

Damping Transients in Polymers during Sorption and Desorption

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Synopsis

It has been found that sudden changes in atmospheric vapor pressure of swelling agents result in a transient increase in mechanical damping in polymers. The effect was observed on both raising and lowering the vapor pressure. The systems investigated were: cellulose (paper)-water; cellulose (paper)-ammonia; gelatin-water; nylon 66-water; cellulose acetate-acetone; poly(vinyl acetate)-acetone; rubber hydrochloride-chloroform; and polystyrene-benzene. The damping was measured with a low-frequency torsional pendulum. The results suggest that the transient damping effect is associated with diffusion processes taking place in the sample during attainment of equilibrium.

A transient increase in mechanical damping has been observed in polymer-solvent (swelling agent) vapor systems after sudden changes in the atmospheric vapor pressure. The effect, which was noted on both raising and lowering the vapor pressure seems to be associated with diffusion processes accompanying the approach to sorption equilibrium. The following systems were investigated: cellulose (paper)-water, cellulose (paper)-ammonia, gelatin-water, nylon 66-water, cellulose acetate-acetone, poly(vinyl acetate)-acetone, rubber hydrochloride-chloroform, polystyrene-benzene. No effect was observed for the polyethylene-water system, apparently owing to the absence of an interaction between the polymer and the vapor.

The damping was determined with a torsion pendulum, by means of which a tensile stress could be applied to the sample during oscillation.^{1,2} The pendulum was placed in a vacuum chamber in which a range of vapor pressures could be produced by evaporating known quantities of liquid. The results were expressed in terms of the loss factor, $\tan \delta$, for a frequency of approximately 1 Hz. The coefficient of variation of $\tan \delta$ was 2-4%. The measurements were carried out at 20°C.

The experiments with cellulose film (cellophane) and paper were performed on commercial samples cut perpendicular to the main direction of anisotropy, i.e., in the cross direction. At 65% R.H. and 20°C. the samples had the properties shown in Table I.

TABLE I
Properties of Paper and Cellulose Film Specimens at 20°C. and 65% R.H.

	Paper	Cellulose film
Specific volume, cm. ³ /g.	1.60	0.68
Thickness, mm. ^a	0.145	0.045
Tensile strength, 10 ⁸ dyne/cm. ²	2.4	5.9
Anisotropy factor $E_{\parallel} / E_{\perp}$ ^b	1.8	1.8
Moisture content, %	9.8	11.3
Degree of polymerization	~1500	290

^a Length 14.0 cm., width 1.5 cm.

^b Static modulus measured parallel and perpendicular to the main direction of anisotropy at a strain rate of 5.0×10^{-3} sec.⁻¹.

The results of experiments using paper and cellulose samples in water vapor and ammonia are reproduced in Figure 1. The initial water content of the samples corresponded to a relative humidity of 65%. They were exposed to vacuum for about 10 min., after which time a relative humidity of 70% or an ammonia pressure of 200 torr were produced in the chamber. The resulting transient changes in damping can be seen in Figure 1 (left). After about 10⁵ sec. the chamber was evacuated to 10⁻² torr. For the two types of samples and for both water vapor and ammonia atmospheres there was a pronounced temporary increase in damping. The transients shown in the middle of Figure 1 start from equilibrium conditions, whereas the

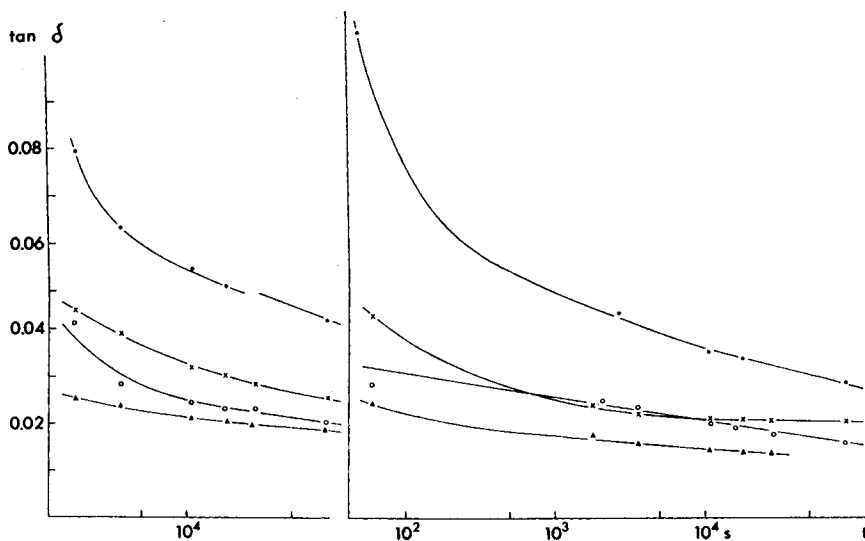


Fig. 1. Damping transients for cellulose film and paper due to diffusion of water vapor and ammonia: (●) cellulose film-water, (×) paper-water, (○) cellophane-ammonia, (Δ) paper-ammonia; (left) relative humidity increased from ~0 to 70% and ammonia pressure from ~0 to 200 torr; (right) measuring chamber evacuated to 10⁻² torr.

initial conditions for the transients shown on the left are not accurately known. The damping behavior was not influenced by longitudinal stresses of 10^5 – 10^7 dyne/cm.². The results were essentially the same for a number of paper and cellulose samples and under differing conditions of humidity and ammonia pressure.

The results for a number of polymer–solvent systems are summarized in Table II. The samples were initially kept at 10^{-2} torr. The vapor pressure of the solvent was then maintained at a certain level for an interval of the order of 10–20 hr. The resulting values for the damping value could be considered as an equilibrium value. The vapor pressure was then reduced to 10^{-2} torr by evacuating the measuring chamber. The resulting transient increase in damping and the approach to the equilibrium damping value can be seen from the results tabulated. As might be expected, lower equilibrium values of $\tan \delta$ were obtained after the solvent vapor had been removed. The magnitude of the transient increase in damping was dependent on the initial pressure and apparently on possible swelling due to the vapor at this pressure. The pressures given in Table II were chosen to give readily observable effects. In experiments with the nylon 66–water system the transient was only weakly developed.

TABLE II
Transient Increase in $\tan \delta$ for Polymers Following Reduction of the Vapor Pressure of the Solvent

System ^a	Solvent pressure, torr	Time after pressure change, hr.	$\tan \delta \times 10^2$
Gelatin–water (thickness: 0.159 mm.)	10	16 ^b	3.42
	0	0	4.96
	0	4/60	4.73
	0	7	2.24
Cellulose acetate–acetone (thickness: 0.026 mm.; molecular weight: 1.5×10^6)	53	16 ^b	0.47
	0	0	0.94
	0	3/60	0.83
	0	4	0.43
Poly(vinyl acetate)–acetone (thickness: 0.032 mm.; molecular weight: 2.4×10^6)	40	5 ^b	2.27
	0	0 ^b	2.97
	0	3/60	3.04
	0	2	1.75
Rubber hydrochloride–chloroform (thickness: 0.038 mm.; molecular weight: 2.4×10^6)	58	17 ^b	1.81
	0	0	2.21
	0	4/60	2.22
Polystyrene–benzene (thickness: 0.027 mm.)	30	20 ^b	0.58
	0	0	0.80
	0	5/60	0.71
	0	2	0.48

^a Length 14.0 cm., width 1.5 cm.

^b Time during which the samples, initially kept at 10^{-2} torr, were in contact with the vapor. The corresponding values of $\tan \delta$ can be considered as approximate equilibrium values.

The symmetry of the described behavior is characteristic of irreversible microprocesses—in this case diffusion—taking place in a stress field.^{3,4} A quantitative relationship is at present difficult to discern, but a closer study of this effect may be rewarding in, for instance, polymer-vapor or polymer-liquid systems, especially with respect to diffusion and relaxation processes. A notable point is the long time required, for instance, by hygroscopic polymers, to reach damping equilibrium after changes in the atmospheric vapor pressure.

References

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Résumé

On a trouvé que les changements brusques de pression de vapeur atmosphérique des agents de gonflement entraînent une augmentation temporaire dans l'amortissement mécanique des polymères. L'effet a été observé lors de l'augmentation et de l'abaissement de pression de vapeur. Les systèmes étudiés sont: cellulose (papier)-eau; cellulose (papier)-ammoniaque; gélatine-eau; nylon 66-eau; acétate de cellulose-acétone; acétate de polyvinyle-acétone; caoutchouc hydrochloré-chloroforme; et polystyrène-benzène. L'amortissement a été mesuré au moyen d'un pendule de torsion à basse fréquence. Les résultats suggèrent que l'influence de l'amortissement temporaire est associé au processus de diffusion qui a lieu dans l'échantillon pendant l'établissement de l'équilibre.

Zusammenfassung

Es wurde gefunden, dass plötzliche Änderungen des Dampfdruckes eines Quellungs-mittels zu einer vorübergehenden Erhöhung der mechanischen Dämpfung bei Polymeren führen. Dieser Effekte wurde sowohl bei der Erhöhung als auch bei der Erniedrigung des Dampfdruckes beobachtet. Untersucht wurden die Systeme: Zellulose (Papier)-Wasser, Zellulose (Papier)-Ammoniak, Gelatine-Wasser, Nylon 66-Wasser, Zellulose-acetat-Aceton, Polyvinylacetat-Aceton, Kautschukhydrochlorid-Chloroform und Polystyrol-Benzol. Die Dämpfung wurde mit einem Torsionspendel niedriger Frequenz gemessen. Die Ergebnisse zeigen, dass der vorübergehende Dämpfungseffekt mit Diffusionsprozessen verknüpft ist, welche in der Probe während der Gleichgewichtseinstellung auftreten.

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