THE DEVELOPMENT OF INTERNAL STRESS IN FILMS OF THERMOPLASTIC POLYMERS CAST FROM SOLUTION

DIANE MORAN AND PAUL M. WHITMORE
Carnegie Mellon University, Research Center on the Materials of the Artist and Conservator,
4400 Fifth Ave., Pittsburgh, PA 15213 USA

ABSTRACT

One of the known contributors to the physical failure of coating or adhesive applications is the shrinkage stress which develops as a solid film is formed from a solution, dispersion, or reactive mixture. As a first examination of the magnitude of such shrinkage stresses in art and restoration materials, we have determined the stresses which develop in films of thermoplastic polymers cast from toluene solutions, by measuring the curvature of a flexible substrate coated on one side with the polymer solution. The polymers studied include several poly (vinyl acetates) and poly (methacrylates), chosen to include several common coating materials and to span a range of physical and chemical properties. The results have been compared with a theory on the development of internal stress in films of solvent-based thermoplastic polymers. The theory correlates the magnitude of internal stress in the film with the amount of solvent which evaporates from the film after it has 'solidified'.

INTRODUCTION

Internal stress is one of the known contributors to the structural failure of polymeric films used as coatings, adhesives, and consolidants. The presence of a high internal stress in a film can cause loss of adhesion and/or cracking. Causes of internal stress in polymeric films include the shrinkage which occurs during film formation; environmental effects, such as changes in temperature or relative humidity;[1-3] and degradation. Whether a polymeric film forms from a solution, dispersion, or reactive mixture, it tends to shrink during formation. If the film is constrained by adhesion to a substrate, shrinkage stresses can result. Internal stresses in excess of the cohesive strength of a film can cause the film to crack. If the strength of a film-substrate bond is exceeded, the film may peel away from the substrate. Even if a film should remain intact following film formation, the inherent shrinkage stresses could put the film at risk to failure due to other stresses. For this study, we have focused on one aspect of internal stress in polymeric films used in art and restoration, shrinkage stress development during film formation.

Stress development in polymeric films has long been recognized as a problem, and has been the subject of much study.[4-19] These studies have found that internal stress can develop in polymeric films formed from solution,[4-10] dispersion,[11-15] or reactive mixtures.[16-19] For films formed from these methods, the magnitude of stress developed can depend on the polymer used,[4,8,11,16] the solvent,[7,12] and particle loading,[9-11,13,15] (including both the type of particle and the volume fraction in the film). In the above studies, the films formed from dispersions generally tended to exhibit less stress than those formed from either solutions or reactive mixtures. For this study, we wish to concentrate on internal stress development in

Mat. Res. Soc. Symp. Proc. Vol. 352 © 1995 Materials Research Society

thermoplastic polymeric films cast from solution. The studies on internal stress development in films of thermoplastic polymers cast from solution have included several in which a theory on the magnitude of internal stress development has been proposed and tested.[4-6]

The previous studies on internal stress development in films of thermoplastic polymers cast from solutions have been limited to a small number of polymers. In this study, we have included a larger number of polymers, most of which find use in art and restoration as adhesives, consolidants, and/or coatings.[20] We have measured internal stress development in a number of poly (methacrylate) and poly (vinyl acetate) films cast from toluene solutions. In an effort to determine the applicability and predictive power of a theory on stress development, we have tested a correlation between the maximum observed stress for each polymer and its measured glass transition temperature.

EXPERIMENTAL

The polymers investigated in this study are listed in Table I. The Elvacite polymers are made by DuPont; the Acryloids are made by Rohm and Haas, and the poly (vinyl acetates) are made by Union Carbide. Glass transition temperatures (T_g) of the polymers were measured with a Seiko Instruments differential scanning calorimeter, Model #220C. The difference in heat flow to the sample and a reference was measured as a function of temperature, while the sample and reference were subjected to the following controlled-temperature program: 1) heat from approximately 50°C below the T_g to approximately 40°C above the T_g at a rate of 10° C/min. and hold for 2 min., 2) cool to starting temperature at 20°C/min. and hold for 10 min., 3) repeat step 1). Sample sizes were between 5 and 10 mg. The glass transition temperature was taken to be the point of maximum change in the plot of heat flow vs. temperature during the second heating step (step 3).

Solutions of the polymers were made with reagent grade toluene (Fisher Scientific) with concentrations of 30-40 % polymer by weight. The films were applied to the substrate using a Boston-Bradley Adjustable Blade from Gardner Laboratory with a clearance of 0.25 mm. The substrate used was stainless steel feeler gage stock (301 stainless, from Precision Brand), 13 mm wide, 140 mm long, and 0.13 mm thick. The thicknesses of the coatings were measured with a magnetic thickness gage, Positector Model No. 6000-F3. Typical dry coating thicknesses were 0.02 to 0.08 mm.

A schematic diagram of the instrument for the measurement of internal stress is shown in Figure 1. (The design was taken from Ref. 4.) The curvature of the steel substrate was measured using a non-contacting capacitive transducer system from Capacitec, Model No. 3101-SP-BNC with HPT-150 probe. The transducer measures the capacitance of the capacitor formed by the detector and the electrically grounded substrate, and this capacitance is proportional to the distance between the detector and substrate. A "zero reading" was obtained with a flat bar, and the deflection of the sample, d, was determined by subtraction of the reading obtained with the sample from the zero reading. The transducer measurement system has a full scale deflection of 2.54 mm with uncertainty of 0.005 mm. The distance between the supports is 73 mm, designed so that the sample is balanced evenly above the transducer and a change in the weight of the film (due to solvent loss) will not cause a change in the amount of deflection in the substrate.[4] The instrument also has posts to guide the sample positioning, to

Table I. Polymers used, composition, and glass transition temperature.

Polymer	Composition	T_g / °C
AYAC	Poly (vinyl acetate), Mw = 12,800[a]	36
AYAA	Poly (vinyl acetate), Mw = 83,000[a]	34
AYAF	Poly (vinyl acetate), Mw = 113,000[a]	27
AYAT	Poly (vinyl acetate), Mw = 167,000[a]	28
Acryloid B-72	Ethyl methacrylate copolymer[b]	40
Acryloid B-67	Isobutyl methacrylate[b]	59
Elvacite 2014	Methyl methacrylate copolymer[c]	64
Elvacite 2045	Isobutyl methacrylate[c]	64
Elvacite 2043	Ethyl methacrylate[c]	76
Acryloid B-60	Methyl/(Normal butyl) methacrylate copolymer[b]	87
Elvacite 2013	Methyl/(Normal butyl) methacrylate copolymer[c]	89
Elvacite 2010	Methyl methacrylate[c]	104

a. See Ref. 20.
b. See Ref. 21.
c. See Ref. 22.

ensure reproducible sample placement above the transducer. Because the steel substrate is so thin (0.13 mm), it is flexible and bends easily. Polymer solutions applied to one face of the substrate cause the substrate to curl as the films dry and shrink. The amount of curvature produced in the steel substrate, along with the elastic properties of the substrate, are used to calculate the stress, S, present in the film using[23]

$$S = \frac{4Et^3d}{3cl^2(t+c)(1-\nu)} \tag{1}$$

where E is the elastic (Young's) modulus of the substrate, t is the thickness of the substrate, d is the measured deflection of the substrate, c is the thickness of the coating, l is the distance between the supports, and ν is Poisson's ratio for the substrate. Eqn. (1) applies if the elastic modulus of the coating is smaller than that of the substrate and if the coating thickness is smaller than the substrate thickness. (See Ref. 20 for more-detailed specifications of the modulus and thickness relationships.) The elastic modulus, E, of the substrate is determined by measuring the deflection of the uncoated substrate when a weight is placed in the center of the span, using[23]

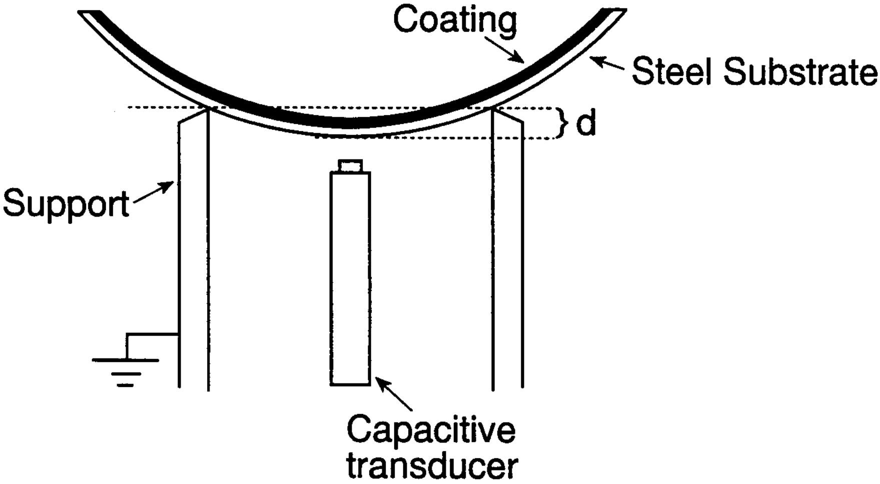

Figure 1. Schematic diagram of instrument to measure internal stress in polymeric films.

$$E = \frac{Pl^3}{4dt^3b} \qquad (2)$$

where P is the mass of the weight used and b is the width of the substrate. The value of E was measured for each substrate, and was typically 160-190 GPa. Poisson's ratio, ν, of the stainless steel substrate was taken to be 0.295.[8,24]

In these experiments, substrates were coated and introduced into a glove box maintained at 25.0 ± 0.2 °C and 50 ± 2 % R.H. The substrates were stored in racks designed to support them evenly and allow them to bend freely during the drying. Curvature measurements were made by placing the substrates on the instrument described above, which was also housed within the glove box. For the first 8 hours after each sample was made, the stress was measured approximately every 30 minutes, and each data point was the average of three measurements. After the first day, since the stress was changing more slowly, it was measured once per day. For these data points, two measurements were made, to ensure that the result was reproducible to within 0.05 MPa.

RESULTS

Table I gives the glass transition temperatures for the polymers under investigation. For all of the polymers, the measured T_g is greater than or equal to the published value.[20-22] The differences could be due to the use of different instruments or measurement techniques.

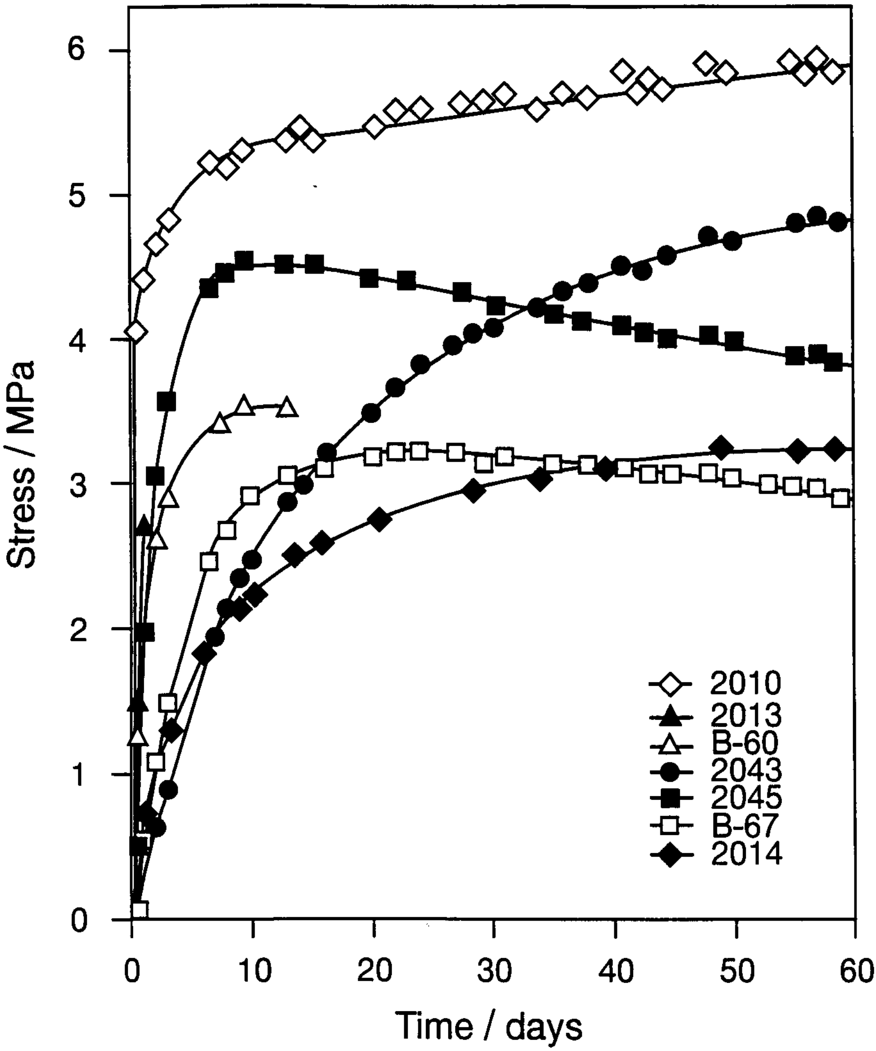

Figure 2. Stress measured during drying for films of polymers cast from toluene solutions. The stresses for the Acryloid B-72 and poly (vinyl acetate) samples were all ≤ 0.2 MPa for the entire time of measurement and are not shown in the figure.

Stresses measured for the film samples during drying are shown in Figure 2. Data is shown for the first 60 days only, although measurements were taken for an additional 100 days. (The curves show little change in days 61 to 160.) The stress development curves for the films differ in several ways, including the rate at which stress develops, whether or not the stress reaches a maximum, and (for those samples which do reach a maximum) whether the stress decreases or remains constant after reaching its maximum. The stress for the Elvacite 2010 sample increased rapidly to 4 MPa after 5 hours, and following this jump the stress continued to increase slowly for the entire time that measurements were taken. For both Elvacite 2043 and 2014, the stress slowly increased to a maximum and remained constant, and the stress for Elvacite 2045 and Acryloid B-67 decreased after reaching a maximum after about 9 days. The maximum stress values ranged from essentially zero for the poly (vinyl acetate) films and for Acryloid B-72 to 6.4 MPa for Elvacite 2010. The magnitudes of these high stresses are comparable to ultimate tensile or film-substrate adhesive strengths for several of the films, as evidenced by the fact that they began to crack and detach from the steel substrate. The samples affected were Elvacite 2013 (1 day), Acryloid B-60 (9 days), and Elvacite 2043 (48 days). The times at which failure was observed are given in parentheses. Although the Elvacite 2043 sample had begun to fail after 48 days, it did not completely detach from the steel substrate. We continued to make measurements on the Elvacite 2043 sample and the stress increased even after it began to crack and detach from the substrate. The stress determined for this sample after it exhibited failure represents the lower limit for the actual value of stress in the sample. Published tensile strengths and maximum stress values measured for the Elvacite polymers are given in Table II.[22] The uniaxial tensile strengths have been converted to biaxial tensile strengths by dividing by (1-ν) (using an approximate value for Poisson's ratio, ν) for comparison with our stress values. Note that the tensile strengths do not increase with the T_g for the polymers (compare with Table I). For the Elvacite samples which failed, 2013 and 2043, the maximum stress measured was comparable to the biaxial tensile strength of the pure polymer. Although the 2045 sample did not exhibit failure which was visually observable, the maximum stress measured for the sample was also comparable to the biaxial tensile strength of the polymer. This sample, along with the B-67 sample, may have failed via microscopic cracks, and the failure may be the reason that the stress decreased for those samples after reaching a maximum.

DISCUSSION

Theory on internal stress development in solvent-cast films of amorphous polymers

A theory on internal stress development in solvent-cast films of amorphous thermoplastic polymers was developed and tested by Croll.[5] This theory does not address the stress development *process* itself, just the stress that results after the coating has dried. According to this model, when a film is cast from a polymer solution, it begins to dry by evaporation of the solvent. As the solvent leaves the film, the polymer molecules, plasticized by the remaining solvent, flow to close the gaps left by the lost solvent molecules. Eventually, enough of the solvent evaporates that the polymer molecules can no longer flow readily to fill the gaps left by evaporating solvent molecules. Croll refers to this point at which the polymer molecules can no longer flow to fill the gaps as the "solidification point" of the film. The volume of solvent which evaporates after the solidification point leaves a void volume within the film which constitutes strain in the film. The strain produces stress via the elastic (Young's) modulus of the polymer (*vide infra*).

than of a good solvent. Thus the strain will tend to be greater for films of high T_g polymers and for films cast from poor solvents. According to the theory by Croll, then, higher shrinkage stresses will occur in films of a polymer having a high Young's modulus and/or a high glass transition temperature, and which have been cast from poor solvents.

Croll's tests of the theory have provided very good agreement between theory and experiment.[4] However, the theory neglects the stress relaxation which may take place in a polymer which is below its T_g. Even after the solidification point, the polymer molecules possess a limited ability to move and close the gaps left by solvent molecules which have evaporated. Thus the actual strain will be smaller than that assumed in the theory. The mobility will be greatest when the film is not far below its T_g, and a polymer with a low Young's modulus will also have more mobility than one with a high modulus.

Comparison of theory with experimental results

Our data set includes films of several methacrylate polymers and poly (vinyl acetates) cast from toluene solution. Since we have used only one solvent, we cannot compare the effects of different solvents on stress development in this study, and we focus instead on the different polymers examined. We have two sets of samples in our data set: the poly (vinyl acetates) and the methacrylate polymers. The relevant parameters in Croll's theory on stress development are the Young's modulus and glass transition temperature of the polymer and the strength of the polymer-solvent interactions. If we assume that within each data set, the Young's moduli will be approximately equal[25] and that the polymer-solvent interactions will also be similar (due to the chemical similarities of the polymers), the remaining parameter affecting the magnitude of stress development is the glass transition temperature of the polymer. Figure 3 shows a plot of the maximum stress measured for each sample versus the glass transition temperature of the polymer. For the poly (vinyl acetates) the stresses are all essentially zero. These polymers all have a T_g just above room temperature, so no stress is expected because the polymer will not reach its solidification point until very little solvent remains. The AYAC and AYAA samples, having T_g's of 36°C and 34°C, respectively, might have had a small volume of retained solvent at their solidification points. It is reasonable to attribute the absence of stress development to relaxation processes occurring in these very soft solids. By contrast, the methacrylate polymers have T_g's ranging from 40°C to 104°C, and for these polymers, the stress appears to increase with T_g. There is some scatter in the relationship between maximum stress and T_g which could be due to differences in the Young's moduli for the different polymers, differences in the interaction of toluene with the individual polymers, or in varying ability to relieve stresses through plastic flow or microscopic fracture. However, it does appear that within the set of methacrylate polymers, the T_g of the polymer is a reasonably good predictor of the maximum shrinkage stress which will develop in films cast from toluene solutions. The point in Figure 3 marked with a question mark represents the Elvacite 2013 sample, which exhibited failure early in the experiment. The stress value for this sample may be lower than the actual value of stress when the sample failed. The stress was increasing rapidly, and our measurements were not made continuously. The value plotted in the figure is from the last measurement made before failure was observed; the actual stress when failure occurred may have been higher.

Table II. Tensile strengths and maximum stresses measured for Elvacite polymers.

Polymer[a]	Biaxial Tensile Strength[b] / MPa	Maximum Stress MPa
Elvacite 2010	68	6.4
Elvacite 2014	43	3.3
Elvacite 2045	5	4.6
Elvacite 2043*	10	5.2
Elvacite 2013*	3.3	2.7

a. The polymers marked with an asterisk exhibited failure by cracking and detaching from the substrate.
b. Uniaxial tensile strengths were obtained from Ref. 22. The value of ν was approximated with 0.4 for all of the polymers in converting from uniaxial to biaxial tensile strengths.

Croll's theory defines the solidification point as the point at which the glass transition temperature of the partially dried polymer solution equals room temperature. The volume of solvent present in the film when it solidifies is the amount required to depress the glass transition temperature of the pure polymer to room temperature. The volume fraction of solvent lost after the film solidifies equals 3ε, where ε is isotropic linear strain.[5] (The volume of solvent lost after solidification is not necessarily the full amount that is present at solidification, for there can be a finite amount of solvent retained in the film indefinitely.) The thickness of the film can contract in response to the component of strain perpendicular to the plane of the film; however, if the film is adhered to a substrate, the strain in the plane of the film results in stress which is biaxial. Assuming that the film behaves as a Hookean material,[25] the stress S is equal to

$$S = \frac{E\varepsilon}{1-\nu} \tag{3}$$

where E is the Young's modulus of the polymer and ν is Poisson's ratio for the polymer (needed because the Young's modulus applies to uniaxial stresses and the stress is biaxial in this case). For thermoplastic materials, ν is generally between 0.35 and 0.45.

The magnitude of the stress in the film, then, is governed by two factors: the Young's modulus (or stiffness) and the strain. The Young's modulus is determined by the choice of polymer, but the strain depends on the polymer/solvent system. As described above, the amount of strain present in the film depends on the amount of solvent lost from the film after the solidification point, which in turn depends on the glass transition temperature of the polymer and on how well the solvent plasticizes the polymer. In general, a polymer with a high T_g will contain more solvent at its solidification point than a polymer of low T_g, for a greater amount of solvent will be required to depress a high T_g to room temperature. Furthermore, for a given polymer, it will take more of a poor solvent to depress its T_g to room temperature

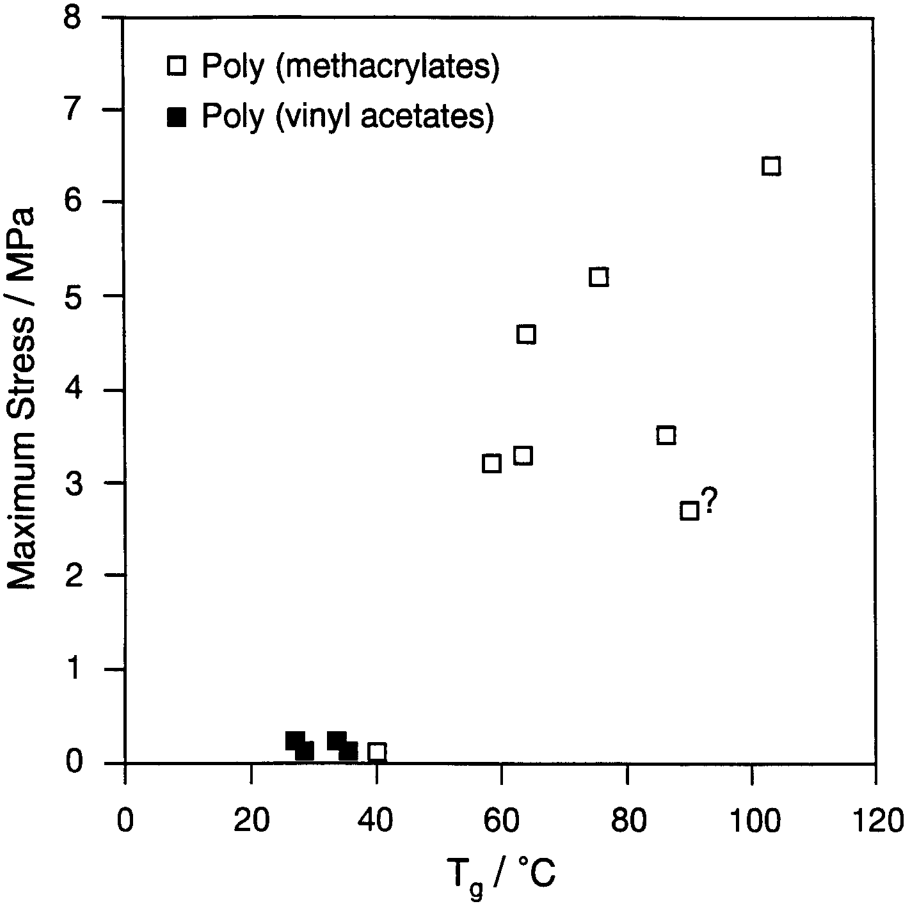

Figure 3. Maximum stress measured for polymer films cast from toluene solutions vs. T_g of pure polymer. The point marked with a question mark represents the Elvacite 2013 sample. The stress value for this point may be lower than the actual maximum stress in the sample.

CONCLUSION

We have measured stress development for films made from a number of polymers cast from toluene solutions. According to the theory on stress development proposed by Croll, the parameters affecting the magnitude of stress in the above films are the Young's modulus and glass transition temperature of the polymer and the strength of the polymer-solvent interactions. For the methacrylate polymers in our study, the magnitude of stress which develops in a film generally increases with the T_g of the polymer in the film, and the results for the poly (vinyl acetate) samples are consistent with this observation. Thus the T_g of the polymer might provide an *a priori* estimate of the likelihood of high shrinkage stresses in films. As several of our samples have shown, high shrinkage stresses can cause failure in films or in film-substrate bonds. However, even if the shrinkage during film formation does not cause failure immediately, these built-in stresses may make more likely subsequent failure due to small stresses from other sources, such as environment, degradation, or physical distortion.

ACKNOWLEDGMENT

This work was performed at the Research Center on the Materials of the Artist and Conservator at Carnegie Mellon University. The financial support of the Andrew W. Mellon Foundation is gratefully acknowledged.

REFERENCES

1. M.F. Mecklenburg in *Materials Issues in Art and Archaeology II*, edited by P.B. Vandiver, J. Druzik, and G.S. Wheeler (Mater. Res. Soc. Proc. **185**, Pittsburgh, PA, 1991) p. 105.
2. M.F. Mecklenburg, C.S. Tumosa, and M.H. McCormick-Goodhart in *Materials Issues in Art and Archaeology III*, edited by P.B. Vandiver, J.R. Druzik, G.S. Wheeler, and I.C. Freestone (Mater. Res. Soc. Proc. **267**, Pittsburgh, PA, 1992) p. 337.
3. J.D. Erlebacher, E. Brown, M.F. Mecklenburg, and C.S. Tumosa in *Materials Issues in Art and Archaeology III*, edited by P.B. Vandiver, J.R. Druzik, G.S. Wheeler, and I.C. Freestone (Mater. Res. Soc. Proc. **267**, Pittsburgh, PA, 1992) p. 359.
4. S.G. Croll, J. Oil Col. Chem. Assoc. **63**, 271, 1980.
5. S.G. Croll, J. Appl. Polym. Sci. **23**, 847, 1979.
6. S.G. Croll, J. Coatings Tech. **50**(638), 33, 1978.
7. D.Y. Perera and D. Vanden Eynde, J. Coatings Tech. **55**(699), 37, 1983.
8. D.Y. Perera and D. Vanden Eynde, J. Coatings Tech. **53**(677), 39, 1981.
9. D.Y. Perera and D. Vanden Eynde, J. Coatings Tech. **53**(678), 40, 1981.
10. S.G. Croll, Polymer **20**, 1423, 1979.
11. D.Y. Perera, J. Oil Col. Chem. Assoc. **68**, 275, 1985.
12. D.Y. Perera and D. Vanden Eynde, J. Coatings Tech. **56**(718), 69, 1984.
13. D.Y. Perera and D. Vanden Eynde, J. Coatings Tech. **56**(717), 47, 1984.
14. G.P. Bierwagen, J. Coatings Tech. **51**(658), 117, 1979.
15. D.Y. Perera, J. Coatings Tech. **56**(716), 111, 1984.
16. D.Y. Perera and D. Vanden Eynde, J. Coatings Tech. **59**(748), 55, 1987.
17. A. Saarnak, E. Nilsson, and L.O. Kornum, J. Oil Col. Chem. Assoc. **59**, 427, 1976.
18. R.N. O'Brien and W. Michalik, J. Coatings Tech. **58**(735), 25, 1986.
19. S.G. Croll, J. Coatings Tech. **51**(659), 49, 1979.
20. C.V. Horie, *Materials for Conservation* (Butterworths, London, 1987), p. 93.
21. *Acryloid Thermoplastic Acrylic Ester Resins*, Rohm and Haas product pamphlet.

22. *Elvacite Acrylic Resins: Properties and Uses*, DuPont product pamphlet.
23. E.M. Corcoran, J. Paint Tech. **41**, 635, 1969.
24. *Smithells Metals Reference Book*, edited by E.A. Brandes and G.B. Brook (Butterworth-Heinemann Ltd., Oxford, 1992), p. 15-3
25. H.-G. Elias, *Macromolecules, Vol. 1*, 2nd ed. (Plenum Press, New York, 1984), p. 425-431.