Viscoelastic Properties of Silicone, Polysulfide, and Polyether Impression Materials

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The viscoelastic properties of nine silicone-, polysulfide-, and polyether-based impression materials were determined using creep tests. During deformation the materials demonstrated linear viscoelastic behavior. The creep compliance curves, recovery, and percent set were calculated. Permanent deformation in these materials is a result of lack of recovery of elastic deformation as well as viscous flow.

The silicone-, polysulfide-, and polyether-based impression materials are commonly called elastic materials because of their rubberlike qualities. These materials are capable of accurate reproduction and are clinically popular. Of particular interest is their ability to recover from strain produced either during removal from undercut areas or during stresses they may encounter during handling before a model is made.

Most of the data on mechanical properties of "elastic" impression materials are obtained from tests similar to those described in American Dental Association Specification no. 19.[1] Bondoc[2] measured the percent permanent deformation and strain in compression for silicone-based materials according to American Dental Association Specification no. 19. Braden, Causton, and Clarke[3] studied both the base paste and set polyether impression material. Their mechanical tests included modulus of elasticity, dissipative modulus, dimensional change, and thermal expansion. MacPherson, Craig, and Peyton[4] determined the stress-strain properties in compression, and resistance to tear of polysulfide and hydrocolloid impression materials. Current books on dental materials list the results of American Dental Association specification tests for several brands of impression materials. Wilson[5] studied the compression and tension set of silicone and polysulfide materials as a function of time after a specified strain had been applied. This approach provides more complete information since in reality these materials are viscoelastic and not elastic. Their stress-strain, recovery, and set properties can only be completely described when a time variable is included. Other advantages of viscoelastic description have been enumerated by Oglesby[6] and include: it has the ability to separate and quantitatively describe the various time-dependent and time-independent mechanical responses, it enables comparison with non-time-dependent materials, it enables comparison of data obtained under different test conditions, and since various mechanical components are individually identified a more satisfactory relationship with the microstructure can be described.

Several test methods are available for studying viscoelasticity. Static tests include stress relaxation, where the stress is measured as a function of time under constant strain, and creep, where the strain is measured against time under a constant stress. Dynamic methods measuring the internal friction and dynamic modulus include the torsion pendulum and forced oscillation techniques.

The creep test was selected as the method for this investigation since it readily enables a comparison with data already in the literature, provides information on the recovery of the materials, and requires only simple instrumentation. A load is applied to a sample of constant cross section, removed at a later time, while the strain is measured as a function of time. The Alfrey[7] generalized mechanical model for creep of amorphous polymers is illustrated in Figure 1. This model contains three components. The in-

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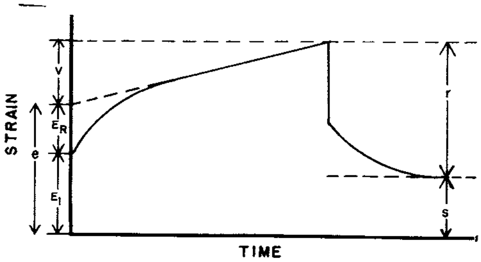

FIG 1.—Strain-time behavior for mechanical model of amorphous polymers.

stantaneous elastic response, E_I, is time independent. The retarded elastic response, E_R, is time dependent. The flow or viscous component, V, is a linear function of time. By use of different loads a family of creep curves can be obtained. If the ratio of the strain to stress is constant at any given time the material is said to be linearly viscoelastic and the entire family of creep curves can be represented by a creep compliance vs time curve. Oglesby[8] has written the analytical equation of the creep compliance curve in the form:

$$J(t) = J_o + t/\eta + \int_{-\infty}^{\infty} L(\tau)\ [1 - e^{-t/\tau}]\ d\tau$$

where

$J(t)$ is the creep compliance, $e(t)$/original stress;

J_o is the instantaneous elastic compliance;

t/η is the viscous response at time t and η is the coefficient of viscosity; and

$\int_{-\infty}^{\infty} L(\tau)\ [1 - e^{-t/\tau}]\ d\tau = J_R$ is the retarded elastic response with $L(\tau)$ the retardation spectrum of the material.

The purpose of this investigation is to characterize the viscoelastic properties of silicone, polysulfide, and polyether impression materials. The linearity of the materials will be evaluated. The amounts of instantaneous elastic response, retarded elastic response, and viscous flow will be illustrated for each material. Finally, the recovery and permanent set of the materials will be characterized.

Materials and Methods

A total of nine different impression materials were tested. Table 1 lists the names, batch numbers, and manufacturers. All materials except product *A* were regular body consistency.

Specimens were prepared according to American Dental Association Specification no. 19. Materials were mixed according to manufacturer's instructions and formed in a cylindrical metal mold 19 mm high and 12.7 mm in diameter. Glass plates were pressed against the ends of the mold to extrude excess material and ensure square edges. The mold containing the impression material along with the glass plates was placed in a 37 C water bath two minutes from the start of the mix. The specimens were removed from the water bath after the minimum time suggested by the manufacturer for leaving the material in the mouth and tested either one minute later or one hour from the start of the mix. In this test the former are referred to as one-minute specimens and the latter as one-hour specimens. All materials were mixed and tested at room temperature (24 C) and humidity.

Specimens were tested in an instrument similar to the one pictured in American Dental Association Specification no. 19 and used for determining strain in compression. The device consists of a dial gauge, graduated in 0.001 inch, a rod to act upon the gauge, and a set of platens for holding the specimen and weights. Specimens were placed in the instrument and loaded with a minor stress of 175 gm/cm^2. Thirty seconds later a major load of either 500, 1,000, or 1,500 gm was applied and this was recorded as time zero. The load was removed either 1, 3, 6, or 12 minutes from time zero. The deflection was recorded as a function of time until a constant value was reached.

The creep compliance, $J(t)$, was calculated for the one-minute and one-hour specimens of each material at times of 0, 15, 30 seconds, and 1, 2, 3, 4, 5, 6, and 8 minutes. The percent set and the percent recovery of the instantaneous plus retarded elastic deformation were tabulated. Although Figure 1 represents the ideal case, the percent set is s/original length × 100, and the percent recovery of instantaneous plus retarded elastic component is r/e × 100.

Results

Figures 2, 3, and 4 are representative creep curves for silicone, polysulfide, and polyether materials, respectively. Each figure

TABLE 1
IMPRESSION MATERIALS STUDIED

Designation	Name	Batch Number	Manufacturer	Type
A	Citricon*	02331003	Kerr Mfg. Co., Romulus, Mich.	Silicone
B	Jelcone	7340B 72339C	L.D. Caulk Co., Milford, Del	Silicone
C	Silicone Impression Material		Columbus Dental, Columbus, Ohio	Silicone
D	Xantopren	A07 311G	Unitek Corp., W Ger	Silicone
E	Permlastic	10221175	Kerr Mfg. Co., Romulus, Mich	Polysulfide
F	Coe-flex	02043	Coe Laboratories, Inc., Chicago, Ill	Polysulfide
G	Rubberjel	7332B 7329C	L.D. Caulk Co., Milford, Del	Polysulfide
H	Neo-flex	828G5	Lactona Corp., Los Angeles, Cal	Polysulfide
I	Polyjel	B72343 C72331	L.D. Caulk Co., Milford, Del	Polyether

* Putty consistency. All other materials are regular body consistency.

contains four creep curves, from tests run with two different stresses on one-minute and one-hour specimens. Each creep curve, illustrated with a solid line, is the average of four tests. The dashed lines are the creep curves for the four individual tests after removal of the load.

The creep compliance, $J(t)$, was calculated for each material at various times, starting at $t = 0$. One-hour specimens were considered independently from one-minute specimens. In all instances, except for products *C* and *E*, the creep compliances calculated from different stresses were equal within experimental error. Table 2 shows typical calculated results. These data allow plotting of just two $J(t)$ vs time curves for each material, one representing the one-hour material. the other representing the one-minute material. The creep compliance vs time curves for the one-hour specimens are shown in Figure 5. The range of $J(t)$ values calcu-

TABLE 2
TYPICAL CALCULATIONS OF $J(t)$ FOR TWO DIFFERENT STRESSES

	1,000 gm = 7.72 Newton/cm^2			1,500 gm = 11.58 Newton/cm^2		
t	Average Deformation	True Strain	$J(t)$ cm^2/Newton	Average Deformation	True Strain	$J(t)$ cm^2/Newton
0	29 ± 4	0.0390 ± 0.0055	$5.1 \times 10^{-3} \pm 0.7$	46 ± 2	0.0640 ± 0.0030	$5.3 \times 10^{-3} \pm 0.9$
15	31	0.0420	5.5	48	0.0670	5.6
30	32	0.0440	5.7	50	0.0700	5.8
1	35	0.0485	6.3	53	0.0730	6.3
2	38	0.0520	6.8	57	0.0790	6.8
3	40	0.0545	7.1	59	0.0830	7.1
4	41	0.0565	7.3	61	0.0850	7.3
5	43	0.0590	7.7	63	0.0880	7.6
6	44	0.0610	7.9	64	0.0905	7.8
8	47	0.0645	8.4	68	0.0955	8.3

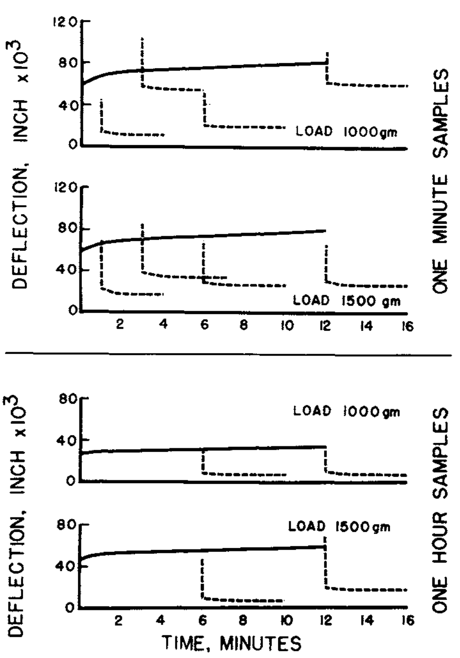

FIG 2.—Creep curves for silicone-based impression material, product *D*.

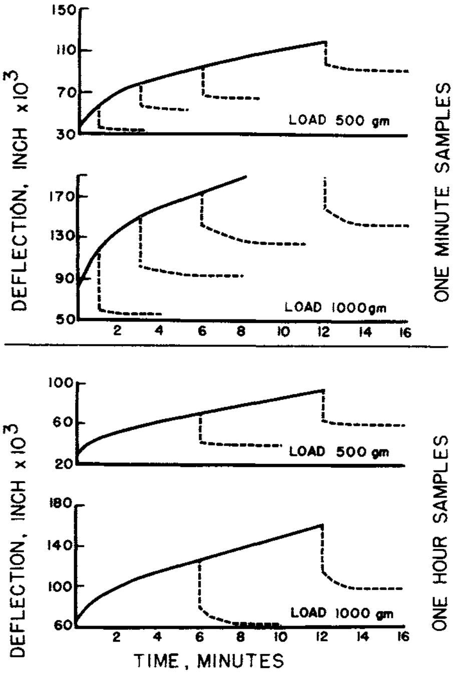

FIG 3.—Creep curves for polysulfide-based impression material, product *E*.

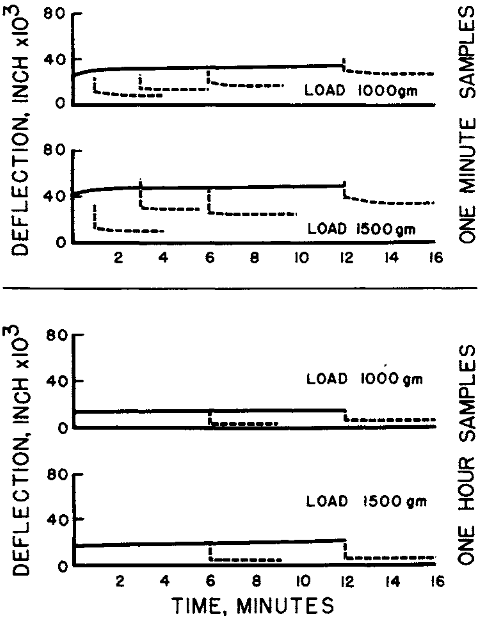

FIG 4.—Creep curves for polyether-based impression material, product *I*.

lated from different loads is shown for each curve. Similar results for the one-minute specimens are shown in Figure 6. The curves are not plotted in the region after removal of the load because the amount of recovery is dependent on the duration of the stress.

The creep compliance curves of the one-minute samples are effected by the length of time in the water bath. All samples were removed from the water bath after the manufacturer's minimum suggested time. Several minutes more in the bath would alter the curves toward the shape and position demonstrated by the one-hour samples. The samples tested at one minute after removal from the bath showed greater variation than the one-hour specimens. The range of $J(t)$ values for the one-minute samples are tabulated in Figure 6.

The recovery of the materials is characterized in Tables 3 and 4. Table 3 contains the data from the one-minute specimens, while Table 4 contains the data from the one-hour specimens. Each table has a section for percent set and percent recovery of elastic deformation. This last variable is a measure of how much of the instantaneous and retarded elastic deformation is recovered after removal of the load. The ideal viscoelastic material recovers 100% of its elastic deformation.

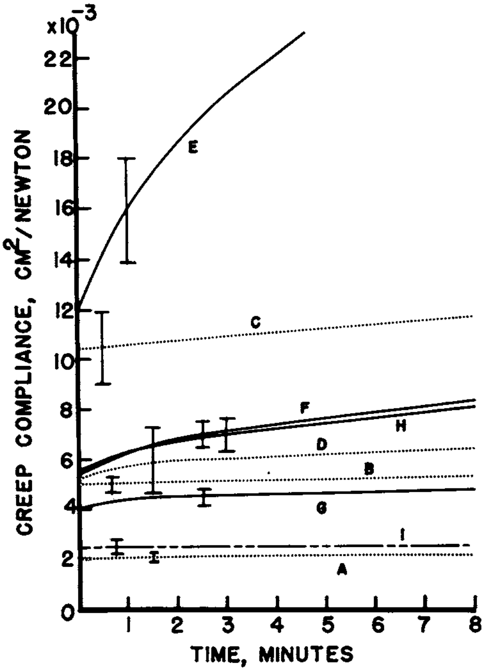

Fig 5.—Creep compliance curves for one-hour samples.

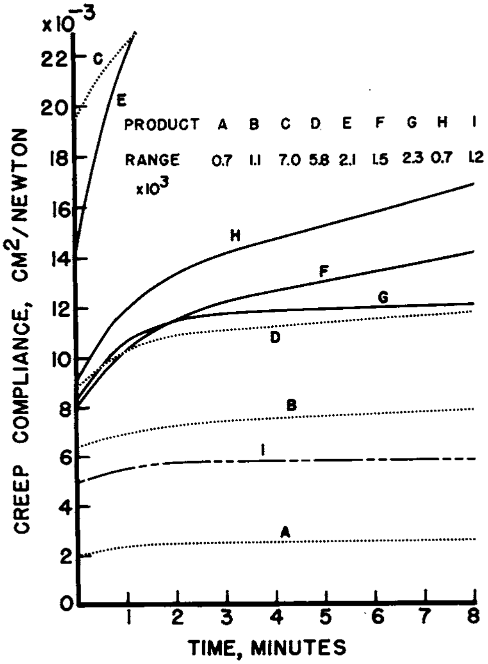

Fig 6.—Creep compliance curves for one-minute samples.

Discussion

The "elastic" impression materials demonstrate linear viscoelastic behavior, although the recovery after removing the stress is not ideally viscoelastic. Since the materials are linearly viscoelastic, the stress-strain time relations over a wide range of values can be characterized by a minimum number of tests.

The creep compliance curves illustrate the three components of deformation experienced by all of these materials. The values for the instantaneous creep compliance, J_o, ranged from 2 to 20 × 10^{-3} cm²/Newton for one-minute specimens, and 2 to 12 × 10^{-3} cm²/Newton for one-hour specimens. All materials showed a decrease in J_o, J_R, and viscous flow with continued polymerization and cross-linking. The retarded elastic response was completed within three minutes for most of the one-minute samples and within two minutes for the one-hour samples.

Produce *A* is a heavy-bodied material and illustrates the typical viscoelastic behavior for the stiffer, heavier consistency impression materials. The following discussion refers primarily to the regular-bodied materials.

Of the regular-bodied materials tested, product *I* (the polyether) had the lowest creep compliance. Of particular interest is its zero viscous flow. Within an hour after removal from the mouth, the polyether functions almost like an "ideal" elastic material. It demonstrates time-independent deformation, with no viscous flow, and nearly complete recovery. Therefore, after removal from the mouth the polyether material is safe from significant permanent dimensional change due to stress. This stability increases its ability to be handled, stored, and shipped. Product *B*, a silicone, demonstrated similar properties. Of course, when discussing dimensional stability consideration must also be given to polymerization shrinkage.

It is difficult to make generalizations about the creep compliance for the silicones or polysulfides as a class; however, the silicones tend to experience less retarded elastic deformation than the polysulfides. Two of the one-hour silicone-based impression materials showed no retarded elastic response.

Product *E* showed considerably more deformation than any of the other materials tested, even one hour after mixing. Product *C* showed the largest change in properties between one minute and one hour. This difference, however, could be decreased with a few extra minutes in the water bath.

TABLE 3

% SET AND % RECOVERY OF ELASTIC DEFORMATION FOR ONE-MINUTE SAMPLES

	% Set											
	500-gm Load				1,000-gm Load				1,500-gm Load			
	Duration of Stress (minutes)				Duration of Stress (minutes)				Duration of Stress (minutes)			
Material	1	3	6	12	1	3	6	12	1	3	6	12
A	0.2	...	0.2	0.5					0.3	...	0.7	0.9
B					0.5	1.3	1.7	2.1	0.8	1.2	1.7	5.3
C	2.2	...	7.7	5.8	3.1	...	12.0	9.5				
D					1.7	7.5	2.8	8.4	2.4	4.5	3.7	3.6
E	4.9	7.3	8.8	12.5	7.7	12.8	16.9	19.2				
F					2.3	3.1	7.2	4.9	5.7	5.5	9.3	7.3
G					6.9	1.7	8.4	3.3	2.0	4.4	7.2	9.9
H					2.7	5.5	7.2	8.8	4.0	7.7	9.6	11.7
I					1.1	1.7	2.3	3.9	1.3	3.6	3.3	4.8
	% Recovery of Elastic Deformation											
A	83	...	90	69					88	...	80	72
B					89	78	70	70	88	87	82	57
C	71	...	45	50	77	...	45	51				
D					73	48	67	36	75	62	65	72
E	44	39	44	39	57	42	44	34				
F					70	65	42	56	60	62	53	59
G					57	76	38	50	75	61	45	33
H					72	51	52	48	73	55	50	44
I					67	54	46	32	74	51	59	33

TABLE 4

% SET AND % RECOVERY OF ELASTIC DEFORMATION FOR ONE-HOUR SAMPLES

	% Set					
	500-gm Load		1,000-gm Load		1,500-gm Load	
	Duration of Stress (minutes)		Duration of Stress (minutes)		Duration of Stress (minutes)	
Material	6	12	6	12	6	12
A	0.2	0.2			0.0	0.2
B			0.3	0.4	0.4	0.3
C	0.5	1.1			1.6	2.4
D			1.1	1.1	1.1	2.4
E	5.3	8.0	8.1	12.7		
F			1.7	2.4	2.1	3.5
G			0.5	0.5	1.1	0.7
H			2.0	2.4	2.1	3.7
I			0.4	0.4	0.4	0.5
	% Recovery of Elastic Deformation					
A	75	80			100	97
B			95	93	95	98
C	93	93			95	91
D			83	90	91	80
E	64	64	74	73		
F			89	97	89	87
G			88	92	88	92
H			81	83	85	79
I			92	87	90	90

Several observations can be made about the set and recovery characteristics of these materials. First it should be noted that percent set in this investigation is not equal to the percent permanent deformation as measured for American Dental Association no. 19, since the later is determined after applying a specified strain. As expected the percent set increased with stress and duration of stress. The samples with higher percent set also had smaller values for percent recovery of elastic deformation. Some of the one-minute specimens recovered only 30 to 40% of their total elastic deformation. The one-hour specimens showed a distinct increase in recovery of elastic deformation, with most specimens recovering at least 80% of their elastic deformation. The materials that have completed their polymerization and cross-linking reactions are more nearly ideal viscoelastic materials, with permanent deformation almost completely a result of viscous flow. In samples that have not completed their polymerization and cross-linking reactions, however, permanent deformation is a result of viscous flow as well as a lack of recovery of elastic deformation. For the one-hour specimens the percent recovery of elastic deformation is independent of stress and duration of stress.

There are several clinically significant observations that can be made from this investigation. First, all materials demonstrated considerable change in viscoelastic properties between the one-minute and one-hour specimens. The most desirable impression materials with regard to viscoelastic properties are those that are most nearly completely elastic, that is, they demonstrate minimum viscous flow and retarded elastic flow. Of the regular-bodied materials tested products *I* and *B* were the most "elastic" materials and demonstrated the lowest percent set, less than 0.5%. With regard to dimensional changes due to stresses experienced during handling, shipping, and storage these materials are, therefore, the most stable. Again, however, note that polymerization shrinkage also affects dimensional stability.

The "stiffness" or "feel" of a material may be deceiving in determining its ability to resist dimensional change due to stress. For example, products *C* and *E* have similar instantaneous elastic compliances, but as can be seen in Figure 5, their total creep compliance curves are quite different. Under a given stress, with time, product *E* would show more strain and permanent deformation.

Conclusions

1. This investigation characterizes the viscoelastic properties of nine polysulfide, silicone, and polyether impression materials.
2. These materials demonstrate linear viscoelastic behavior during deformation. All three components of deformation—instantaneous elastic, retarded elastic, and viscous flow—decrease with continued ploymerization and cross-linking of the materials.
3. Permanent deformation in these materials is a result of lack of recovery of the elastic components of deformation as well as viscous flow.
4. The polyether and one silicone material most closely approach ideal elastic behavior. This characteristic is desirable for it minimizes dimensional change due to stresses encountered during handling, shipping, and storage of the impression.
5. The silicone materials in general exhibit less retarded elastic deformation than the polysulfide materials.
6. The creep test provides a more complete characterization of the mechanical properties of impression materials and requires only simple instrumentation.

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