량비율로37%의 스티렌이 함유된 UPR이었다. 적층 공정의 FRP분무 작업자와 보조 작업자들 모두 스티렌의 8시간 가중평균 노출기준(20 ppm)을 초과하였다. 단시간 노출평가 결과 FRP 분무 작업자의 경우 45.9 ppm에서 86.1 ppm 수준으로 FRP를 사용하지 않는 작업보다 통계적으로 유의하게 높은 수준이었다(P<0.01). 가장 높은 수준의 스티렌에 노출되는 단위작업은 FRP를 이용하여 1차 코팅 하는 작업으로 특별한 관리가 필요하였다.

결론: 보건진단을 위해 실시한 이중벽 탱크 제조 사업장의FRP 적층 공정 작업자의 스티렌 노출수준은 노출기준을 초과할 정도로 높은 수준이었다. 그러나 탱크를 천장에 매달고 돌리면서 적층작업을 수행하기 때문에 적절한 국소환기 시스템을 구축하는데 어려움이 있다. 따라서 적절한 방독마스크 착용으로 스티렌 노출 예방이 필요하였다.

Key words: FRP, mandelic acid, styrene

I. Introduction

Styrene is the ideal monomer used for cross linking Fiberglass-Reinforced Plastic(FRP) resins. Thus, workers in the lamination process of the FRP manufacturing industry are still a high risk group for exposure to styrene in Korea(Cho et al., 2008). Various studies on possible adverse health effects on workers exposed to styrene have been reported such as neurotoxic effects on color vision(Paramei et al., 2004),

*Corresponding author: Sangjun Choi, Tel: 82-53-850-3738, Fax: 82-53-850-3736, E-mail: junilane@gmail.com
Department of Occupational Health, Catholic University of Daegu, 13-13, Hayang-ro, Hayang-eup, Gyongsan, Gyongbuk, 712-702, Korea
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the peripheral and autonomic nervous system(Yuasa et al., 1996), neurobehavioral performance(Seeber et al., 2004) and the vibration perception threshold(Sato et al., 2009).

During styrene's human metabolic process, approximately 85% of the inhaled amount is eliminated as mandelic acid(MA) in urine, 10% as phenylglyoxylic acid(PGA), and 1% as styrene in exhalation(ACGIH, 2001). MA can be used as biomarker of exposure to styrene.

In the 2007 special health examination, the biological exposure index of styrene exceeded the criteria for 2 workers in a small sized under storage tank(UST) manufacturing company, and the Ministry of Labor called for the health diagnosis based on this result. So, we conducted an identification of styrene sources, a characterization of workers' exposure to styrene by jobs and tasks, as well as biological monitoring.

Ⅱ. Materials and methods

1. Subjects

We surveyed a factory which has a lamination process with FRP for manufacturing double walled UST between July and August in 2008. FRP lamination is a process to manufacture double walled tanks by spraying FRP with unsaturated polyester resin(UPR), hardner and toner on the surface of UST made of bare steel.

2. Identification of styrene

The major sources of styrene were evaluated by a review of the material safety data sheets(MSDS) of raw materials used and ingredient analysis using gas chromatography with mass spectrometry(GC-MS; HP 6890 plus, Agilent 5973, USA). Each sample was collected at 10 ul with a micro syringe, diluted with methanol, and analyzed with GC-MS. In case of viscous samples, some amount was weighed, followed by dissolution in methanol, and a part of upper liquid separated was analyzed. For qualitative analysis, the substance with match rate of 80% or higher with Wiley-library at scan mode were estimated as ingredients; contents of styrene ingredients were verified with quantitative analysis at SIM mode.

3. Air sampling and analysis

The attempted measurements were both long-term (8h-TWA) to evaluate total exposure from all occupational sources and short-term(task based samples with duration of less than one hour) to investigate identified tasks with potentially elevated exposures. For assessment of 8h-TWA styrene in air, consecutive two samples were taken from one worker by considering breakthrough. The flow rates(0.2 L/min for short-term sampling and 0.1 L/min for long-term sampling) of portable sampling pumps(LFS-113, Sensidyne, LP) used to collect samples were selected to ensure that sufficient contaminants were collected on the samples for analysis. All pump flow rates were calibrated before and after sampling using a primary flow calibrator(Gilian Gilibrator 2 Calibration System; Sensidyne, LP).

All charcoal tube(SKC 226-01, SKC Inc.) samples were analyzed for styrene by gas chromatography with flame ionization detector using National Institute for Occupational Safety and Health(NIOSH) method 1501 (NIOSH, 2003) in Wonjin Institute for Occupational and Environmental Health laboratory that are being quality controlled under the NIOSH proficiency analytical testing program. The results of analysis were adjusted by analyzing blanks and desorption efficiency with each batch of samples analyzed.

4. Measurement of mandelic acids(MA) in urine

Five workers in lamination process with FRP were classified as a styrene exposure group and 3 office workers with no occupational exposure to styrene were classified as a control group. The participating subjects signed informed consent forms and urine samples were collected at pre- and post-shift work. Collected samples were stored as frozen, rapidly transferred to a laboratory to be analyzed for MA, a styrene metabolite within 24h.

Urinary MA concentrations were measured by high performance liquid chromatography(Waters 2690, USA) with ultraviolet detector(Waters 2487, USA) according to the methods developed by Occupational Safety and Health Research Institute(OSHRI) in Korea(OSHRI, 2006). Urinary MA concentrations were expressed in mg/g creatinine Cr). In addition, as a variable with potential influence on the MA concentration, the amount of alcohol consumption in the evening prior to sampling was investigated.

5. Statistical analysis

An 8h-TWA styrene in air were calculated with consecutive two samples taken in the morning and afternoon. Statistical analyses were performed by Student's t-test for short-term exposure levels by tasks and MA concentrations in urine by shifts or exposure groups. $P<0.05$ was considered to be significant. The data were analyzed using SPSS version 12.0K for windows.

III. Results

1. Characteristics of subjects

The operation process of manufacturing a major product, a 50,000 L tank, was to clean the surface with an air gun after the feeding of a steel tank, followed by spraying with the mixture of UPR(400 kg), hardner(400 ml) and toner(500 ml) along with fiber glass(80 kg). Coating takes placed over 4 times and after the first coating, mesh and polyethylene film are attached upon the tank surface to form a double wall. Basic characteristics of FRP lamination process is presented in Table 1.

There were a total of 5 workers including one sprayer who conducted coating by spraying the mixture of FRP, UPR, hardner and toner, three helpers engaged in rolling to prevent bubble formation during coating and for even lamination of the surface, and one inspector who undertook the examination of the final product quality. In terms of job characteristics of 5 workers, a sprayer conducted coating by spraying with the mixture of FRP, UPR, hardner and toner on a tank, helper 1 and helper 2 did rolling operation next to and on the opposite side of a sprayer, respectively around the tank, and helper 3 was assisting the helper 1 or helper 2.

Figure 1. Photograph of local exhaustive ventilation in the lamination workplace

Table 1. Basic characteristics of lamination process

Item	Characteristics
Product	Double wall underground storage tank(Capacity ; 50,000 ℓ)
Major tasks	Coating, Spraying, Rolling, Inspection
Workers	Sprayer(1), Helper(3), Inspector(1)
Raw materials per tank	Fiberglass 80 kg, Resin 400 kg, Hardener 400 ㎖ and Toner 500 ㎖
Temperature	28~32℃
Relative humidity	30~50%
Control strategy	Local ventilation, Personal protective equipment(Purifying respirator)

For a LEV system for the lamination process, a steel tank was installed as shown in Figure 1 and hoods were installed to the upside of a tank at 3 sites where lamination operation can be conducted. The ordering of the components to a LEV system was hood, duct, fan, and stack, without air cleaner. The second LEV system placed at the center of the workplace was not functioning as the duct linked to the fan outside the workplace was disconnected. The capture velocity for two functioning LEV systems measured at the 20 cm apart from the top surface of a tank was 0 m/s, and exhaustive velocity at the stack was measured as 2-3 m/s. PPEs including cotton gloves and air purifying respirator for organic solvents(3M, 6006 multi gas & vapor cartridge) were provided but the exchange period of cartridge was irregular.

2. Identification of styrene within raw materials

The major raw materials used in lamination operation were fiber glass, UPR, hardner, and toner. Cleaner was also used for rolling operation. A

Table 2. Identification of raw materials

Classification	MSDS		GC/MS		
	Chemical name	Amount, %	Chemical name	Relative abundance, %	Amount, %(w/w)
Cleaner	Acetone*	100	Acetone*	98.2	
			Isopropyl alcohol	1.8	
Hardner	Methyl ethyl ketone*	50-56	Acetaldehyde	0.1	
	Methyl phthalate*	50-44	Acetic acid	0.9	
			Ethanol	0.4	
			Ethyl acetate	0.2	
			Methyl benzoate	0.1	
			Methyl ethyl ketone*	8.7	
			Methyl phthalate*	87.9	
			Phthalic anhydride	0.1	
			Unknown	1.7	
Resin	Styrene*	31-39	N,N-dimethyl bezenamine	0.4	
	Unsaturated polyester	61-69	Phthalic anhydride	3.2	
			Styrene*	90.2	36.8
			Toluene	0.3	
			Unknown	5.9	
Toner	Pigments	70-30	1,2-propanediol	4.2	
	Unsaturated polyester	30-70	2-(2-butoxyethoxy)ethanol	31.1	
			2-ethoxyethyl acetate	21.7	
			Butyl phthalate	3.5	
			Ethyl benzene	0.5	
			Phthalic anhydride	6.6	
			Styrene	8.3	0.6
			Xylene	1.3	
			Unknown	18.3	

* : chemicals matched with MSDS

comparison of the analysis result of UPR, hardner, toner and cleaner with MSDS and GC-MS is presented in Table 2.

From GC-MS analysis results, styrene was identified in UPR and toner that were used during lamination operation at the largest amount. In the case of UPR, the styrene content was 37%(w/w) which was comparable to MSDS. Although not specified in MSDS, toner was found to contain 0.6%(w/w) of styrene. In all 4 substances, additional substances were identified other than ingredients specified in MSDS; in particular, 8 substances including styrene were detected in toner although specific ingredients are not described in MSDS.

3. Exposure assessment of airborne styrene

For assessment of 8h-TWA styrene in air, two consecutive samples were taken from one worker by considering breakthrough; the results are shown in Fig. 2. In terms of jobs, measurements in the morning when most of the lamination operation took place were from 37.8 ppm to 52.5 ppm for all 4 workers after excluding the inspector who conducted the inspection outside the process, all exceeding the Korean occupational exposure limit(20 ppm); The 8h-TWA concentration was 26.7-29 ppm for 3 workers excluding the inspector and helper 3, also exceeding the exposure limit.

In the operation steps in the lamination process, the tank is put in the workplace, followed by preliminary coating with only a hardner and UPR, not using FRP, followed by the first coating with FRP, the second coating, the third coating with hardner and UPR only, and finally, the fourth FRP coating for the sides of the tank. The short-term exposure concentration of styrene was measured for 15 min in each operation step, and the results are shown in Fig.3. The short term exposure level of styrene for spraying with FRP ranged from 45.9 ppm to 86.1 ppm, significantly higher than the case without FRP(P<0.01). In particular, the short-term exposure concentration showed a mean of 82.5 ppm during the first FRP coating, almost two times higher than STEL of 40 ppm.

4. Biological monitoring of styrene

The results of the MA concentrations in urine are presented in Table 3. The MA concentrations in urine

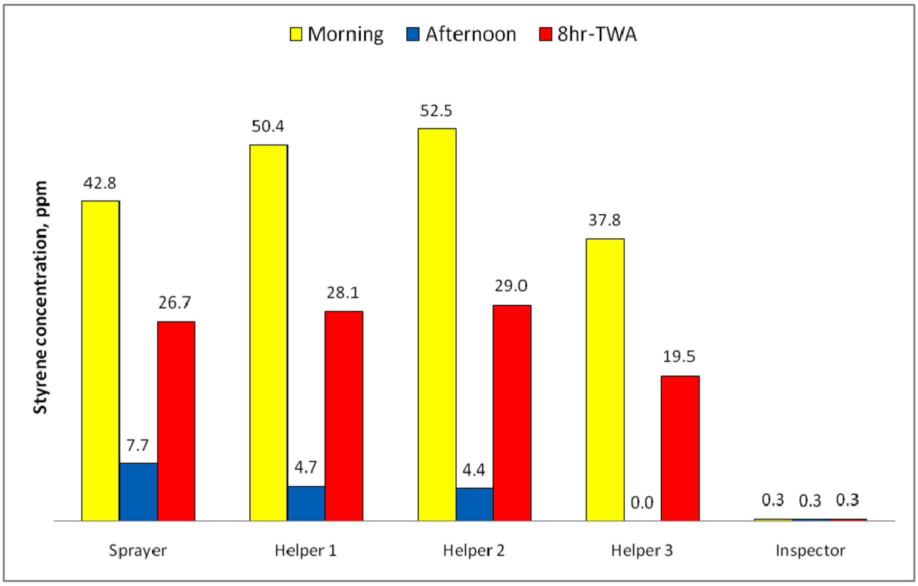

Figure 2. Airborne 8-hr time weighted average concentrations of styrene by job

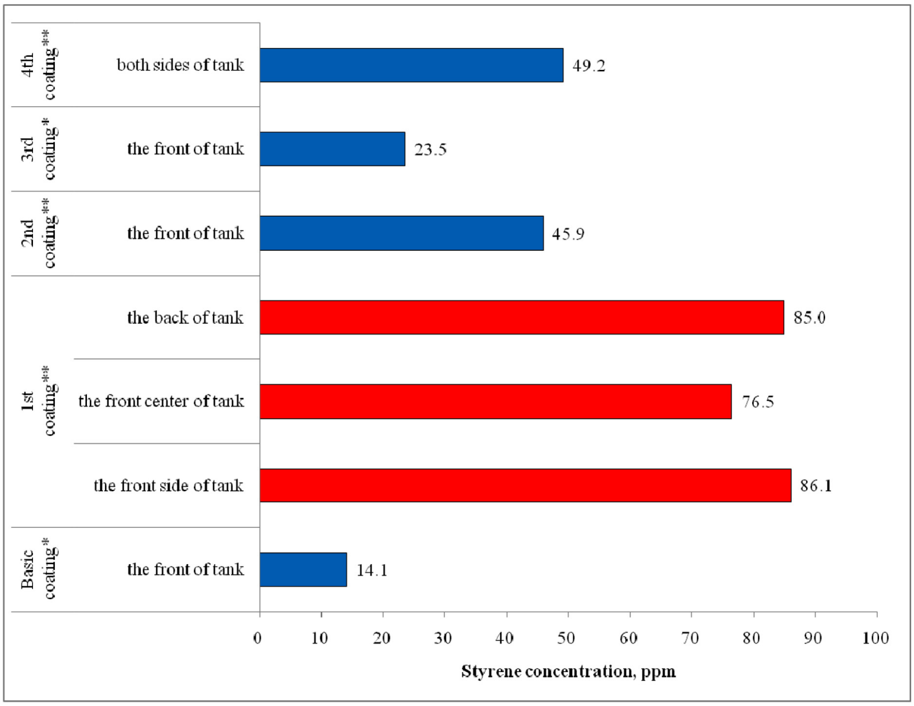

Figure 3. Airborne short term exposure level of styrene by tasks. *Coating without FRP. **Coating with FRP

Table 3. The concentration of styrene in air and mandelic acid in urine

Group	Job	Gender	Major workplace	Mandelic acid in urine, mg/g creatinine		Styrene in air, ppm	Ingestion of alcohol[a], g
				Pre-Shift	Post-Shift		
Exposure	Sprayer	Male	In the lamination process	37.7	42.3	26.7	None
	Helper 1	Male	In the lamination process	35.0	31.8	28.1	None
	Helper 2	Male	In the lamination process	76.0	84.8	29.0	None
	Helper 3	Male	In the lamination process	114.2	118.6	19.5	118
	Inspector	Male	Out of the lamination process	33.9	51.5	0.3	142
	Arithmetic mean			59.4	65.8		
	Standard deviation			35.3	35.6		
Control	Office worker1	Male	In the office	47.0	50.8	NA[b]	None
	Office worker2	Male	In the office	66.6	56.3	NA	None
	Office worker3	Male	In the office	55.2	54.2	NA	None
	Arithmetic mean			56.3	53.8		
	Standard deviation			9.8	2.7		

[a]: Alcohol ingestion of the evening before urine sampling[b] : Not available

ranged from 31.8 mg/g Cr to 118.6 mg/g Cr. The results were less than 15% of the domestic biological exposure index standard, and there was no statistical difference between the exposure group and the control group(pre-shift, P=0.89; post-shift, P=0.59). In addition, when drinking in the evening of a pre-shift day was investigated, helper 3 consumed a half bottle of vodka(250㎖) with 60% alcohol concentration, the inspector was found to have consumed 2 bottles of soju, Korean distilled spirits, with 25% alcohol concentration;

when the amount of ethanol was calculated by using ethanol density(0.789 g/㎖ @ 20℃), they had consumed 118 g and 142 g, respectively.

IV. Discussion

UPR used in the lamination process is known as a major source of styrene generation, and the styrene contents for optimizing the property of UPR as a linkage is known as 30-45%(Fradet & Arlaud, 1989). In this study, the UPR with the highest amount of use was also found to contain 37%(w/w) styrene, followed by toner with 0.6%(w/w)(Table 2).

The 8h-TWA exposure level of styrene for the spryer and helpers ranged from 19.5-29.0 ppm, similar to the exposure level in Europe in the 1990s(Van et al., 2008)(Figure 1). In details by each operation, styrene exposure level was helper 2(29 ppm) > helper 1(28.1 ppm) > sprayer(26.7 ppm) > helper 3(19.5 ppm) > inspector(0.3 ppm), showing the highest concentration for helper 2.

The short-term exposure assessment of styrene by operation steps showed that the exposure level during coating with FRP was significantly higher than the exposure level without FRP. In addition, the styrene exposure concentration during the first coating after the initial preliminary coating(82.5±5.2 ppm) was more than double the exposure limit, showing a statistically significant difference from the exposure level during other operation steps(33.2±17 ppm) (P=0.005). The current Regulation on Dangerous Goods Safety Management Act in Korea for underground storage double wall tank manufacturing stipulates that FRP is to be coated on tank surfaces at 3mm or more thickness(MGAHA, 2004). Therefore, during the first FRP coating, the spray pressure is almost maximized to achieve a thickness of approximately 3mm, and only a small quantity is subsequently sprayed during the second and the third coating so that the thickness standard can be achieved. This suggests that the first FRP coating operation step is the operation with the highest risk of styrene exposure, and, correspondingly, calls for careful control.

The MA concentrations in urine ranged were less than 15% of the domestic biological exposure index standard, and there was no statistical difference between the exposure group and the control group. In the exposure group, helper 3 and the inspector were found to have consumed 118 g and 142 g of alcohol, respectively; helper 3 showed the highest MA concentration, possibly reflecting the influence of alcohol(Alessio et al., 1995). However, the overall urine MA concentration level in the exposure group was very low compared to the standard, and when compared to the measurements of MA in FRP operation workers in Europe by a time trend, the levels were similar to the level in the 2000s. This reflects the effect of wearing personal protective equipment(PPE). At the time of this survey, all workers were wearing purification masks for organic solvents and the cartridge was replaced pre-shift on the day of measurement.

In this study, the local exhaustive ventilation(LEV) system with an upper side hood is not appropriate, as the subject of operation has a large volume and the surface area of styrene generation is large. In particular, the stack was placed lowly at 2 m from the floor beside the resting space of workers, calling for improvement. However, as tank lamination is conducted by fixing a tank in the air and rotating it, as shown in Fig.1, it is highly difficult to adequately introduce a LEV system. Therefore, PPE can play a crucial role in workers' protection in such a work environment. Workers were using respirators with a cartridge for organic solvents. Using the mask service life prediction program provided by the manufacturer of the respirator that the workers were wearing, the service life of masks were predicted to be 49-53h under the condition of 8-h TWA concentration of 50 ppm, workplace temperature 10℃-30℃ and relative humidity of less than 65%, indicating that the masks are to be replaced every 7-8 days based on an 8hr working day.

V. Conclusion

We surveyed a small sized factory which has a lamination process with FRP for manufacturing double walled UST under the health diagnosis. In this study, we found that UPR with the highest amount of use was a major source of styrene generation, followed by toner. Although the MA concentration in urine was low, the airborne styrene exposure level exceeded the exposure limit. Short-term exposure assessment of styrene by operation steps showed that the exposure level during coating with FRP was significantly higher than exposure level without FRP. It is difficult to properly design a ventilation system because of the nature of the UST production system(e.g., hanging the tank on the ceiling during lamination). Therefore, it is suggested that the cartridge in the respiratory protective equipment be used with appropriate replacement and that engineering improvement be pursued by considering the characteristics of the work process.

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