

Physical Properties of Oxidative Polymerized Films Prepared from Polymerized Oils, Alkyd Resins, and Phenolic Varnishes: Transition by Dynamic-Mechanical Method and Line-Width Measurement (NMR)

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Synopsis

Glass transition temperatures of oxidative polymerized films were measured by the dynamic-mechanical method and by line-width measurements (NMR). The correlation was studied in relation to the chemical structure. The films investigated were polymerized linseed oil, alkyd resins, phenolic varnishes, and polyester-urethane films. It is found that the effects of chain stiffness and the degree of crosslinking predominate in T_g measured by the dynamic-mechanical method, whereas the effect of polar groups is most important on T_g measured by line-width measurement. It was previously reported that T_g as measured by the line-width measurement increased with the degree of crosslinking in vulcanized rubbers. This was not observed in films of phenolic varnishes, as the variation of the polar groups was involved. The meaning of T_g measured by different methods is also discussed from the thermodynamic standpoint.

INTRODUCTION

It is well known that film formation by oxidative polymerization proceeds with the formation of hydroperoxide and its decomposition, leading to crosslinking. Representative of such polymers are polymerized drying oils, alkyd resins, ester gum varnishes, and phenolic varnishes. The oxidative polymerized films have network structures which differ from the polymers of linear structure (thermoplastics). The methods of investigation employed previously for studying such films are as follows:¹⁻³ infrared spectra; viscoelastic properties; swelling and solubility characteristics; practical testing.

Recently, nuclear magnetic resonance (NMR) techniques have been widely employed to investigate the structure and molecular motions in polymers. In order to get more information about film formation of oxidative polymerized films, especially the correlation of reactivity, structure, and molecular motion, the NMR technique was employed in addition to infrared spectral methods and viscoelastic measurements. As film-forming

materials, polymerized oils, alkyd resins, and phenolic varnishes were used to show their differences in chemical structure and reactivities of film formation.

METHODS

Preparation of Films

The varnishes, for example, a solution of prepolymer in an equal weight of xylene, were coated on tin plates under film-forming conditions detailed below. The coating procedure was repeated several times in order to get the desired thickness of films. Then the films were stripped off by the amalgam method.

Torsional Pendulum Method

The temperature (T) dependence of shear modulus G and logarithmic decrement λ of the films were measured by the torsional pendulum method.⁴ The following data are obtained from the G - T and λ - T curves: the glass transition temperature measured by a dynamic-mechanical method (T_g)_d, i.e., the temperature is maximum at λ (λ_{\max}); the shear modulus at high temperatures G_h , the shear modulus obtained from the plateau at high temperatures, which is a measure of degree of crosslinking;⁵⁻⁷ the shear modulus at room temperature G_r , i.e., the shear modulus at 20°C., a measure of rigidity of the films at room temperature.

Infrared Spectra

The process of film formation was examined by an infrared method. After coating the varnishes on rock salt prisms and removal of solvent at 10 mm. Hg vacuum for 1 hr., the infrared spectra were measured. Films stripped off from tin plates were ground and their infrared spectra were measured by means of the potassium bromide pellet technique. The change of functional groups is expressed by optical density D or the ratio of that of the related functional groups.

Line Width by NMR

Measurement of line width (ΔH) at different temperatures by nuclear magnetic absorption was carried out for the films. The temperature at which the $d(\Delta H)/(dT)$ is maximum is expressed as the transition temperature measured by the NMR method (T_g)_n. NMR spectra were obtained by a JEOL, JNM-BL-2 type instrument (30 Mcycles).

EXPERIMENTAL AND RESULTS

Polymerized Oil and Alkyd Resins

Generally speaking, alkyd resins are considered to consist of a polyester backbone from phthalic anhydride and glycerine, with unsaturated ali-

phatic side chains. When the alkyd resins are compared with polymerized oil, some steric effects due to the phthalate group may be expected to show up as differences in the viscoelastic properties of the films.

Materials

Polymerized Oil. Linseed oil (commercial grade, iodine value 183) was heated in air at 210°C. for 8 hr. (M.W. 1730; measured by Mechrolab vapor pressure osmometer).

Alkyd Resins. Glycerine (chemical grade), phthalic anhydride (chemical grade), and linseed oil fatty acid (commercial grade, iodine value 187) were heated together at 230°C. in a stream of nitrogen. The reaction times to obtain resins of oil length 50 (M.W. 1400) and 60 (M.W. 1710) were 7 and 9 hr., respectively.

Film-Forming Conditions

The varnishes were coated on tin plates and heated at 105°C. for 2 hr.; this coating process was repeated six times.

Results and Discussion

The results are shown in Figures 1-3 and Table I. As the concentration of the aliphatic component of the prepolymer increased, $(T_g)_d$ and G_r decreased, and $(T_g)_n$, G_h , and D_{OH} increased. These results indicate that the effect of the phthalate group is to raise $(T_g)_d$ and G_r , i.e., to increase the rigidity of the films, and to decrease the degree of crosslinking and the

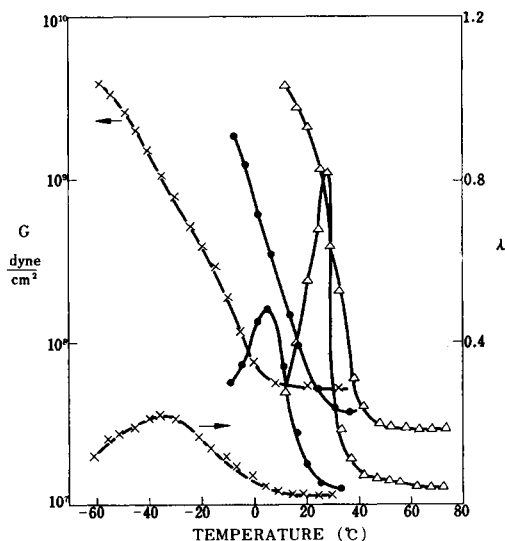


Fig. 1. G - T and λ - T curves of films of polymerized linseed oil and alkyd resins: (×) polymerized linseed oil; (●) alkyd resin, oil length 60; (Δ) alkyd resin, oil length 50.

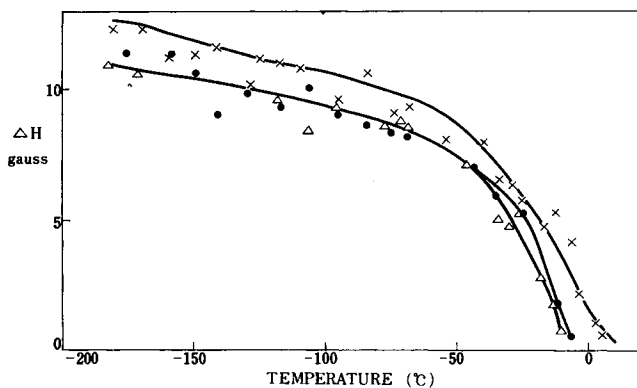


Fig. 2. ΔH - T curves of films of polymerized linseed oil and alkyd resins: (X) polymerized linseed oil; (●) alkyd resin, oil length 60; (Δ) alkyd resin, oil length 50.

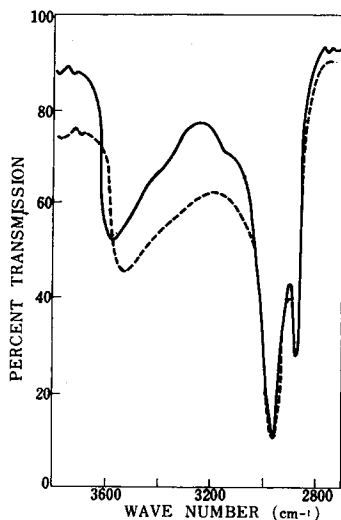


Fig. 3. Infrared spectra (near 3μ) of films of polymerized linseed oil and alkyd resin: (---) polymerized linseed oil; (—) alkyd resin, oil length 60. KBr pellet, 6 mg. of sample/700 mg. of KBr.

concentration of polar group in the films. It is also suggested that the decrease of $(T_g)_n$ is due to the decrease in the concentration of polar groups.

TABLE I
Physical Properties of Films of Polymerized Linseed Oil and Alkyd Resins

Films	$(T_g)_d$, °C.	G_h , dyne/cm. ²	G_r , dyne/cm. ²	$(T_g)_n$, °C.	D_{OH}
Polymerized linseed oil	-35	5.2×10^7	5.2×10^7	0	0.367
Alkyd resin (oil length 60)	5	3.6×10^7	7.0×10^7	-10	0.257
Alkyd resin (oil length 50)	28	3.0×10^7	2.0×10^8	-15	

The results also may be explained reasonably on the basis of the facts that the unsaturated part of aliphatic constituent of prepolymer is the functional group of oxidative polymerization and that the content of the unsaturated groups is proportional to oil length.

Phenolic Varnishes

These prepolymers are considered to be partially or wholly mixtures of polymerized oils and phenol-formaldehyde resin, and they differ in homogeneity from alkyd resins. The effect of this difference on physical properties of films was investigated.

Materials

For the drying oil (O), a mixture of tung oil (iodine value 168) and linseed oil (iodine value 187), (1:1) was used. For resins, two types of *p*-tert-butylphenol-formaldehyde resins were prepared by conventional methods; these were a resole type (R) (M.W. 650, m.p. 65–72°C.) and a novolac type (N) (M.W. 375, m.p. 55–62°C.).

Preparation of Prepolymers. Oils only, or mixtures of oils and resin (3:2) were heated in air at 210°C. The reaction times were 8 hr. for the novolac type (N-O), 3 hr. for the resole type (R-O), and 5½ hr. for oils (PO). Each of the prepolymers was then dissolved in an equal weight of mineral turpentine.

In addition to these varnishes, two other varnishes were prepared by dissolving each of the mixtures of polymerized oils and resin (3:2) in an equal weight of mineral turpentine containing 2–3% methyl ethyl ketone at room temperature (N + PO, R + PO).

Film-Forming Conditions

Drying agents were added to the varnishes (Co 0.02%, Mn 0.02%). Air-dried films were prepared by coating on tin plates and allowing the coated plates to stand in a room temperature for 24 hr. (20°C., 68% R.H.); this was repeated 10 times. To prepare baked films, the samples were coated on tin plates and heated at 80°C. for 2 hr., and the process repeated 10 times.

Results and Discussion

Chemical Reaction Involved in Film Formation. To determine the effect of polar groups on $(T_g)_n$, the change of D_{OH} near 3μ in film formation was measured (Fig. 4). The increase of D_{OH} of phenolic varnishes was much less compared with that of polymerized oils in the case of air drying, and their D_{OH} decreased on continuing heating in the case of baking. Elementary analysis was also carried out on the films in order to get information on the oxygen absorbed during film formation (Table II). It is obvious that the amount of oxygen absorbed in films of phenolic varnishes was similar to that absorbed by polymerized oil films. It is also known that a reaction between drying oils and phenol-formaldehyde resins takes place

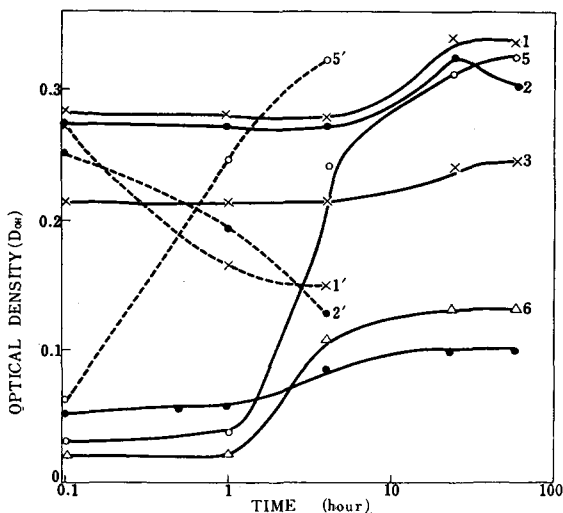


Fig. 4. Relation of optical density D_{OH} and drying time in phenolic varnishes: (1) N + PO, air drying; (2) R + PO, air drying; (3) N—O, air drying; (4) R—O, air drying; (5) PO, air drying; (6) N-Ac + PO, air drying; (1') N + PO, baking; (2') R + PO, baking; (5') PO, baking.

in the course of oxidative polymerization⁸ and a reaction between hydroperoxide and phenols takes place in the presence of catalyst.⁹ It is seen that the change in D_{OH} of the mixture of acetylated *p*-tert-butylphenol-formaldehyde resin and polymerized oils is similar to that of polymerized oils in case of air drying (Fig. 4, N-Ac + PO).

These data and the above results on oxygen absorption lead to the conclusion that the hydroperoxide produced by the autoxidation of oils reacts with the phenolic resin, with a concomitant decrease of phenolic hydroxyl groups, though the reaction is still not fully understood.

TABLE II
Elementary Analysis of Oxidative Polymerized Films

Films	Drying method	C, %	H, %	O, %	Number of oxygen atoms per acyl group in the films ^a
N-O	Air drying	71.91	8.53	19.56	3.9
N-O	Baking	71.74	8.54	19.72	4.0
Alkyd resin (oil length 60)	Air drying	63.78	7.46	28.76	3.8
"	Baking	64.29	7.39	28.32	3.6
Polymerized linseed oil	Air drying	65.12	9.18	25.70	4.6
"	Baking	65.20	8.58	26.36	4.6

^a Assuming no scission of acyl groups during film formation.

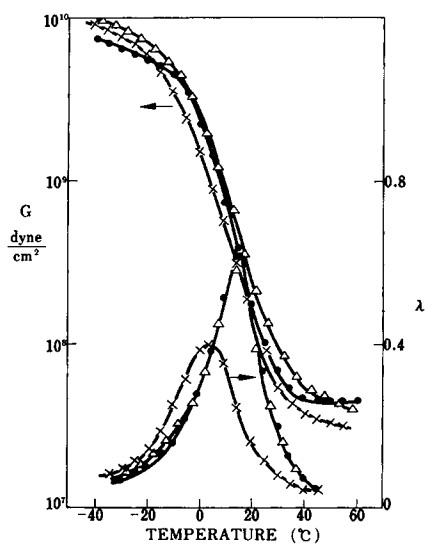


Fig. 5. G - T and λ - T curves of films of phenolic varnishes (air drying): (●) N-O; (Δ) R-O; (×) N + PO.

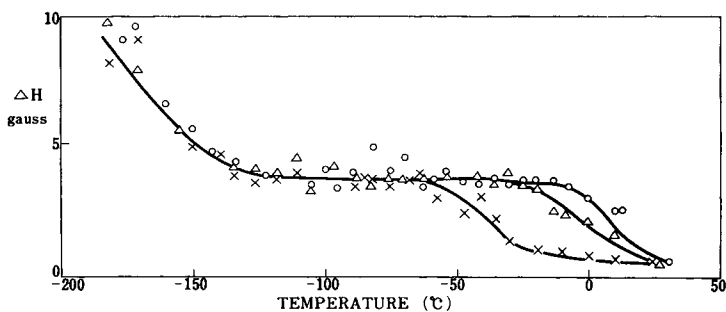


Fig. 6. ΔH - T curves of films of phenolic varnishes (air drying): (O) N-O; (Δ) R-O; (×) N + PO.

TABLE III
Physical Properties of Films of Phenolic Varnishes

Films	Drying method	$(T_g)_d$, °C.	$(T_g)_n$, °C.	$D_{OH}/D_{C=O}$ of ester ^a
N-O	Air drying	15	10	0.22
N-O	Baking	45	-70	0.125
R-O	Air drying	15	0	
R-O	Baking	45	-70	
N + PO	Air drying	5	-35	0.197
N + PO	Baking	30	-70	0.129

^a Obtained from the infrared spectra of the films.

Physical Properties of Films. The results are shown in Figures 5-8 and Table III. Larger values of $(T_g)_d$ and G_h and smaller values of $(T_g)_n$ and D_{OH} were observed in the baked films than the air-dried films. Crosslinking took place on heating, accompanied by a decrease in D_{OH} , and it suggested that the phenolic hydroxyl groups take part in the crosslinking.

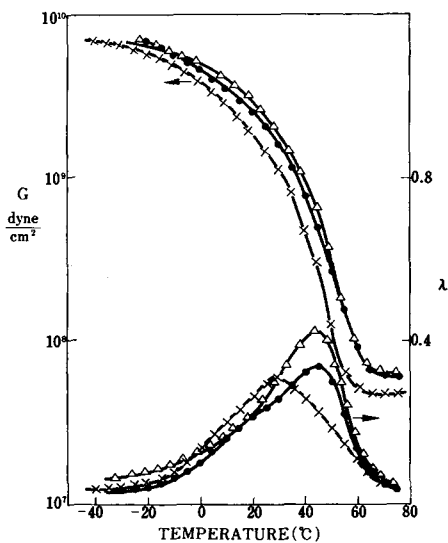


Fig. 7. G - T and λ - T curves of films of phenolic varnishes (baking): (●) N—O; (Δ) R—O; (×) N + PO.

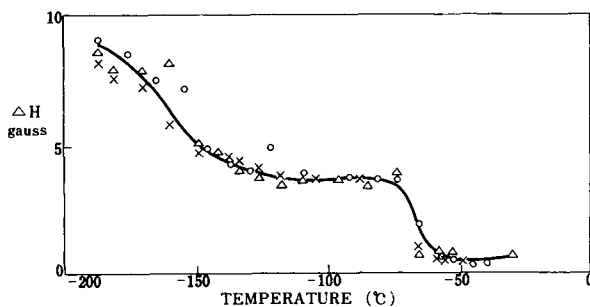


Fig. 8. ΔH - T curves of films of phenolic varnishes (baking): (O) N—O; (Δ) R—O; (×) N + PO.

It was reported that $(T_g)_n$ increases with the increase of the degree of crosslinking in vulcanized rubbers.¹⁰⁻¹⁴ The results obtained from alkyd resins and polymerized oil were in agreement with these reports, but the results obtained from the investigation of the phenolic varnishes were reversed. It is suggested that the polar groups are important in determining the $(T_g)_n$ of phenolic varnish films.

Effect of Polar Groups on $(T_g)_n$

In order to understand the effect of polar groups on $(T_g)_n$, two polyester-urethane films were synthesized which differed in chain stiffness and the concentration of polar groups, and $(T_g)_d$ and $(T_g)_n$ values were compared.

Materials

Two samples of polyesters were synthesized at 230°C. for 3 hr. in a stream of nitrogen. Their composition and molecular weight are shown in Table IV.

TABLE IV
Composition and Molecular Weight of Polyesters

Polyesters	Adipic acid, mole	Ethylene glycol, mole	1,4-Butanediol, mole	Glycerine, mole	molecular weight
I	1.0	0.36		0.7	1440
II	1.0		0.24	0.8	1360

Film Preparation

Toluene diisocyanate (TDI, chemical grade, *ortho/para* = 2/8) was mixed with each of the solutions of the polyester in an equal weight of cyclohexanone (0.7 mole TDI/mole adipic acid used in the preparation) in a dry box. The mixtures were coated on tin plates and allowed to stand in air for a week. The $(T_g)_d$ and $(T_g)_n$ of the films were measured.

Results and Discussion

The results are shown in Figures 9–11 and Table V. I, which contained fewer methylene groups, had a larger $(T_g)_d$ than II, but as expected, $(T_g)_n$ was smaller for I because of its lower content of polar groups such as hydroxyl and urethane.

TABLE V
Physical Properties of Polyester-Urethane Films

Films	$(T_g)_d$, °C.	$(T_g)_n$, °C.	$D_{OH, NH}$
I	-15	-32	0.242
II	ca. -60	-26	0.348

Generally speaking, T_g is thermodynamically proportional to $\Delta H/\Delta S$. As the frequency of the torsional pendulum method is about 0.1–1 cycle/sec., accompanying the deformation of sample, the units of segmental motions would be larger. On the contrary, as the frequency of the NMR method is about 10^4 cycle/sec. and the line width is a measure of interaction of proton magnetic moments, and the interactions involved are

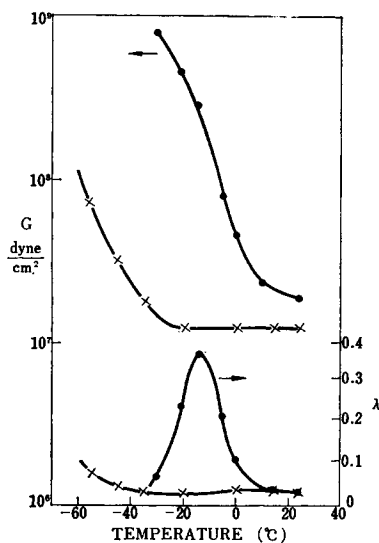


Fig. 9. G - T and λ - T curves of polyester-urethane films: (●) I; (×) II.

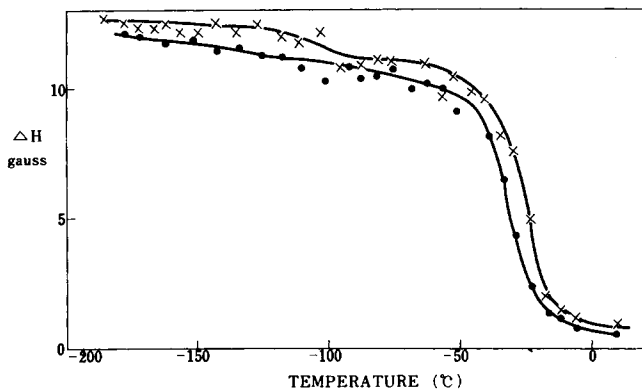


Fig. 10. ΔH - T curves of polyester-urethane films: (●) I; (×) II.

short-range, a smaller scale of molecular movements would be observed. Then, it is suggested that the entropy effect is predominant with $(T_g)_d$ and the enthalpy effect is predominant with $(T_g)_n$.

From the above discussion, it is obvious that the effects of chain stiffness and the degree of crosslinking predominate with $(T_g)_d$ and the effect of polar groups predominates with $(T_g)_n$.

In vulcanized rubbers, both $(T_g)_d$ and $(T_g)_n$ increase with the increase of the degree of crosslinking, no effect of polar groups being involved. In case of oxidatively polymerized films, a relation of $(T_g)_d$ and $(T_g)_n$ to the degree of crosslinking was not observed in the case of films of phenolic varnishes, because of the change in polar groups present during the course of film formation.

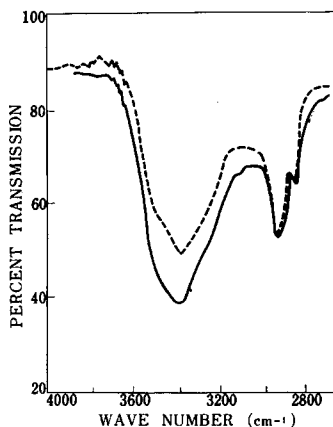


Fig. 11. Infrared spectra (near 3μ) of polyester-urethane films: (—) I; (---) II. KBr pellet, 6 mg. of sample/700 mg. of KBr.

In other words, by applying a NMR technique together with the dynamic-mechanical measurements, the effect of polar groups on physical properties of films was observed, although the quantitative relation of chain stiffness and the degree of crosslinking to the polar groups on the glass transition of films still requires further investigation.

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Résumé

On a mesuré les températures de transition vitreuse de films polymérisés par oxydation, en utilisant la méthode dynamique-mécanique ainsi que la mesure de la largeur de

raie (NMR). On a étudié la corrélation avec la structure chimique. On a travaillé sur des films polymérisés à partir d'huile de lin, de résines alcoyles, de vernis phénoliques et de polyester-uréthane. On a trouvé que les effets de rigidité de la chaîne ainsi que le degré de pontage prédominaient lors de la mesure de T_g par la méthode dynamique-mécanique, tandis que les groupes polaires prédominaient dans la détermination de T_g par la mesure de la largeur de raie. On a montré que la mesure de T_g par la largeur de raie augmentait avec le degré de pontage dans les caoutchoucs vulcanisés. Ceci n'est pas observé dans les films de vernis phénoliques; comme cela est impliqué par la variation des groupes polaires. La signification de T_g mesurée par les différentes méthodes est également expliquée thermodynamiquement.

Zusammenfassung

Die Glasumwandlungstemperatur von oxydativ polymerisierten Filmen wurde nach dynamisch-mechanischen Methoden und durch Linienbreitenmessung (NMR) bestimmt. Die Korrelation zur chemischen Struktur wurde untersucht. Es wurden Filme aus polymerisiertem Leinöl, Alkydharzen, phenolischen Firnissen und Polyester-Urethan untersucht. Der Einfluss der Kettensteifigkeit und der Vernetzungsgrad waren bestimmend für den nach der dynamisch-mechanischen Methode bestimmten T_g -Wert, die polaren Gruppen hingegen für den durch Linienbreitenmessung bestimmten T_g -Wert. Es wird angegeben, dass der durch Linienbreitenmessung bestimmte T_g -Wert bei vulkanisiertem Kautschuk mit dem Vernetzungsgrad zunimmt; diese Beobachtung konnte bei Filmen von phenolischen Firnissen, bei welchen eine Variation der Polymergruppen beteiligt war, nicht bestätigt werden. Die Bedeutung des mittels verschiedener Messungen bestimmten T_g -Werts wurde auch thermodynamisch erklärt.

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