Polyurethane Sealants

TECHNOLOGY AND APPLICATIONS

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To my wife, Sylvia

Without her "noodging" this book would never have been finished.

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1

URETHANE CONSTRUCTION SEALANTS

1.1 Introduction

The first chapter of this book deals with construction sealants. Construction is a very large market for adhesives and sealants. Estimated sales are $455 million [1]. Of these sales, sealants account for about 60% [2]. In recent years, however, automotive and aerospace, with a total use of $600 million, have surpassed the construction market.

1.1.1 Sales

Sales to the construction market rely on ability to meet the relevant specification. U.S. requirements are not as rigorous as those of France. There the sealant supplier must comply with AFNOR national standards if he wants insurance coverage. With the growing importance of the European Community, ISO standards grow increasingly important for exporting U.S. companies. Sales in either market require compliance with ASTM or foreign standards. To tap these markets requires knowledge and understanding of the existing specifications.

While this chapter will discuss the requirements of the specifications, the chemical means of formulation required to meet these criteria are discussed in the following chapters.

1.2 Market Data

Urethanes are sold as high performance sealants. The other high performance sealants are silicones and polysulfides. A study by Frost and Sullivan gives sales of caulks and sealants for 1990 as well as projections for 1995 [3]. Table 1.1 summarizes some of their findings.

1.2.1 Comparison of High Performance Sealants

High performance is primarily defined by movement capability. In the field, however, several other attributes determine sealant life expectancy.

Table 1.1. Sales of Caulks and Sealants by Product.

Product	1990 (Million Dollars)	1995
Silicone	275	404
Butyl	191	211
Acrylic	148	180
Polyurethane	124	167
Polysulfide	88	76
Oleoresinous	35	35
Asphaltic	33	38
Other	135	

Of the high performance sealants, polyurethane sealants have moved to the forefront because their properties are superior in so many other respects. Such properties are summarized. Tables 1.2, 1.3, and 1.4 compare properties of urethanes with silicones and polysulfides.

While movement capability is very important, other important properties are unprimed adhesion to concrete,[1] resistance to hydrolysis,[2] color, paint-

Table 1.2. Comparison of Properties of Polysulfide, Silicone and Urethane.

Property	Polysulfide	Silicone	Urethane
Recovery from stress	−	++	++
Ultraviolet resistance	−	++	+
Cure rate[a]	−	++	− to ++
Cure rate, two component[b]	+		++
Cure rate, latent hardener[c]	NA	NA	++
Low temperature gunnability	−	++	−
Tear resistance	−	−	++
Cost	−	−	++
Paintability	++	−−	++
Available in colors	+	−	++
Unprimed adhesion to concrete	−	−	++
Resistance to hydrolysis		−	++
Non-bubbling[d]	++	++	−
Self levelling available[e]	++	−	++

[a]One component sealant.
[b]Silicone is available only as one component
[c]Latent hardeners as described in Chapter 5.
[d]See Chapter 4 for discussion.
[e]Desirable for plaza decks and pavements.

1 Concrete is especially difficult because it usually has a chalky surface which is difficult to penetrate.
2 Concrete has a very high pH. See Chapter 7 for discussion on the nature of concrete.

Table 1.3. Advantages and Disadvantages of Silicone Sealants.

Advantages	Disadvantages
Low temperature gunnability	Poor unprimed adhesion to masonry
Glass adhesion	Dirt pickup
UV and ozone resistance	Poor tear resistance
Fast cure	Short tooling time
No shrinkage	Liable to stain substrate due to low modulus weep out
20 Year durability	
/±50% Movement	Poor resistance to hydrolysis

ability and cost. Both unprimed adhesion to concrete and hydrolysis resistance are required for precast concrete applications. The slow cure rate of one component urethanes is one of the subjects discussed in subsequent chapters.

1.3 Defining Movement Capability

1.3.1 Joint Movement of Modern Buildings

The need for high performance sealants arose after the end of World War II. At that time, new types of buildings whose outer surface was a skin rather than a support member were introduced. This had a tremendous economic and architectural advantage over the masonry and mortar construction that had prevailed in the past. But the new construction materials had much higher expansion coefficients than brick and mortar (see Figure 1.1). The sealants used on the curtain wall buildings did not have the movement

Table 1.4. Advantages and Disadvantages of Polyurethane Sealants.

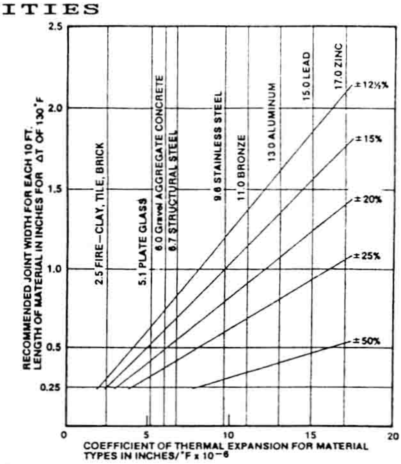
Advantages	Disadvantages
Excellent recovery	Light colors discolor
Excellent UV resistance	Some require priming
Fast cure for multicomponent	Relatively slow cure for one component (1K) sealant
Fast cure for latent hardeners	
Negligible shrinkage	
Excellent tear resistance	
Excellent chemical resistance	
Meets ASTM C920	
±40% Movement capability	
Unprimed adhesion to concrete	
Paintable: available in colors	

capability required to seal its joints. Consequently most of the buildings leaked. It took new types of sealants to meet the requirements of these buildings. These were the high performance sealants.

The joint moves in response to daily and seasonal temperature changes. Figure 1.2 shows how a joint alternates between compression and extension – with compression in the summertime,[3] extension in the winter [4].

Figure 1.1 shows how the lighter construction materials required sealants with higher movement capability. Defining movement capability is a complex process. Temperature, test rate, and test configuration influence test results. Hence, test methods are developed by national standards making bodies [5].

FOR MODERN CONSTRUCTION
EXPANSION COEFFICIENTS OF MATERIALS
INCREASED, MODULES GREW LARGER.
THIS REQUIRED HIGHER MOVEMENT
CAPABILITIES



MOVEMENT CAPABILITY NEEDED FOR
10 FOOT MODULE WITH 12.5 MM
JOINT ASTM C962, figure 7

MATERIAL	MOVEMENT CAPABILITY
BRICK	<12.5%
GLASS	15%
CONCRETE	20%
ALUMINUM	50%

FIGURE 1.1. Movement capability required for 10 foot (2.9 m) modules and a 0.5 inch joint (12.25 mm or 12.2 mm).

[3]The tests were run in Philadelphia.

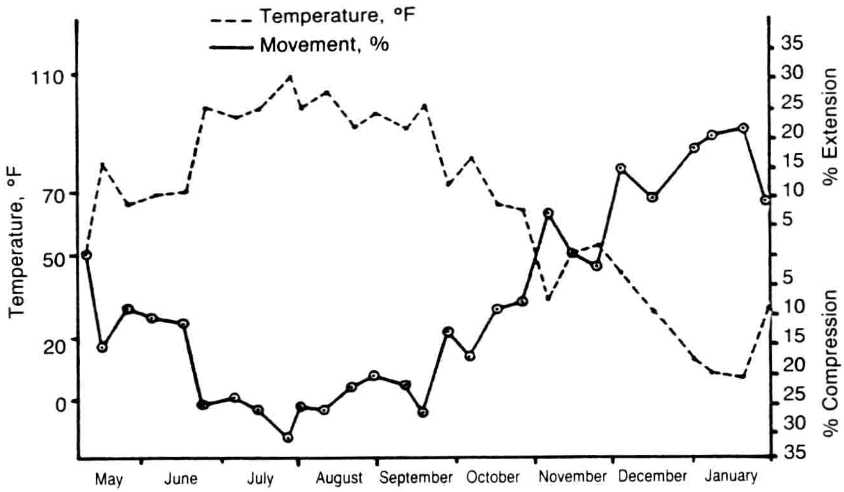


FIGURE 1.2. Movement of joints during seasonal changes.

1.3.2 Daily Variations

Diurnal variations are those that happen on a daily basis. Substantial temperature variations also take place due to changes from sun to shade exposure. The temperature of an aluminum sheet when it goes from sun to shade, Panek reports, can vary 60° between the sunny and the shady side [6]. Adding a daily fluctuation of 30°F, diurnal variations could equal 90°F (32°C). The rate of movement of seasonal variations is slow – for a concrete roof coping, for instance, it is .020 inches per hour. Daily variations, on the other hand, can be very rapid. An aluminum mullion (sash), for instance, will move at a rate about 1000 times faster than the masonry coping – 120 inches/hour [7]. Since this movement will take place while the sealant is fresh, it constitutes a serious problem for one component sealants.

1.3.3 Movement Requirements

Examination of Figure 1.2 shows that the joint is in compression in the summertime – in extension in the winter. Consequently most test methods for movement capability require a test of the effect of compression at high temperatures, of tension at low temperatures.

As Figure 1.1 showed, while brick and mortar construction required a movement capability of only ±12.5% for a 0.5 inch (12.2 mm) joint. Precast concrete requires a sealant with ±20% capability for a joint size of 0.5 inches. Steel panels would require ±25%, while aluminum sheets require ±50%.

1.4 Specifications

To function in the environment required of a high performance sealant, many different properties are required. Some of them are peculiar to high performance sealants, some of them are required of all sealants. Each requirement must be put in concrete terms. This is done with specific test methods. The group of test methods which profiles a sealant for a particular usage is a specification. In the United States, the operative specification for high performance sealants for building construction is ASTM C 920. The International Standards Organization (ISO) is writing test methods and specifications for, mostly, European countries. This is done by an ISO Technical Committee (TC). Construction sealants are dealt with by TC 59 (Construction) Subcommittee 8 (SC-8).

1.4.1 The U.S. Specification

This is ASTM C 920. In effect, a sealant specification is composed of a group of tests which defines the properties of the high performance sealant. In the following section, we shall discuss some of these properties and the tests which determine whether they meet the requirements for a high performance sealant.

1.4.2 Types of Joint Configuration

Many of the tests that will be discussed are of the behavior of sealants in joints. There are two types of joints – butt joints and lap joints. In the former, as temperature rises, the joint will go into compression. As temperature declines the building components will shrink and the joint will go into tension (see Figure 1.3).

While early test methods used dog-bone tensile specimens to determine elongation capacity and tensile strength, the results did not coincide with field behavior. Peterson showed that this was a result of unequal stress distribution in butt joints [8]. Figure 1.4 shows the multiplication of stress at corners. Consequently, test methods for construction sealant capability

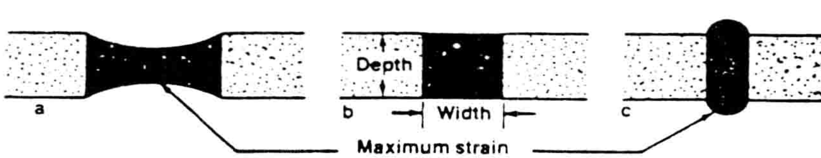


FIGURE 1.3. Movement of a butt joint.

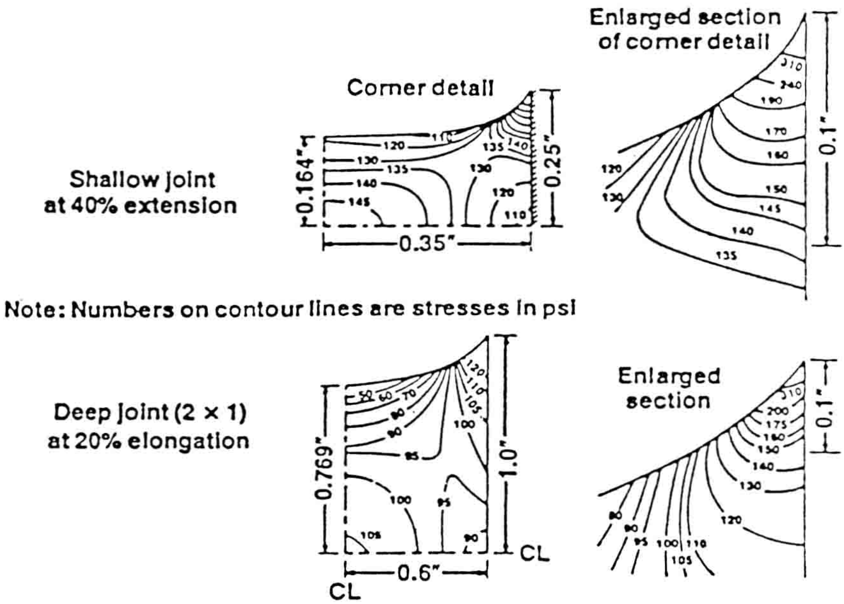


FIGURE 1.4. Unequal stress distribution in butt joints.

use butt joint samples whose width equals its depth (not its length). This is, generally, 12.25 mm (0.5 inch) square.

Lap joints are shown in Figure 1.5. Strain in these joints can be less, for a given thickness, than for butt joints. For instance, the strain on the sealant, when the joint moves 50%, is only 25%. However, the movement is in shear which can cause catastrophic failures in certain circumstances [9].

1.5 Generic Types

It is generally accepted that high performance chemically curing sealants are required to withstand the temperature variations of North America. We discuss the characteristics of the polysulfides and silicones because understanding them is needed to understand the evolution of polyurethane sealants.

1.5.1 Polysulfides

Polysulfides were the first elastomeric sealants.[4] They are formed by the reaction of dichlorethylformal with sodium polysulfide [Equation (1.1)].

[4]Morton Thiokol, Inc., 110 N. Wacker Dr., Chicago, IL 60606.

$$nClC_2H_4OCH_2OC_2H_4Cl + nNa_2S_{2.25} \rightarrow$$

$$HS[C_2H_4OCH_2OC_2H_4SS_{2.25}]n - C_2H_4OCH_2OC_2H_4SH + nNaCl \quad (1.1)$$

Equation (1.2) shows that chain extension is achieved with such oxidizing agents as manganese peroxide.

$$HSRSH + MnO_2 \rightarrow RSMSR + H_2O + MnO \quad (1.2)$$

While polysulfides were the first high performance construction sealants – they had two faults which made them easy prey to the polyurethanes and the silicones. One of these was excessive compression and extension set caused by the unstable disulfide linkages. The other was the high material cost characteristic of a material supplied by a single supplier.

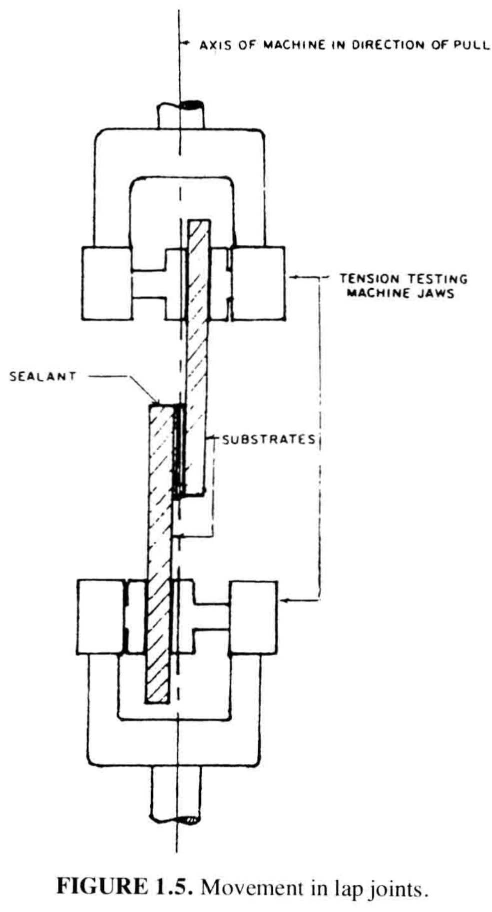


FIGURE 1.5. Movement in lap joints.

In important work by Burstrom, compression and extension set of polysulfides was compared to that of silicones [10]. Figure 1.6 shows his results. To develop the data shown in Figure 1.6, Burstrom elongated specimens the amount shown in Figure 1.6 at −25, −5 and +23°C and compressed specimens the amounts shown at 23 and 55°C. The test rate was .001 mm/min (1.5 inches/hr). Remaining elongation or compression was measured after one hour. The polysulfide sealant which had been elongated 25% at 23°C retained 5% elongation. The silicone, treated equally, retained almost none. When compressed 25% at 55°C the polysulfide and the silicone retained, respectively 20% and 4% compression.

As one would expect, the retained compression of the polysulfide was the source of failure in the field. This was graphically confirmed by samples exposed on an out of doors cycling rack devised by Karpati [11]. Figure 1.7 shows samples exposed ±35% annual movement. Viewed in summer, the photograph shows the uneven configuration resulting from tensile and compressive creep. In the winter, when the joint opens up, this has become the locus for incipient failure by cracking.

It was this sort of behavior in the field – compression set leading to failure in tension – which prompted Arthur Hockman to require one week of compression at 70°C before cyclic testing in the federal specification for chemically curing sealants [12]. This was later adopted by ASTM C-24 in test method C-719 and specification C 920 (see Figure 1.8). It was the adoption of these specifications, among other reasons, that signalled the takeover of the construction market by silicones and polyurethanes.

1.5.2 Silicone Sealants

The covalent bonds of silicones are more stable than the disulfide bonds of polysulfides, improving their resistance to compression set. Acetoxy terminated and acetamide terminated are two major chemical varieties.

Acetoxy Terminated Silicone

$$RSi(O(CO)CH_3)_3 + 3H_2O \rightarrow RSi(OH)_3 + 3CH_3(CO)OH \qquad (1.3)$$

Acetamide Terminated Silicone

$$-\overset{|}{\underset{|}{Si}}OH + C_2H_5(CO)NH_2 \leftrightarrow -\overset{|}{\underset{|}{Si}}NH(CO)C_2H_5 + H_2O \qquad (1.4)$$

The curing reaction of the two materials is shown by Equations (1.3) and (1.4). The acetoxy cure had the advantage of excellent adhesion – particularly to glass. However, the acetic acid which was released ate away