WATER-BASED POLYURETHANE DISPERSIONS FOR DIPPING APPLICATIONS

Hiroyuki Suzuki
Covestro Japan Ltd.
1-7-6 Shibakoen, Minato-ku, Tokyo 105-0011
Japan

Khoo Siong Hui
Le Inoova Sdn Bhd
116(a) Jalan Zapin 3A/KU5, Bandar Bukit Raja, 41050 Klang, Selangor
Malaysia

Marc-Stephan Weiser
Covestro Deutschland AG
Kaiser-Wilhelm-Allee 60, 51373 Leverkusen
Germany

Approx. 2%[1] of the global population suffers from natural latex sensitization with employees in the medical area being even more affected. Natural latex, due to its availability, competitiveness and mechanical properties, is still the major raw material for dipped articles such as gloves and condoms. The market is looking for a non-allergenic alternative formulation to natural latex. Synthetic latex based on polyisoprene is costly and can also elicit hypersensitivity[1]; most other materials such as nitrile and polychloroprene do not correspond to the desired properties for high-end applications in medical, such as probe covers and surgical gloves.

New water-based polyurethane dispersions (PUD) may be an important alternative to latex in the future as it is confirmed to be non-sensitizing to skin. With innovative formulations, they significantly strengthen the durability, oxidation and chemical resistance of dipped articles without the need to use accelerators and sulfur, which are particularly related to Type I and IV hypersensitivities[1]. These PUD innovative solutions do not contain divalent or trivalent ions, for example zinc oxide, which allow reducing such emissions through waste into the environment. Even more advantageously, these innovative PUD solutions allow for the use in gamma sterilization processes for dipped elastomer films and increase mechanical properties particularly high in tensile strength, tear strength and elongation, but yet being low in modulus. Polyurethane gloves aim to provide improvement in flexibility, durability, elasticity, barrier protection, chemical resistance, whilst being friendly to skin and environment.

The key feature of polyurethane glove is that the elastomeric composition does not require the addition of sulphur, activator and accelerator. The accelerators, such as thiurams, mercaptobenzothiazole, and carbamates can be potential irritants that could cause chronic dermatitis (Type I and Type IV hypersensitivity) with users[2]. Additionally, both sulphur components and accelerators will react and produce nitrosamine and nitrosatable substances, that often being described as carcinogenic and mutagenic[3]. The absence of zinc oxide is less harmful to the environment, as less effort is used in the water treatment process[4]. Table 1 gives an overview about additives used in alternative raw materials.

Without the presence of sulphur, zinc oxide and accelerators, polyurethane gloves not just avoid the negative effects associated with said additives, it has also produced comparatively higher tensile strength, better elongation, and yet remained low modulus film. From the perspective of better barrier, polyurethane glove also demonstrates comparable resistance to commonly used chemicals in medical industry. Therefore, polyurethane gloves are superior over conventional gloves in this regard.

	Zinc	Accelerator*	Sulphur	Extractable Protein	Plasticizer	Solvent Processing
Polyurethane	**X**	**X**	**X**	**X**	**X**	**X**
Synthetic Polyisoprene	√	√	√	**X**	**X**	**X**
Polychloroprene	√	√ **or X**	√ **or X**	**X**	**X**	**X**
Styrene Ethylene Butylene Styrene	**X**	**X**	**X**	**X**	√	√
Natural Polyisoprene	√	√	√	√	**X**	**X**

** indicates ZMBT, ZDEC, ZDBC etc.*
X: unnecessary, √**:** necessary

Table 1: Typical raw materials for the glove industry and additives used during the manufacturing process

Polyurethane dispersions show more mechanical properties comparable with natural latex (and synthetic latex) than other alternative materials. By tailoring the microstructure of the polymer, these innovative raw materials combine low 100% modulus, representing softness as well as high elongation and flexibility and high tensile strength (Table 2). High breathability of the polyurethane films leads to comfortable wearing even over prolonged times. All dispersions are fully miscible at any ratio and allow for tailoring mechanical properties to the exact desired range.

Property (method)	PU dispersion 1	PU dispersion 2	PU dispersion 3
100% modulus [MPa] (DIN EN ISO 572-2)	1.5	1.6	5.8
Tensile strength [MPa] (DIN EN ISO 572-2)	30	18	35
Elongation at break [%] (DIN EN ISO 572-2)	1,750	1,100	700
pH value (DIN ISO 976)	5.5-7.5	6-8	5.5-7.5

MVTR [g/(24h•m²)] at 50 µm thickness (DIN EN 13726-2)	To Be Determined.	2,000	1,400

Table 2: Typical parameters of films made of different polyurethane dispersions:

They can be readily used in the dipping process. Adjusting the pH value is not necessary. The dispersions are very stable in neutral pH range and avoid the use of ammonia which contributes to a working environment with less exposure to this chemical in the factories. Figure 1 shows a typical dipping process with polyurethane dispersions:

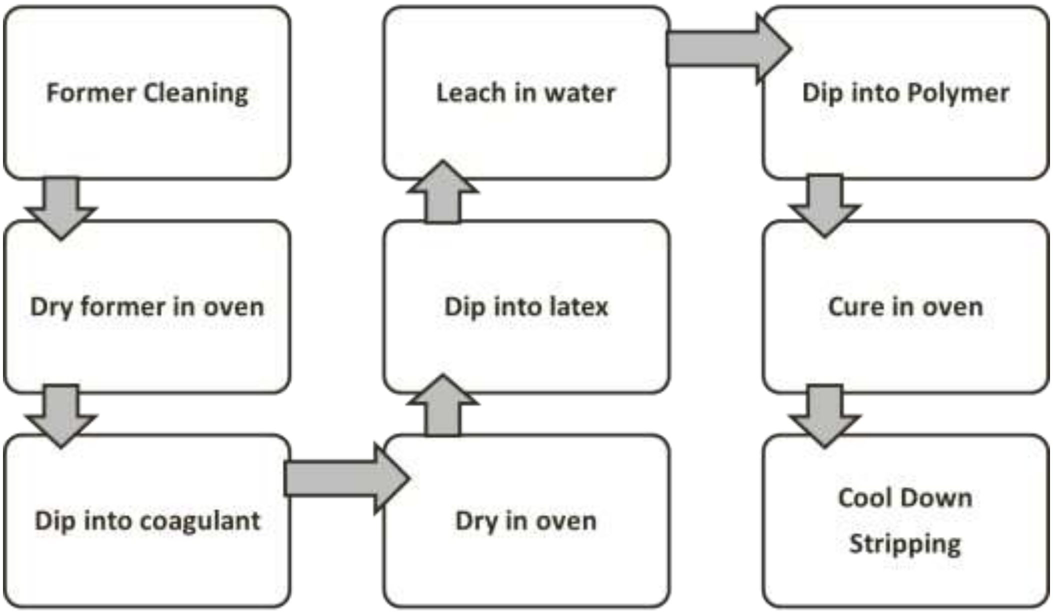

Figure 1: Lab dipping process flow

Due to its medium polarity and hydrophilic nature, typical weaknesses of polyurethanes are in the area of solvent and chemical resistance. The research which was leading to this paper has shown that an appropriate formulation 1 (Figure 2) is enabling polyurethane films to withstand solvents to an extent comparable with alternative materials.

Ingredients	**Description**
PU Dispersion 1	Aliphatic water-based polyurethane dispersion
Additive 1	Crosslinking agent
Additive 2	Anti-aging agent

Figure 2: Formulation 1

Solvent resistance is determined via swelling in different solvents at ambient temperature. Table 3 gives an overview about the swelling characteristics of films made of PU dispersion 1 using Formulation 1. Herewith, PU is meeting the acceptable range particularly for ethanol.

	Time (Minutes)	0	1	2	3	4	5	6	7	8	9	10	15	20	25	30
Solvent	ISO Propyl Alcohol	0	0	0	4	8	8	12	12	16	16	16	16	16	16	**16**
	Toluene	0	56	64	68	72	72	72	72	72	76	76	76	76	80	**80**
	Acetonitrile	0	36	40	40	40	40	40	40	40	40	40	40	40	40	**40**
	NaOH 50%	0	0	0	0	0	0	0	0	0	0	0	0	0	0	**0**
	Acetone	0	60	68	76	76	76	76	76	80	80	80	84	84	84	**84**
	MEK	0	64	88	100	108	116	116	120	124	124	128	132	136	136	**136**
	Ethanol	0	8	12	16	20	20	20	20	20	20	20	20	20	20	**20**
	DCM	0	124	140	148	156	164	164	168	172	172	172	184	188	192	**196**

(Source: in-house test data from Inoova)

Table 3: PU Glove – Chemical Resistance (Swelling Index, %)

Polyurethane films do not need post-treatment such as cross-linking and vulcanization used in process with natural latex. Their mechanical properties arise directly from the design of the polymer material. Therefore, polyurethane films keep their thermoplastic nature and save additional processing steps. Nevertheless, due to the lack of cross-linkage, polyurethane films are more susceptible for loss of mechanical properties during sterilization and/or accelerated ageing processes. This is particularly true for soft polyurethanes alone that are typically used in this study.

However, gloves made by dipping into Formulation 1 showed no reduction in mechanical properties during 7 days ageing at 70°C. Table 4 shows the results of mechanical tests prior and after ageing studies carried out at polyurethane gloves prepared in laboratory.

Non- sterilized glove samples

Product Type		ASTM - D3577					Tear Resistance (Initial), kN/m	EN 455-2 Force at Break, N	Durability (stop @16hrs)
	Thickness, mm	Tensile Strength, MPa	M100, MPa	M300, MPa	M500, MPa	EAB, %			
Unaged									
PU	0.11	28.2	1.2	1.8	2.7	1,048	26.0	10.5	16 hrs
Aged 7days @ 70°C									
PU	0.11	31.7	1.3	1.7	2.5	1,139	25.0	10.3	16 hrs

(Source: in-house test data of Inoova)

Table 4: PU Glove physical properties, aged and unaged.

Gloves for medical uses such as surgical gloves need to be sterilized prior to application. The most common and safest way of sterilization is gamma-radiation. This is also the method of choice to treat large quantities of articles. This process is fixed in the value chain and cannot be substituted. Therefore, newly developed materials need to keep their properties during sterilization conditions. Soft polyurethanes are more susceptible to scission reactions in this environment and lack the degree of cross-linkage to suppress degradation of polymer chains. Thus, the mechanical stability under sterilization conditions can only be achieved using the right additives to suppress chain scission.

Table 5 shows a comparison of polyurethane gloves versus commercial market products and their behavior after sterilization. It is demonstrated that the polyurethane gloves keep their tensile strength and softness.

Sterilized glove samples

Product Type		**ASTM - D3577**					**Tear Resistance (Initial), kN/m**	**EN 455-2 Force at Break, N**	**Durability (stop @16hrs)**
	Thickness	**Tensile Strength, MPa**	**M100, MPa**	**M300, MPa**	**M500, MPa**	**EAB, %**			
Unaged									
PU	0.11	28.0	1.2	1.6	2.8	930	25.0	10.3	16 hrs
PI	0.20	24.5	0.9	1.2	2.1	1,100			16 hrs
CR	0.18	23.8	1.0	1.4	2.4	870			16 hrs
SEBS	0.21	17.1	0.7	1.3	2.8	980			
NR	0.22	23.5	0.8	1.6	2.7	850			16 hrs
Aged 7days @ 70°C									
PU	0.11	28.0	1.1	1.5	2.7	1,000	23.0	9.3	16 hrs
PI	0.20	17.5	0.6	0.8	1.5	1,020			
CR	0.18	20.2	1.3	1.8	4.1	740			
SEBS	0.21	15.2	0.7	1.3	2.3	1,066			
NR	0.22	21.5	0.7	1.4	2.7	800			

(Source: in-house test data from Inoova)

Table 5: Physical properties comparison of different polymers, aged and unaged, sterilized (potentially different sterilization parameters).

Only the PU glove samples were prepared in the lab. The other glove samples used are commercially available. They have been used as purchased and had been priorly sterilized by the manufacturer. They were not further sterilized prior to the tests. There are several commonly available glove sterilization processes, like electron beam (EB), ethylene oxide gas (EtO) and gamma-radiation, that may have impacted the film properties. Our test results are actually based on assumption that different sterilization process will have no impact to glove properties.

Conclusions:

Formulation work in this collaboration paired with unique innovative new polyurethane dispersions lead to a new invention that is able to overcome many conventional glove chemistry challenges. Polyurethane is a highly recognized material in medical industry for contact lenses, wound dressings, medical sheets and tubing, material which is now being formulated to lead to non-skin sensitizing, breathable, high strength, durable and soft medical gloves. Its high strength enables the gloves to achieve comparable performance with lower thickness, that eventually provide cost down options and allows for a better and more precise feeling for the surgeon.

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