NATIONAL RESEARCH COUNCIL OF CANADA
CONSEIL NATIONAL DE RECHERCHES DU CANADA

Mechanical Properties of Sealants: I. Behavior of Silicone Sealants As A Function of Temperature

by
K. K. KARPATI

Reprinted from
Journal of Paint Technology
Vol. 44, No. 565, February 1972
p. 55-62

Research Paper No. 515
of the
Division of Building Research

OTTAWA

February 1972

Price 25 cents

NRCC 12477

LES PROPRIETES MECANIQUES DES PATES A JOINTS: I. LE COMPORTEMENT DES PATES DE SILICONES EN FONCTION DE LA TEMPERATURE

SOMMAIRE

Une série d'études ont déjà examiné les propriétés mécaniques des pâtes à joints. La présente étude examiné, en fonction de la température de l'expérience, l'étendue et la charge, lors de la défaillance, des pâtes traîtées chimiquement et ayant une partie de silicone. Les échantillons reproduisent approximativement la géométrie des passes à pâte utilisées dans les joints de construction. On remarque un changement des propriétés d'adhésion lorsque la température varie. Enfin, à la lumière des résultats obtenus, l'auteur énumère certaines conditions de recherche pour l'avenir.

ANALYZED

Mechanical Properties of Sealants: I. Behavior of Silicone Sealants As a Function of Temperature

K. K. Karpati
National Research Council of Canada*

The mechanical properties of sealants have been examined in a series of studies. The present paper examines the extension and load at failure of chemically cured, one-component silicone sealants as a function of test temperature. The test specimens were an approximate representation of the geometry of sealant beads used in building joints. It is shown that there is a change in adhesive properties as the temperature varies. Test conditions for further investigations are selected on the basis of the results obtained.

INTRODUCTION

Sealants can be used in the joints of the inner or outer skin of buildings. Since requirements for exterior use are usually more severe, any sealant that performs well on the outside should perform well on the inside. Similarly, if a sealant passes a test of outside performance, it should be suitable for inside use. Development of test methods for sealants on the outside of buildings should be given priority because of their widespread use; the level of requirements can be later lowered for inside application if necessary. It is essential, however, that the test should be relevant to outdoor performance, and one should have accurate knowledge of the correlation between the particular test conditions and the outdoor conditions. The most promising way of achieving this is by thorough investigation of the basic properties of sealants. The present test methods used in specifications are not based on theoretical considerations, and it is not clear how relevant they are. The ultimate aim of the work undertaken on the mechanical properties of sealants is to fill this gap and find the necessary link between test methods and practical performance of sealants. This paper, the first in a series, has the task of assessing the problem in general and of defining the course for further investigations.

On the outside of buildings sealants are expected to act as water, dust, insect, and air barriers in the joints, and are required to perform this task under wide temperature variations and for considerable lengths of time. The sealant is most extended at the lowest outside temperature and most compressed by joint contraction during periods of high temperatures. In Canada the demands made on sealants are severe because even in moderately cold regions like Ottawa, air temperatures regularly reach near —30 F (—35 C) in winter and near 100 F (38 C) in summer. However, more extreme temperatures occur on buildings, depending on their orientation, surroundings, and color of the surface. Stephenson[1] gives, for example, possible extremes of 230 F (110 C) for a dark-colored horizontal roof and, at the lower end of the temperature scale, a surface temperature 10 F (5.6 C) lower than air temperature.

Because these demanding performance requirements have occasionally been combined with poor joint design and little knowledge of the mechanical properties of sealants, failures of sealed joints have occurred. This has probably led to a decreased confidence in the ability of sealants to perform satisfactorily. It is hoped that work undertaken here will improve this situation in part by studying the behavior of sealants with temperature changes. The problem of rate of movement will be investigated in a later paper.

This paper deals with the results obtained with silicone sealants only, but subsequent work will consider other types of polymers used for sealants. The order in which the various chemical types of materials will be tested and reported is not a reflection of their relative importance.

EXPERIMENTAL

Two commercially available, one-component white silicone sealants of the chemically curing type were investigated. Several different batches of the same commercial product were used in the test series.

* Building Materials Section, Division of Building Research, Ottawa, Canada. K1A OR6.

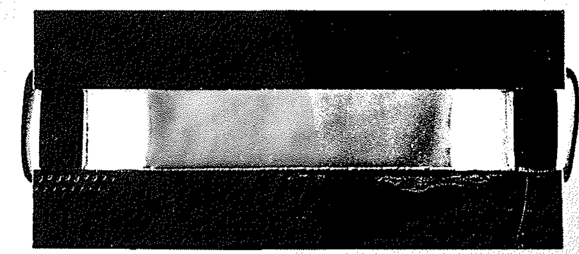

Figure 1—Specimen on spacers

The influence of substrate was investigated by using both aluminum and cement mortar as supporting bars for the samples. These substrates are the ones most frequently encountered on buildings. The investigation was not extended to other substrates, partly because the adhesive properties of the sealants were not the main object of this work and partly because the number of variables had to be kept to a minimum. The use of two types of substrates made it possible to choose the best one for further investigation. Sealants were cast on primed and unprimed substrates to obtain information about the importance of priming.

The size and shape required of specimens to duplicate service conditions is subject to various considerations. Theoretical investigations of polymeric materials use ring- or dumbbell-shaped specimens. The samples tested here are of the size and shape many standards use: ½ in. × ½ in. × 2 in. (1.3 cm × 1.3 cm × 5.1 cm) sealant bead attached to the substrate with the ½ in. × 2 in. side forming a butt joint. The samples were prepared in a constant temperature room at 77 F (25 C) and 50% relative humidity. They were cast between pieces of substrate using polyethylene or cellophane film for a base and cellophane-coated end spacers, to which the cured samples had little adhesion. After the samples had been cured overnight, they were removed from the film and new spacers placed at the end of the specimen. *Figure* 1 shows a sample on square aluminum tubing, the latter having the dimensions of ½ in. × ½ in. × 3¼ in. (8.2 cm). The spacers at the ends of the sample and the clips (which have a spring action) maintain the sample in the desired shape during the curing period, which is three to four weeks with conditions the same as during the preparation.

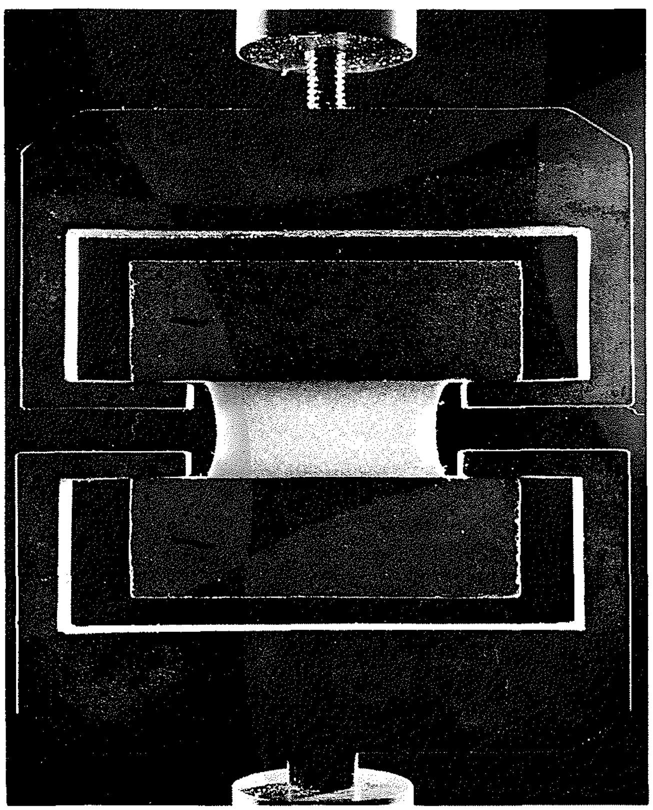

Figure 2—Extension of specimen

The cement-mortar bars shown in *Figure* 2 with dimensions of ½ in. × 1 in. (2.5 cm) × 3¼ in. were prepared from one part by volume cement (normal Portland, type I) and two parts by volume Arnprior sand. To 662 g cement and 1667 g sand, 300 g water was added and mixed according to CSA Standard A8-1956, paragraph B7.8.[2] The mortar flow determined by B8.5.1 was found to be 110%. After casting, the blocks were cured for a month at 73 F (23 C) and 95 to 100% relative humidity.

As indicated in *Figure* 2, the exposed surfaces, which are flat on all four sides in the initial unstressed state, become concave when subjected to extension (or become convex on compression). Although this sample geometry is difficult to treat theoretically it was chosen because the aim was to provide information related to building practice. This could be done only by using a specimen which was, in a way, a model of sealant beads used on builidngs.

The advantage of the selected specimen is that the sealant may fail either cohesively or adhesively as occurs in practice. Because of stress concentration at the end, failure can start there and propagate through the material. The shortness of the specimen amplifies the end effect in comparison to the sealant bead on an actual building, so it is probable that a sealant that does not fail when tested in this manner will not fail in practice, providing environmental conditions are similar. Although a longer specimen might be more representative of actual joints, the advantage of this particular one is that many standards call for the same sample geometry, so the results obtained by various investigators can, therefore, be more easily compared.

The tensile test consisted of pulling the sample in the direction perpendicular to the attached surfaces until failure occurred either cohesively or adhesively. A Tinius Olsen testing machine was used for the purpose. The tests explored the mechanical properties in the temperature range occurring on vertical surfaces in inhabited parts of Canada. This range, which is slightly wider than the air temperature range, is from about —60 F (—51 C) to 120 F (49 C). Tests were done with about 10 F (5.5 C) increments within this range using a constant extension rate of 0.05 in. per minute (0.127 cm per minute).

DISCUSSION

Tensile curves typical of the many tests performed with silicone sealants are illustrated in *Figure* 3. In the temperature range investigated, the stress-strain curves show a progressive hardening at lower temperatures. At elongation below 50% and loads less than 50 psi (3.5 kg/cm^2) there is little, if any, difference in results at different temperatures. Above —30 F the differences are less than the precision limits of the test. As the elongation and load increase, however, the curves differ considerably, demonstrating a hardening of the material with decreasing temperature.

With regard to sealant performance the failure points are the most important feature of *Figure* 3. The conditions under which failure occurs will, therefore, be examined in more detail in the succeeding figures.

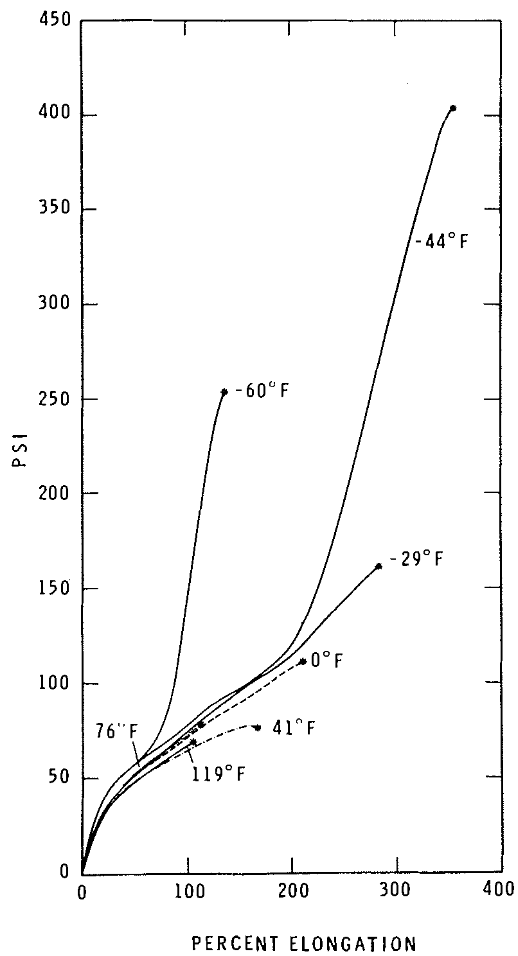

Figure 3—Tensile tests at various temperatures and at constant strain rate 0.05 in./min. White silicone sealant, Brand I, primed aluminum substrate

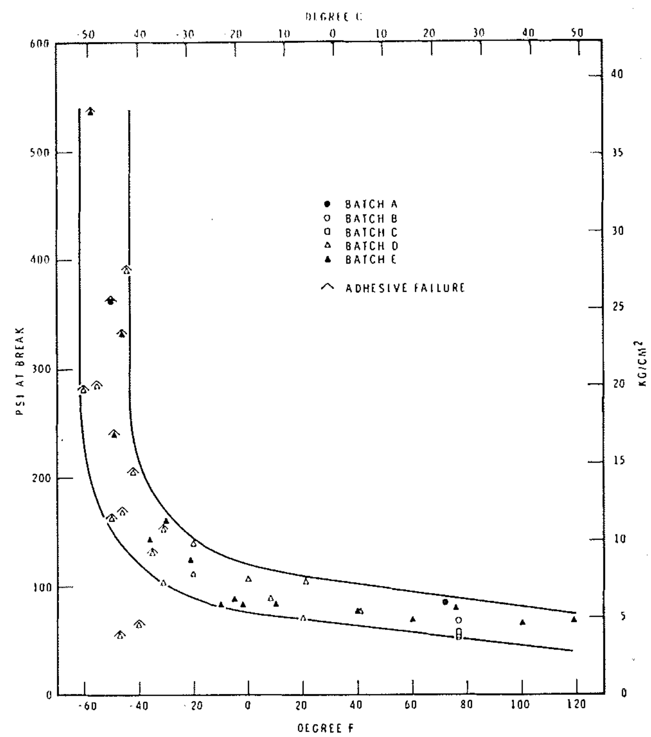

Figure 4—Load at break as a function of temperature. Brand I; primed aluminum substrate

Figure 4 represents the load at break as a function of temperature. The sealant used here was Brand I applied on primed aluminum substrate. In this figure as well as in succeeding ones different symbols are used for different batches of the sealant. An inverted V over a symbol indicates that the break occurred adhesively, that is, most of the sealant was removed in the test from one of the supporting bars. If only one side of the inverted V is shown at a symbol, it means that the failure occurred about 50% adhesively and 50% cohesively. A circle around a symbol indicates that the failure occurred in the substrate, as sometimes happened when cement mortar blocks were used as substrate (see Experimental). The blocks that failed usually did so in the middle, perpendicularly to the longest side. If none of the above signs are placed at a symbol, the failure was cohesive. The latter was a propagation of failure through the middle of the specimen parallel to the longer side. In most cases failure initiated near one of the corners of the material at about 1 mm or less from the substrate. The break tapered off toward the middle. In many cases, however, the break started in the middle of one edge of the sample. The propagation through the middle of the specimen was the same in either case. *Figure* 5 illustrates propagation of cohesive failure. The tip of the failure is actually not round but has a sharp edge which is not clearly shown in the photograph.

Figure 4 illustrates that the failure points fall within a broad band which rises abruptly to higher load values at about —40 F (—40 C) as the temperature decreases. One can observe as well that as the

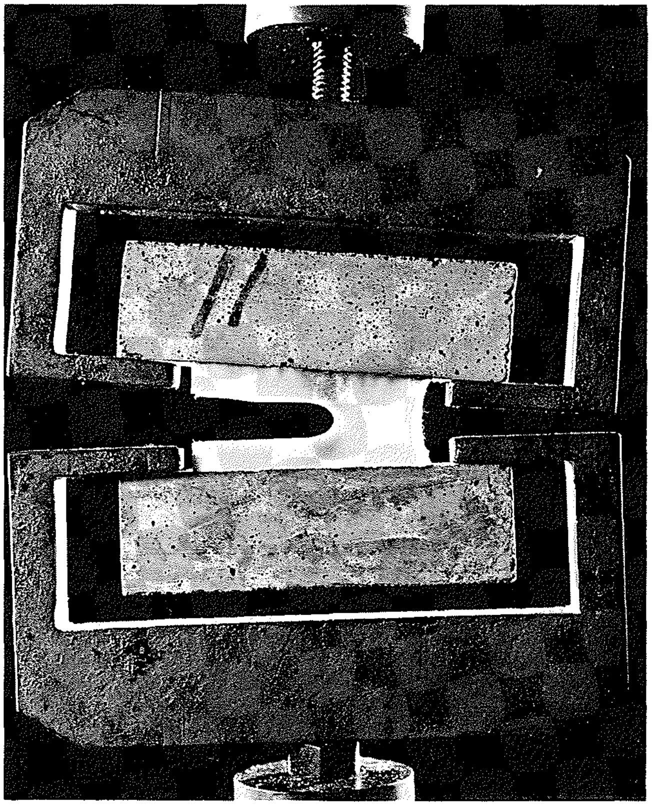

Figure 5—Progress of cohesive failure

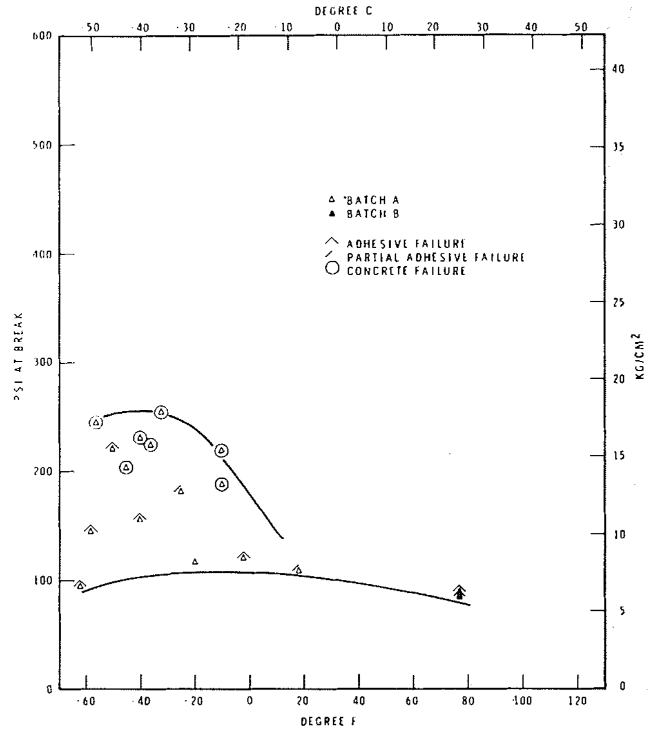

Figure 7—Load at break as a function of temperature. Brand II; primed cement mortar substrate

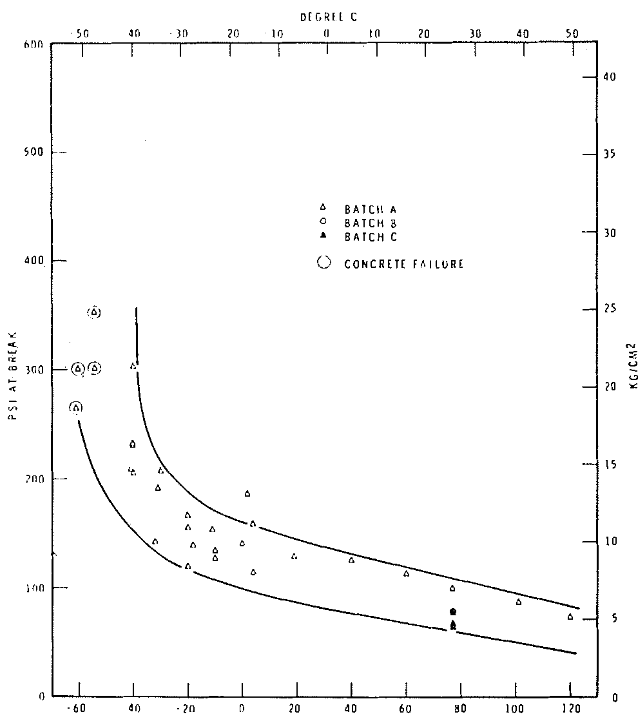

Figure 6—Load at break as a function of temperature. Brand I; primed cement mortar substrate

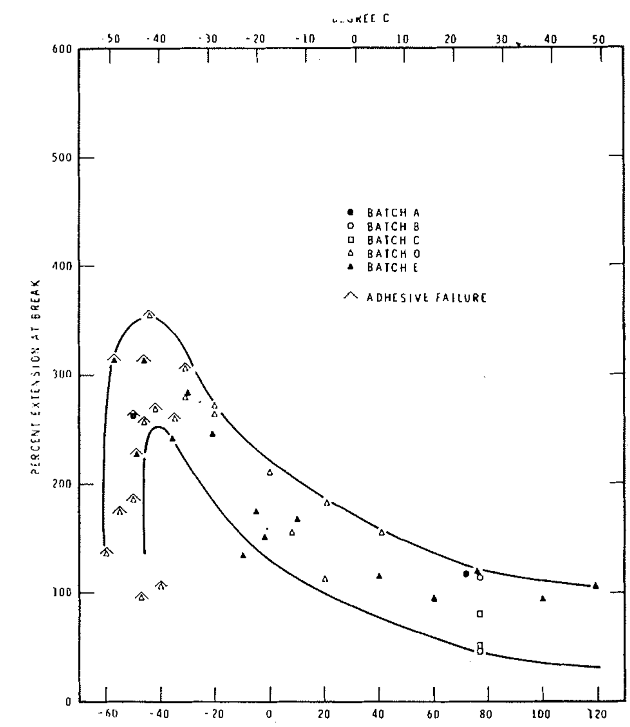

Figure 8—Extension at break as a function of temperature. Brand I; primed aluminum substrate

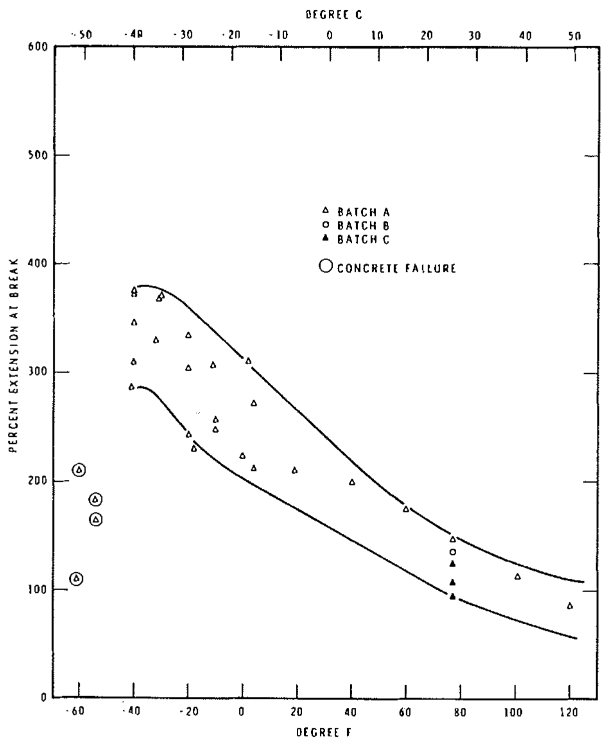

Figure 9—Extension at break as a function of temperature. Brand I; primed cement mortar substrate

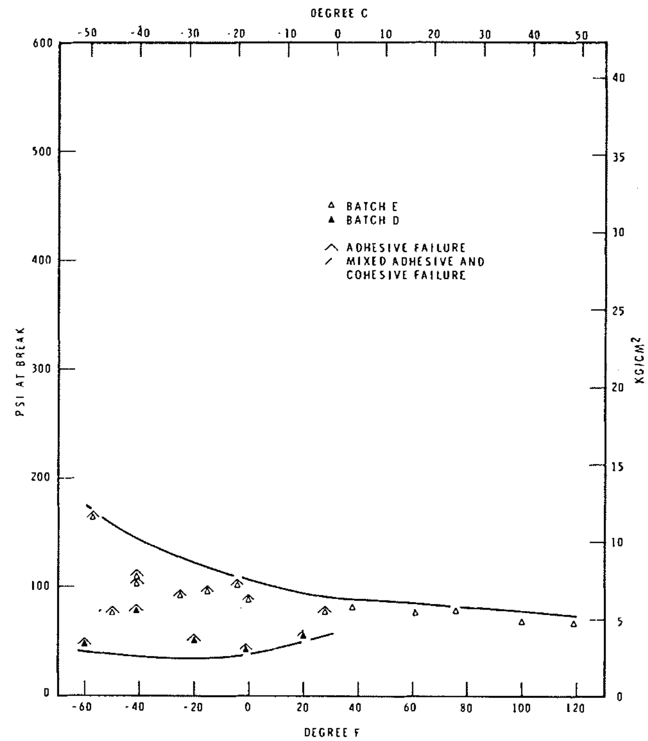

Figure 11—Load at break as a function of temperature. Brand I; cement mortar substrate, not primed

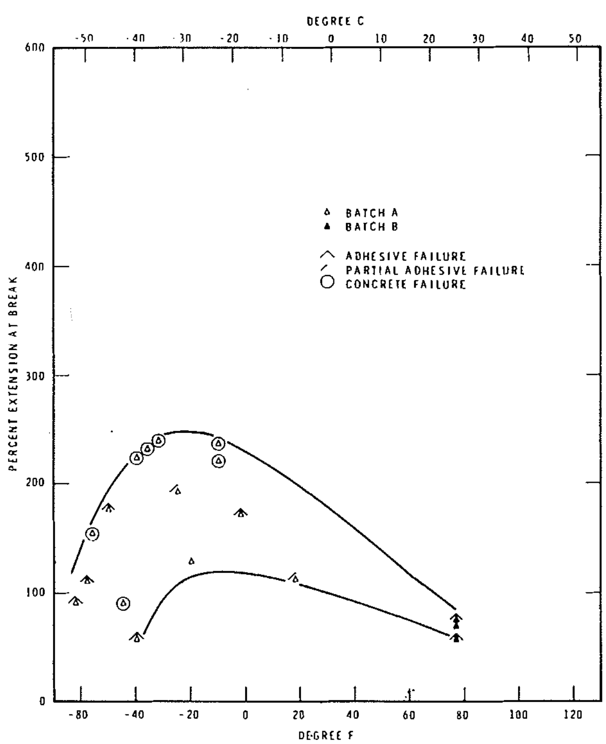

Figure 10—Extension at break as a function of temperature. Brand II; primed cement mortar substrate

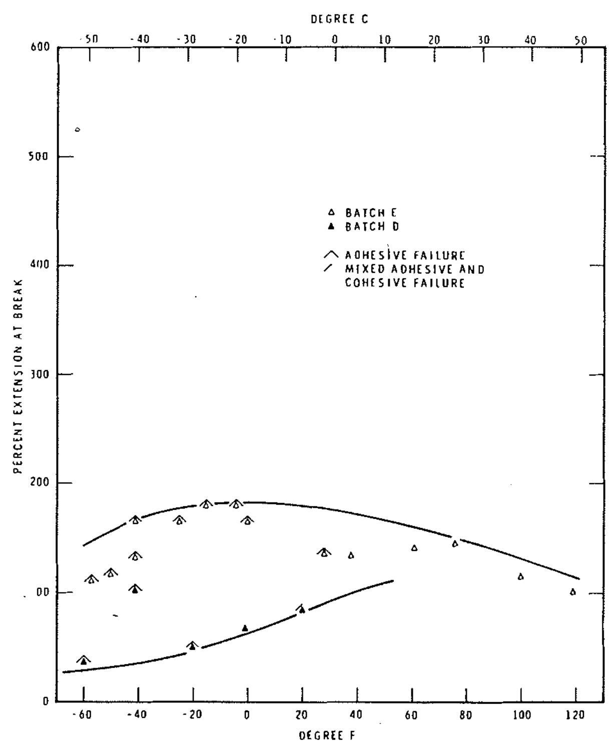

Figure 12—Extension at break as a function of temperature. Brand I; cement mortar substrate, not primed

Klara K. Karpati has been associated with the Division of Building Research of the National Research Council of Canada since 1965. Previously, she was employed by Imperial Chemical Industries, England, and by Trimetal Paint Co., Belgium, working in paint research and development. She obtained the Licence Speciale en Chimie Industrielle from the University of Brussels and graduated in chemistry from the University of Sciences of Budapest.

temperature decreases, starting at around —30 F (—34.5 C), the failures occur adhesively. The general trend of grouping of the failure points within a broad band is observed for 37 points out of 39. The two odd points failed adhesively and it is possible that their behavior, which did not fit the general pattern, was simply due to contaminated surfaces.

The general trend of break points being grouped in a band and, therefore, the fact that the two odd points can be discarded are confirmed by *Figure* 6, which presents load at break as a function of temperature for the same brand of sealant but on primed cement mortar substrate. Here the adhesion was excellent in all cases and no failure occurred adhesively. The broad band within which the points have fallen and its curving to higher load values is similar to that obtained on aluminum substrate. At the low end of the temperature scale examined, the failure occurred in the cement mortar substrate as indicated by the circles around the symbols.

It should be noted that, as the variations in the symbols indicate, tests were carried out on five different batches of Brand I sealant. This is a reasonable assurance of the reproducibility of the general pattern of behavior obtainable with this material.

The behavior of another brand of silicone sealant is illustrated in *Figure* 7. The specimens were applied on primed cement mortar substrate similarly to those in *Figure* 6. With two exceptions out of the 18, all failures occurred either adhesively or in the cement mortar. Even at room temperature the failure was adhesive in two cases out of three. Brand II was not tested on aluminum substrate because experience had shown that on outdoor weathering it detached itself from the substrate after six months to a year of exposure, even without movement of the sealant.

The extension at failure as a function of temperature is a more pertinent characteristic of sealant behavior than the load at failure because joint width has to be designed, and a sealant chosen, according to the extensibility of the available sealants. In *Figures* 8 to 10 the extension at break as a function of temperature is examined for the two brands of silicone sealants. The points illustrated in *Figure* 8 are derived from the same tensile experiments as those of *Figure* 4 and, similarly, *Figures* 6 and 9 and *Figures* 10 and 7 represent the same tensile tests. The behavior of Brand I on primed aluminum substrate is illustrated in *Figure* 8, and on primed cement mortar substrate in *Figure* 9. The failure points in both figures are arranged in a broad band which has a maximum at around —40 F (—40 C). The higher extensibility with decreasing temperature is a useful characteristic of the sealant since on outside performance the latter is subject to increasingly more extension as the temperature decreases.

Figure 10 illustrates the extensibility of Brand II. There is a maximum occurring between —20 F and —30 F (—29 C and —34.5 C) which is, however, much less well-defined than the curves for Brand I because the scatter of the readings is much larger.

In order to obtain information concerning the influence of priming on the failure characteristics of sealants, Brand I was applied on unprimed cement mortar substrate and on unprimed aluminum. The results obtained for the former case are illustrated in *Figures* 11 and 12. Comparison of *Figure* 11 with *Figure* 6 and of *Figure* 12 with *Figure* 9 illustrates that both the load and extension at break occurred at much lower values without primer than on primed substrate at temperatures under 40 F (4.5 C). Above this temperature the failure points seem to fall within the same band whether the substrate is primed or not. Due to the low number of observations, the temperature range within which the departure from the primed behavior occurs can not be given with accuracy.

Another observation one can make when comparing primed and unprimed samples is that the lowering of the break values, both load and extension, occurs simultaneously with the appearance of adhesive failure. It is interesting to note that at room temperature, where the testing of adhesive properties of sealants is usually done according to standards at date of writing this paper, the primer has no influence on the results obtained.

The occurrence of failure on unprimed aluminum was examined as well, although not so extensively as for cement mortar. Since *Figures* 4 and 8 illustrated that adhesive failure started to occur with equal chances under —30 F (—34.5 C) tests were done only in this temperature region. *Table* 1 presents the results. Tests were in triplicate without primer, with a fresh primer and with a primer several months old. Without primer the failure occurred at extremely low elongation and load values. The results obtained with the fresh primer fit the general picture obtained in *Figures* 4 and 8. Failure occurred at very high elongation and load values and at the two higher values it was adhesive, while at the lowest elongation and load the failure was cohesive. When the old primer sample was used, although the elongation and load at failure were higher than without the primer, the values were still far below the failure region represented in *Figures*

Table 1—Effect of Priming on the Failure of Brand I Silicone Sealant. Aluminum Substrate

Sample No.	Primer	Temperature °F	Temperature °C	% Elongation	Load psi	Load kg/cm²	Type of Failure
1	None	—33	(—36.1)	12	15	1.1	Adhesive
2	None	—33	(—36.1)	10	12	0.8	Adhesive
3	None	—33	(—36.1)	7	6	0.4	Adhesive
4	Fresh sample	—34	(—36.7)	240	135	9.5	Cohesive
5	Fresh sample	—33	(—36.1)	271	166	11.6	Adhesive
6	Fresh sample	—34	(—36.7)	310	160	11.2	Adhesive
7	Old sample	—32	(—35.6)	25	24	1.7	Adhesive
8	Old sample	—32	(—35.6)	29	34	2.4	Adhesive
9	Old sample	—32	(—35.6)	38	41	2.9	Adhesive

4 and 7. The old primer was a clear solution but with a very slight deposit on the bottom of the can. As the results illustrate, even this small quantity was enough to make the primer ineffective.

There are significant observations from the point of view of establishing adhesion tests for sealants. The adhesive failure on the samples results from a peeling action. Standards which call for a peel test on sealants usually specify a sample with the sealant adhering to a substrate on only one side and some kind of fabric embedded in the sealant on the other side. The test is done with the fabric folded back 180° and pulled in this position after undercutting at the substrate to start the peel. The angle is not the same as in a joint and is not well defined either. It depends, among other things, on thickness, rate of peel and viscoelastic properties of the sealant. Failure often occurs at the fabric, and therefore gives no indication of the adhesive properties to the substrate. Because the peeling conditions and the whole configuration of the peel test sample are different from the conditions occurring in practice, it seems to be necessary to use tensile adhesion tests for establishing the adhesion characteristics of sealants.* Furthermore, as concluded from this work, adhesion should not be tested at room temperature only but preferably at a minimum of three different temperatures covering the full operating range.

It is pointless to test adhesion only at room temperature when the adhesive properties of viscoelastic materials may go through tremendous changes at the glass-transition temperature, as indicated by the works of Bright[3] and Voyutskii.[4] These workers investigated peel strength of polymers as a function of temperature and found similar transitions from cohesive failure to adhesive failure with decrease of temperature and at increasing loads as was found in this work.

The changing character of the failure as a function of temperature cannot be attributed to stress concentration at the corners exerting a peeling action on the sample. The stress concentration existed for all recorded failures and if it were the only factor inducing adhesive failure, all samples should have failed in adhesion, which was not the case. The explanation for the changing type and changing load at failure in silicone sealants probably lies in the change of the thermal coefficient of expansion of the materials involved and in crystallinity. The coefficient of thermal expansion of the polymer changes faster with temperature change than does that of the substrate. Since sealants are usually applied on buildings when the temperature is at the middle of the temperature range occurring in the geographic region, considerable stresses can be built up at the interface as a consequence of the difference in contraction of the substrate and of the sealant when the weather gets cooler. If the sealant were applied at a temperature higher than the middle temperature, the total stresss buildup on cooling would be greater because of the larger temperature difference. In addition, there is very likely some degree of crystallinity occurring in the polymer under the effect of stress and it probably increases as the temperature decreases. Since the formation of crystallites is accompanied by volumetric change, crystallinity can add to the stresses building up in the interface. It also has a reinforcing effect on the polymer, with the result that the load at failure increases with decreasing temperature.

It has to be noted that the failure described as adhesive in this work is probably a weak boundary failure[5] in the sealant, but it is so close to the substrate that, observed by the naked eye, it seems to be adhesive. The surface appears as though a thickness of material comparable to the primer were left on the substrate.

CONCLUSION

Testing of the sealant bead specimens illustrated that the tensile test curves varied considerably with varying temperature using a constant rate of elongation. The differences were very small below about 50% elongation and 50 psi (see *Figure* 3). Above these values, however, the curves differed considerably. Because the conditions under which failure occurs are the most important performance characteristic of a sealant, the occurrence of failure points was examined from various aspects. The distribution of the failure

* Peel tests could be used, complementing tensile adhesion tests, for testing comparative adhesion among substrates for a given sealant.

points on both aluminum and cement mortar substrates followed the same pattern. The break points were arranged in a broad band which, for load at break as a function of temperature, increased slightly as the temperature decreased until a sudden increase occurred around —40 F (—40 C). The elongation at break as a function of temperature showed the points gathering in a band as well, the value of which shifted progressively to approximately triple the values obtained at room temperature when the temperature was lowered to about —40 F. In this temperature region the band had a maximum and then it steeply decreased.

Consequently, the silicone sealant can undergo larger extension with the lowering of temperature without failure, provided the temperature does not drop below —40 F. This is a definite advantage since a sealant must undergo increasingly more extension as the temperature decreases. Under —40 F the extensibility of the silicone sealant is considerably reduced, although it is not less than at room temperature.

The above findings were obtained with one of the brands examined. The second brand showed a much larger scatter of the results, failure at lower loads and elongation and mainly adhesive failure even at room temperature. One can conclude that Brand II silicone sealant has not reached the stage of development where its adhesive properties are satisfactory. Consequently, for future work only Brand I silicone sealant will be used.

On primed cement mortar, no adhesive failure occurred with Brand I sealant above —50 F (—45.5 C). Below this temperature the type of failure was camouflaged by failure occurring in the cement mortar substrate. On primed aluminum the failure changed from cohesive to adhesive at around —30 F (—34.5 C). The importance of priming has been further demonstrated around this temperature: the absence of primer brought the extensibility reading down to practically nothing.

On cement mortar substrate the full temperature range has been explored without primer. It has been found that cohesive failure occurs at about 40 F (4.5 C) and the failure is adhesive at lower temperatures. Without primer the extensibility can drop to dangerously low levels at low temperatures. It is advisable, therefore, to do adhesion testing not only at room temperature but also at the lowest temperature which occurs in practice and preferably at an intermediate temperature as well. A suitable choice would be room temperature, +20 F (—6.7 C), and —40 F (—40 C) for regions similar to Ottawa or, if the air temperature never drops under, for example, —10 F (—23.3 C), —20 F (—28.9 C) would be sufficient as the lowest test temperature for the region in question.

All tests have been done at a constant rate of extension of 0.05 in./min (0.127 cm/min). This may be several orders higher than the average rate at which movement occurs in practice. The test results presented here do not give an indication of the behavior at other rates of extension. The influence of rate of extension on the failure of sealants should, therefore, be investigated as a next step toward the understanding of sealant performance. As demonstrated in this paper, only Brand I silicone sealant should be used for further examination, partly because Brand II does not have sufficiently good adhesion and partly because even if the lack of adhesion is discounted the tensile properties are not very different for the two types and it decreases the workload if only one of them is investigated. As substrate, aluminum is preferable because its strength is high enough and the type of failure in the sealant is not camouflaged by a failure in the substrate. Another point in favor of choosing aluminum is that both the load and extension at failure occurred at lower values on aluminum than on cement mortar. Consequently, results which will be obtained on aluminum could be obtained on cement mortar as well, or the performance would be better on the latter. The effect of moisture could alter this picture, of course, but this effect is a separate variable which should be kept constant while the effect of rate of extension is investigated.

ACKNOWLEDGMENT

The author wishes to acknowledge the assistance of G. M. Wallace and C. C. Barrett in executing the tests discussed in this paper.

This paper is a contribution from the Division of Building Research, National Research Council of Canada, and is published with the approval of the Director of the Division. ♦

References

(1) Stephenson, D. G., "Canadian Building Digest," No. 47, Division of Building Research, National Research Council of Canada. Nov. 1963.

(2) CSA Standard A8, Masonry Cement, Canadian Standards Assoc., Rexdale, Ont., 1956.

(3) Bright, W. M., "Adhesion and Adhesives," p. 130, Soc. Chem. Ind., John Wiley & Sons, 1954.

(4) Voyutskii, S. S., Markin, Yu. I., Gorchakova, V. M., and Gul, V. E., *Adhesive Age, 8*, 24. (Nov. 1965).

(5) Bikerman, J. J., "The Science of Adhesive Joints," Academic Press, 1968.

Publications of the Division may be obtained by mailing the appropriate remittance (a Bank, Express, or Post Office Money Order, or a cheque, made payable to the Receiver General of Canada, credit NRC to the National Research Council of Canada, Ottawa. K1A0R6. Stamps are not acceptable.

A list of all publications of the Division is available and may be obtained from the Publications Section, Division of Building Research, National Research Council of Canada, Ottawa. K1A0R6.