Journal of Thermal Analysis, Vol. 9 (1976) 205—215

THERMAL ANALYSIS AND DEGRADATION KINETICS OF THERMOPLASTICS

I. STAYBELITE RESIN AND ITS DERIVATIVE STAYBELITE ESTER 10

J. W. LIN and *W. Y. WEN

Honeywell Inc., Corporate Research Center, Bloomington, Minnesota, 55420;
**Honeywell Inc., Plastics Laboratory, Hopkins, Minnesota, 55343, USA*

(Received May 23, 1975)

The thermal mechanical properties and degradation kinetics of Staybelite Resin, a thermoplastic, and its ester derivative Staybelite Ester 10 have been investigated using thermoanalytic methods. The thermogravimetric analyzer applied in the degradation studies has been interfaced with a minicomputer for data acquisition. The degradation kinetics of each thermosplastic have been satisfactorily attributed to an associated first-order process using a differential method.

The results indicate that the esterified resin has an improved durability over the original material with regard to thermal cycling between ambient temperature and 60°. This observation is consistent with the finding that the esterified resin was thermally more durable than Staybelite Resin for holographic recording use.

Staybelite Resin (SR) is a thermoplastic that has been broadly applied in household and industrial uses. The resin is obtained from hydrogenation of a rosin containing as many as 20 resin acids [1]. Data concerning the physical and chemical properties of most resin acids are available [2]. However, the thermal mechanical properties and stability of the SR system had not been studied, even though this information is of prime importance to specific applications such as holographic recording. It is apparent that the complex nature of the SR system has made detailed thermal analysis and degradation kinetic studies extremely difficult, if not impossible.

Our interest in SR as well as its derivative Staybelite Ester 10 (SE-10) has been stimulated and promoted by the discovery of their potential application to holographic memory [3—5] that can be employed directly in computer storage systems [6—8]. The fundamentals of holographic recording on thermoplastics have been described elsewhere [4—6]. This paper concentrates on thermal analysis and degradation kinetic measurements of SR and SE-10. It is hoped that the results of the present study can be correlated with the observed holographic recording performance of the materials. We believe this information will enhance future investigation in this particular area.

Experimental

The thermal mechanical properties were determined by thermomechanical analysis and differential scanning calorimetry, and the degradation kinetics by thermogravimetry. These thermoanalytic methods have been reviewed extensively [9–11]. SR and SE-10 were tested as received (Hercules Inc., Wilmington, Delaware). Atmospheric air was introduced into the thermogravimetric analyzer as an ambient gas for the measurement.

Spectrophotometry

Beckman IR-12 and Varian Cary 14 UV spectrophotometers were applied to identify the chemical structures of the resins. A sample for IR measurements was prepared by dissolving an adequate amount of a resin in chloroform, which was then coated on a NaCl substrate. The IR spectra were measured in the region of 3600–600 cm^{-1} as indicated in Fig. 1. In UV measurements, a 10-mm quartz cell was used and the sample concentration was approximately 1 mg ml^{-1} in chloroform. The spectral region studies covered from 250 to 330 nm as shown in Fig. 2.

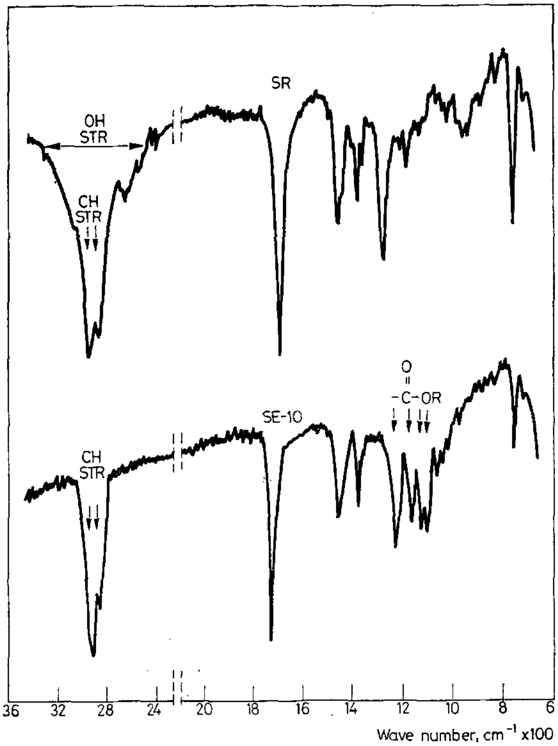


Fig. 1. Infrared absorption spectra of SR and SE-10

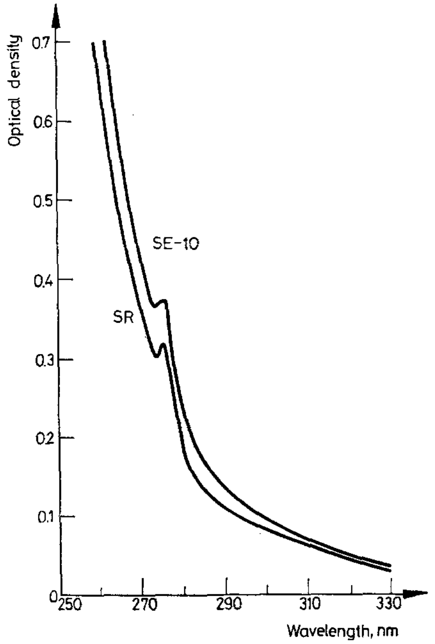


Fig. 2. Ultraviolet absorption spectra of SR and SE-10

The IR spectrum of SR in Figure 1 shows a broad absorption band of bonded O−H stretching in the region of 3400−2400 cm^{-1}, typical for carboxylic acid $(-\overset{\overset{O}{\|}}{C}-OH)$. These acid groups probably were inherited from the raw rosin. On the other hand, the spectrum for SE-10, indicates a considerably smaller absorption band for the carboxyl group $(-\overset{\overset{O}{\|}}{C}-OH)$. This decrease of the carboxyl group absorption appears to be compensated by a corresponding increase of absorption at around 1200 cm^{-1}, characteristic of ester groups $(-\overset{\overset{O}{\|}}{C}-OR)$. Other absorptions apparently are common to both resins.

The UV spectra in Fig. 2 show that both SR and SE-10 have similar absorptions. The peak at 275 nm is characteristic of $\pi \rightarrow \pi^*$ transition from substituted aromatic nuclei. The general absorption at shorter wavelengths indicates that both SR and SE-10 contain an appreciable amount of $-C{=}C-$ and conjugated types of unsaturation.

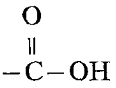
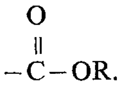
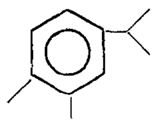
A qualitative picture of the materials derived from the spectrophotometric measurements is summarized in Table I. The results indicate that the compositional difference between SR and SE-10 is mainly in the contents of their chemical functional group, i.e., the  $-\overset{O}{\overset{\|}{C}}-OH$ and  $-\overset{O}{\overset{\|}{C}}-OR$.

Table 1

Major difference in chemical structures among the raw material, Staybelite Resin (SR), and Staybelite Ester 10 (SE-10) as derived from IR and UV measurements

Material	$-\overset{O}{\overset{\|}{C}}-OH$	$-\overset{O}{\overset{\|}{C}}-OR$	$-C=C-$ and/or conjugation	
Raw	Original	None	Original	None
SR	Original	None	Partially reduced	Some
SE-10	Partially reduced	Some	Partially reduced	Some

Thermomechanical Analysis (TMA)

The mechanical transitions or the softening and melting behavior of a sample were measured on a DuPont 942 TMA or a Perkin-Elmers TMS-1. The sample was prepared by careful shaping an as-received resin block into a disc measuring 1.5 – 2.0 mm in thickness and weighing approximately 40 mg. TMA displacements were determined at a heating rate of 10° min^{-1} and a weight load of 2 g on the DuPont analyzer. Experiments on the Perkin-Elmer TMS-1 were performed at 5° min^{-1} heating rate with a 10 g weight load. Penetration mode was used with both analyzers.

The measurements determined mainly the softening and melting behaviors of the materials. The glass transition temperatures appeared to have no direct relation to holographic application and therefore were not studied in this investigation.

Differential scanning calorimetry (DSC)

Calorimetric measurements were conducted on a DuPont 900 DSC. Samples were packed in aluminum pans in as identical a manner as possible. The program heating rate was 10° min^{-1} and the temperature region covered was 0° to the inception temperatures of the degradation reaction. The sensitivity of ΔT measurements was 0.1° in^{-1} on the coordinate of the X – Y plotter. Purified benzoic acid, which has a heat of fusion of 33.9 cal g^{-1}, was used as a standard of the calorimetric measurement.

Thermogravimetry (TG)

A Cahn RG electrobalance with a Perkin-Elmer furnace and a UU-1 programmer were employed in the TG measurements. The sample temperature was recorded with a chromel-alumel thermocouple placed immediately above the sample pan. The samples were prepared by cutting the resins into small particles of different sizes and 4 – 10 mg of a sample was placed in an aluminum or a platinum crucible for measurement. The program heating rate was 2.5° to 10° $\min^{-1}$. Air was admitted into the system slowly with the flow rate regulated carefully to avoid disturbances from thermal gas flow [14, 15] and apparent weight gain [16]. With the samples studied, the resins usually decomposed completely within an appropriate temperature range, and the weight of the residual ash was negligible.

The TG analyzer was interfaced with a Honeywell H112 minicomputer to monitor the data acquisition process automatically. Under the computer-controlled mode, as many as 1000 data points, (corresponding to weight loss as a function of time) could be collected in the computer memory. The data then could be displayed on an oscilloscope, traced on a X – Y plotter, printed on a teletype, or punched on a paper tape in digital form with the option of outputting any desired number of points. For convenience of data processing, usually 50 points were used. The hardware and software techniques for this computer-controlled system have been reported recently [12]. A similar system has been developed at the General Electric Company [13]. The General Electric equipment apparently is less flexible and sophisticated than the present minicomputer system.

Kinetic analysis

During the last decade, many efforts have been dedicated to kinetic analysis of TG data. The topic has been extensively reviewed in a series of articles [17] and elsewhere [18, 19]. The basic mathematic models for most of the nonisothermal methods fall into one of the following five categories: (1) Integrated Method, (2) Differential Method, (3) Differential-Differential Method, (4) Initial Rate Method, and (5) Non-Linear or Cyclic Heating Method [18]. Even with the simplest first-order degradation process, the rate equations involved cannot be integrated in a close form [20]. Hence the integral method has to be done by series expansion [19, 20] or graphical techniques [21, 23]. All these methods are tedious and time-consuming. The shortcoming in the differential-differential method lies in its critical dependence on the measured reaction rates because it requires the differences between consecutive rates in the calculation. The initial rate method depends significantly on the early stages of a reaction and is usually difficult to measure precisely. The non-linear or cyclic heating method was ruled out because it is not a conventional experimental technique. The differential method, with the assistance of numerical method, has been shown to be a powerful technique for solving kinetic problems [24]. Hence, for this study, the differential method is employed.

The rate law of a simple degradation reaction in solid state can be described by Equation 1,

$$V = -\frac{\mathrm{d}\alpha}{\mathrm{d}t} = kf \tag{1}$$

where V and α are the instantaneous rate and the weight fraction of materia[1] remaining at time t respectively; k and n are the rate constant and reaction order, and f is a function of α and n. For a first-order reaction ($n = 1$), f is equal to α. By substituting the Arrhenius equation into Equation 1, then taking natural logarithm one obtains:

$$\ln\frac{V}{\alpha} = -\frac{E_a}{RT} + \ln A \tag{2}$$

where T is the absolute temperature, R is the gas constant, A and E_a are the pre-exponential factor and activation energy respectively. For a temperature-programmed experiment with a linear heating rate r, the reaction rate V can be easily obtained from Equation 3,

$$V = -\frac{\mathrm{d}\alpha}{\mathrm{d}t} = -r\frac{\partial\alpha}{\partial T} \tag{3}$$

where $\frac{\partial \alpha}{\partial T}$ is the partial derivative of the associated quantities. Conventionally, reaction rates are calculated by the point-to-point techniques which generally are susceptible to experimental errors of consecutive measurements. In this study the rates were obtained from a TG curve by a numerical differentiation technique using a second-order Lagrangian interpolation polynominal. A sub-routine for numerical differentiation [24] was adopted in a FORTRAN program which performed a linear-least-squares [25] fit on Equation 2 and calculated the kinetic parameters from the derived slope and intercept. All computations were performed on a timesharing terminal of the Honeywell Computer Network within Honeywell Inc.

Results and discussion

It is apparent from the TMA measurements that the softening and melting behaviors of SR and SE-10 are different. The esterified resin has shown a smaller transition temperature range and has a melting point 12° higher than the original resin. Typical TMA traces of both substances as determined by the DuPont TMA are shown in Fig. 3, and the derived results of the tests are summarized in Table 2. Measurements on the Perkin-Elmer TMS-1 generally agreed within 5° with those on the DuPont analyzer.

Table 2

Softening and melting behaviors of SR and SE-10 as determined by a DuPont TMA

Sample	Inception of softening, °C	Melting point, °C	Peak, °C	End of melting, °C
SR	23	32	54	80
SE-10	38	44	62	83

Table 3

Softening and melting behaviors and enthalpies of melting for the first transition peaks and the degradation inception points of SR and SE-10 as determined by a DuPont 900 DSC

Sample	Inception of softening, °C	Melting point, °C	ΔH_m, cal g^{-1}	Inception of degradation, °C
SR	20	26	0.8	170
SE-10	34	42	4.2	195

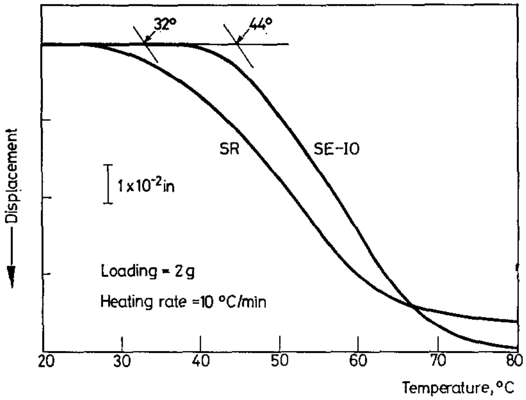


Fig. 3. Thermomechanical analysis of SR and SE-10

As indicated in Table 3, agreements of the DSC results with the corresponding TMA measurements are good. It is readily seen from the DSC curves in Figure 4 that the transition peak for SE-10 at 42° is sharper than that for SR at 26°, a result that is consistent with the bulk melting points of the associated resins as determined by the TMA. Apparently, these distinctive endotherms reflect the major components in the resins, presumably resin acids in SR and resin esters in SE-10. The heat of fusion ΔH_m of these transitions are 4.2 and 0.8 cal g^{-1} for SE-10 and SR respectively. The fact that there is a sharper melting transition temperature and a higher transition enthalpy for SE-10 than for SR indicates that either SE-10 has a higher purity due to processing or the morphology of the esterified resin is more regular than its parent substance, or both.

Figure 5 shows the TG curves of two typical thermal degradation runs of the different resins. The reaction rates derived from numerical differentiation of each curve are plotted on the same graph. It is interesting to note that the inception

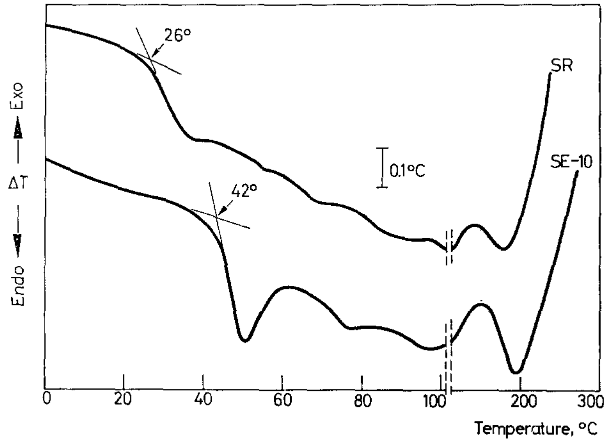


Fig. 4. Differential scanning calorimetric analysis of SR and SE—10. Sample weight: 35 mg; heating rate: 10° min.$^{-1}$

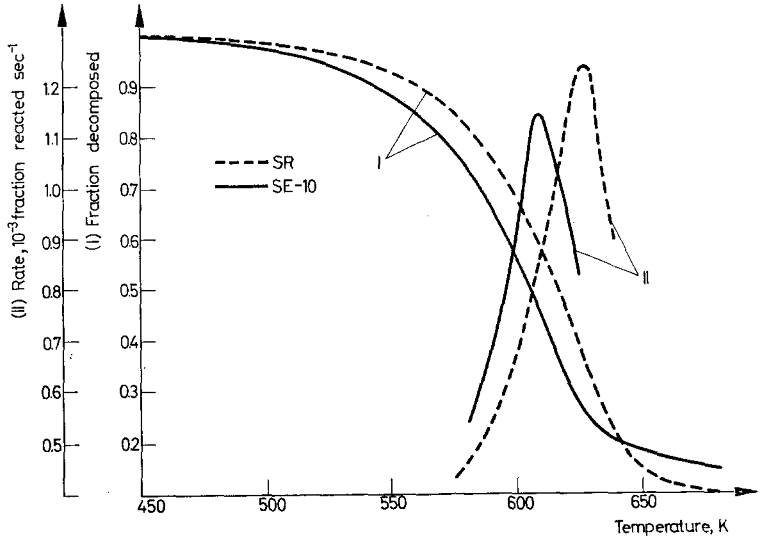


Fig. 5. Thermogravimetric and the derivative thermogravimetric curves of SR and SE-10

point for the thermal degradation of SR obtained from the TG curve agrees well with that derived from the corresponding DSC curve (Table 3), but a similar analysis on the TG measurements of SE-10 shows a difference of approximately 25° higher than the DSC result. The reason for this discrepancy is unknown. The derivative curves in Fig. 5 show that the degradation temperature range is sharper for SR than SE-10 and that the esterified resin has higher reaction rates at temperatures below 620 K.

The data from a TG curve are calculated using Equation 2 with $n = 0, 1/2, 2/3$, and 1. These reaction orders have been discussed in solid-state reactions [26]. The first-order results appear to be the best fit for the data. The consistency of this data analysis technique is shown in Table 4. The fact that a 2.5 fold change of sample weight and varying sample particle size had no detectable effect on the degradation kinetics is good evidence that the degradation processes were not diffusion controlled reactions. Because of the complex nature of the systems, no attempt is made to study in detail the mechanistic analysis on either of the reactions. The purpose of this study is to determine the relative thermal stability of these two thermoplastics. The information we have obtained has satisfied this need. However, the similarity in the thermoanalytic results of both resins suggests that they decompose through a similar reaction scheme. The observed first-order decomposition kinetics indicate that both resins decompose by initially splitting into small molecules followed by decomposing into gas products, which is probably the rate determining step. The results also imply that SE-10 takes a shorter step in the initial degradation process. Apparently, the replacement of the carboxylic group by an ester group results in a slightly higher activation energy and a corresponding increase in entropy effect. The results in Table 4 show that the program heating rate has no observable effect on the degradation reaction. If a decomposition reaction in solid state is unaffected by the shape of a sample, the reaction rate should be independent of the program heating rate [27].

Table 4

Kinetic results for first-order thermal decomposition of SR and SE-10 in air at various conditions of temperature-programmed TG experiments

Sample	Heating rate, °C min. $^{-1}$	E_a, kcal mole^{-1}	A, 10^6 sec^{-1}
SR	10	25.0±1.0	1.96
	5	24.7±1.4	1.24
	2.5	24.8±1.4	1.28
SE-10	5	27.0±1.9	11.0

Conclusion

According to the results obtained from this analysis, esterifying the SR has not effectively varied the stability of the thermoplastic toward degradation. Nevertheless, the softening and melting behavior of the resin is significantly altered. The higher melting point and greater heat of fusion of SR-10 may well be the major factors that contribute to the repeatability of the material morphology during heating-cooling cycles. Furthermore, the small thermal mechanical transition region for SE-10 may correlate with its better resolution for "writing" and less residual image for "erasing" as found in the holographic recording [8]. Even with SE-10, it is not economical and practical for use in holographic memory systems. However, we believe that the information we have collected will be very useful for future research in this area. Rigorous investigation for an economical holographic recording material is still underway and results will be released at some appropriate time in the future.

*

The research was initiated by T. C. Lee at the Corporate Research Center of Honeywell Inc. The authors owe their thanks to H. Heist, K. Plant, and F. Swanson for their enlightening discussions and inspiration. Our gratitude is due J. Madsen for TG measurements. The publication is made possible by Honeywell Inc.

References

1. H. I. Enos, Jr., G. C. Harris and G. W. Hednick, Encly. Chem. Techn., 17 (1968) 475.
2. G. C. Harris and T. F. Sanderson, Am. Chem. Soc., 70 (1948) 334; ibid., 70 (1948) 339; ibid., 70 (1948) 2079; 70 (1948) 2081; G. C. Harris, ibid., 70 (1948) 3671; G. C. Harris and J. Sparks, ibid., 70 (1948) 3674; G. C. Harris and T. F. Sanderson, ibid., 70 (1948) 3870.
3. J. C. Urback and K. W. Meier, Appl. Opt., 5 (1966) 666.
4. L. H. Lin and H. L. Beauchamp, ibid., 9 (1970) 2088.
5. T. C. Bellamy, D. B. Ostrowsky, M. Poindron and E. Spitz, ibid., 10 (1971) 1958.
6. T. L. Credelle and F. W. Spong, RCA Rev., 33 (1972) 206.
7. W. C. Stewart, R. S. Mezrich, L. S. Cosentino, E. M. Nagle, F. S. Wendt and R. D. Lohman, RCA Rev., 34 (1973) 3.
8. T. C. Lee, Appl. Opt., 13 (1974) 888.
9. W. J. Smothers and Y. Chiang, Handbook of Differential Thermal Analysis, Chemical Publishing Co., Inc., New York, 1966.
10. W. W. Wendlandt, Thermal Methods of Analysis, Interscience Publishers, 1964.
11. T. Daniels, Thermal Analysis, John Wiley & Sons, New York, 1973.
12. W. Y. Wen and M. Dole, Computer in Chemistry and Instrumentation Series, Vol. VI, J. S. Mattson, H. B. Mack, Jr. and H. C. MacDonald, Jr., Editors, (in press).
13. G. Romco, E. Lifshin, M. F. Ciccarelli and D. B. Soresen, Anal. Chem., 45 (1973) 2444.
14. E. Robens, Vac. Microbalance Tech., 8 (1971) 73.
15. L. Reich and S. S. Stivala, Elements of Polymer Degradation, McGraw-Hill Co., New York, 1971, p. 84.
16. A. E. Newkirk, Anal. Chem., 3 (1960) 1558.

17. C. B. MURPHY, ibid., 36 (1964) 347R; ibid., 38 (1966) 443R; ibid., 40 (1968) 380R; ibid., 44 (1972) 513R.
18. C. H. FLYNN and L. A. WALL, J. Res. Nat. Bur. Std., A70 (1960) 487.
19. L. REICH and S. S. STIVALA, loc. cit., p. 81.
20. L. REICH and S. S. STIVALA, ibid., p. 89.
21. R. W. FARMER, Technical Report AFML-TR-65-246, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, January 1966.
22. W. W. WENDLANDT, loc. cit., p. 43; J. FOCK, Some applications of thermal analysis, Proceedings of a Seminar, Cambridge, September, 1966, p. 12.
23. W. Y. WEN J. Thermal Anal., (in press).
24. W. Y. WEN, Intern. J. Chem. Kinet., 5 (1973) 621.
25. Y. BEERS, Introduction to the Theory of Errors, 2nd ed., Addison Wesley Publishing Co., 1962, p. 68.
26. A. W. COATS and J. P. REDFERN, Nature, 201 (1964) 68.
27. L. REICH and S. S. STIVALA, loc. cit., p. 84.
28. T. C. LEE, private communication.

RÉSUMÉ — On a étudié par les procédés thermoanalytiques les propriétés thermomécaniques et la cinétique de la dégradation de la résine thermoplastique Staybelite et de son dérivé éthérifié Staybelite Ester 10. L'acquisition des données s'est effectuée en couplant la thermobalance à un miniordinateur. A l'aide d'une méthode différentielle, on a pu attribuer d'une manière satisfaisante la cinétique de dégradation de chacune des deux résines thermoplastiques à un processus associé du premier ordre.

Les résultats indiquent que la résine éthérifiée possède une durée de vie supérieure à celle du matériau original en ce qui concerne le cyclage thermique entre la température ambiante et 60°. Cette observation est en accord avec le résultat selon lequel la résine éthérifiée résiste plus longtemps lors de l'enregistrement holographique que la résine Staybelite.

ZUSAMMENFASSUNG — Die thermischen mechanischen Eigenschaften und die Zersetzungskinetik des Harzes Staybelite, eines thermoplastischen Materials und seines Esterderivats Staybelite Ester 10 wurden unter Verwendung thermoanalytischer Methoden geprüft. Der bei den Zersetzungsuntersuchungen eingesetzte thermogravimetrische Analysator wurde zwecks Datensammlung mit einem Minikomputer gekoppelt. Unter Anwendung einer Differentialmethode konnte die Zersetzungskinetik jedes der beiden thermoplastischen Materialien befriedigend einem assoziierten Vorgang erster Ordnung zugeordnet werden.

Die Ergebnisse zeigen eine verbesserte Beständigkeit des veresterten Harzes gegenüber dem Originalmaterial hinsichtlich der thermischen Zyklisierung zwischen Zimmertemperatur und 60°. Diese Beobachtung stimmt mit dem Befund überein, nach welchem das veresterte Harz im Einsatz bei holographischen Aufzeichnungen hitzebeständiger war als das Harz Staybelite.

Резюме — Исследованы, используя термоаналитические методы, термические механические свойства и кинетика деградации Staybelite Resin, термопластика и его сложноэфирное производное Staybelite Ester 10. Термогравиметрический анализатор, используемый при изучении деградации, был соединен с малой вычислительной машиной для сбора данных. Используя дифференциальный метод, было установлено, что кинетика деградации каждого термопластика удовлетворительно описывается каким-либо действующим процессом первого порядка. Результаты показывают, что этерифицированная смола, относительно теплового цикла от окружающей температуры и до 60°, обладает большей стойкостью по сравнению с начальным материалом. Это наблюдение согласуется с найденным, что этерифицированная смола была термически более устойчивой при голографическом использовании, чем исходная — не этернифицированная смола.