Modification of Poly(vinyl alcohol) with Aliphatic and Aromatic Epoxides in the Molten Phase

A. A. HARALABAKOPOULOS, D. TSIOURVAS, and C. M. PALEOS*

NCSR "Demokritos", 15310 Aghia Paraskevi, Attikis, Greece

SYNOPSIS

A new method for improving the processability and thermal stability of commercially available poly(vinyl alcohol) is presented involving the reaction of the hydroxyl group on the polymer backbone with long-chain aliphatic, cycloaliphatic, and aromatic epoxides. The reaction was performed in the molten phase using a laboratory-scale thermostated reactor. As expected, the extent of the reaction varied with the chemical structure of the epoxide, the properties of polymers obtained being dependent on the amount of the incorporated side group. Specifically, the reactivity of long aliphatic chain epoxides was low and the polymers obtained exhibited a small decrease in the melting points, being directly proportional to the length of the aliphatic chain. They displayed, however, improvement in thermal stability compared to the parent polymer. Cyclohexene oxide was appreciably more reactive and it exhibited a larger melting point reduction and satisfactory thermal stability. Polymers functionalized with aromatic rings and prepared under the same conditions were mostly amorphous, not showing melting point transition or improvement in their thermal stability. Finally, the reactions with aliphatic epoxides were catalyzed with phosphoric acid and the modified polymer exhibited a large decrease in the melting point but not a concomitant improvement in thermal stability. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Poly(vinyl alcohol) (PVOH),[1] among other useful properties, displays an extremely low gas permeability.[2] However, it presents melt-processing problems since it shows little thermoplasticity at its melting temperature where decomposition occurs quickly.[3] For this reason, PVOH copolymers with ethylene are employed in extrusion with somewhat reduced gas barrier properties but better thermal stability, processability, and mechanical properties.[4,5] In addition, the processability problem associated with PVOH has been treated by the following two modes: (a) processing of PVOH in the presence of water and water-soluble hydroxylated plasticizers[6] and (b) plasticizing PVOH with non-hydroxylated plasticizers in the absence of water.[7] Other methods for the improvement of the processing properties have been used including copolymer-

ization of PVOH with a long aliphatic chain co-monomer,[8] melt processing PVOH with metal salts,[9] and esterification of the hydroxyl group in solution to lower the processing temperature.[10] In all these cases, enhancement in processability and modification in the resin properties were claimed.

In this work, a new mode for enhancing the processability and thermal stability of PVOH is presented, involving the interaction of the polymer with aliphatic and aromatic epoxides. To our knowledge, some work with low boiling point epoxides in solution has been reported[11] for the preparation of PVOH soluble in organic solvents. The reaction of epoxides with simple alcohols is catalytically induced and the subject was exhaustively discussed several years ago.[12] In our study, the reaction was conducted under conditions of complete exclusion of water, in the molten state, and under experimental conditions that simulate those occurring in reactive extrusion processes.[13,14] The enhancement in processability should be followed by a parallel decrease in hydrophilicity to the extent that it would not be detrimental to certain technological applications such as

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* To whom correspondence should be addressed.

good barrier properties. Nuclear magnetic reso-
nance,[15-19] differential scanning calorimetry, and
thermogravimetry[20] are the techniques employed for
structure elucidation of PVOH and evaluation of its
properties.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (PVOH) grade Mowiol M8-88
obtained from Hoechst with a degree of hydrolysis
of 87.7 (87.7% hydroxyl, 12.3% vinyl acetate func-
tion) and molecular weight of 67,000 g/mol was used
for the reactions. Dodecyl-, tetradecyl-, hexadecyl-,
and octadecylepoxides as well as styrene oxide (SO)
and phenyl glycidyl ether (PGE) were purchased
from Aldrich and used as obtained. Cyclohexene ep-
oxide (CHE) was kindly provided by BASF and used
as obtained. The reactions were performed in a cus-
tom-made reactor, shown in Figure 1, comprising a
stainless-steel thermostated reactor and a rotating
shaft. The reactor was analogous to the one recently
described in the literature.[21] The rotating shaft, in
addition to mixing, was also exercising pressure on
the melted reactants. The quantities of materials
that can be processed in this reactor range from 3
to 15 g. PVOH was dried at 80°C under vacuum.
The materials were premixed before their introduc-
tion in the thermostated reactor where the temper-
ature was kept at 190°C. The shaft during the ex-
periments was rotating with a speed of 500 rpm, the
quantities used for each reaction ranged from 5 to
7 g, while the time of mixing was kept short (5–7
min) to avoid thermal degradation. At the end of
the reaction, the polymer mixture was cooled rapidly
by immersion in acetone. The unreacted epoxides
were removed by dissolving the polymers in water
at 70°C with subsequent precipitation by the addi-
tion of acetone. The pure polymers were dried under
a vacuum at 70°C for 24 h, finely ground, and dried
again at 70°C over phosphorus pentoxide for about
8 h.

Nuclear Magnetic Resonance

Proton and carbon-13 NMR spectra of polymers
were obtained employing a Bruker AC 250 spec-
trometer operating at 250 MHz. Sample concentra-
tions were approximately 8–10% w/v in perdeuter-
ated dimethyl sulfoxide which also served as the in-
ternal locking agent. The spectra were obtained
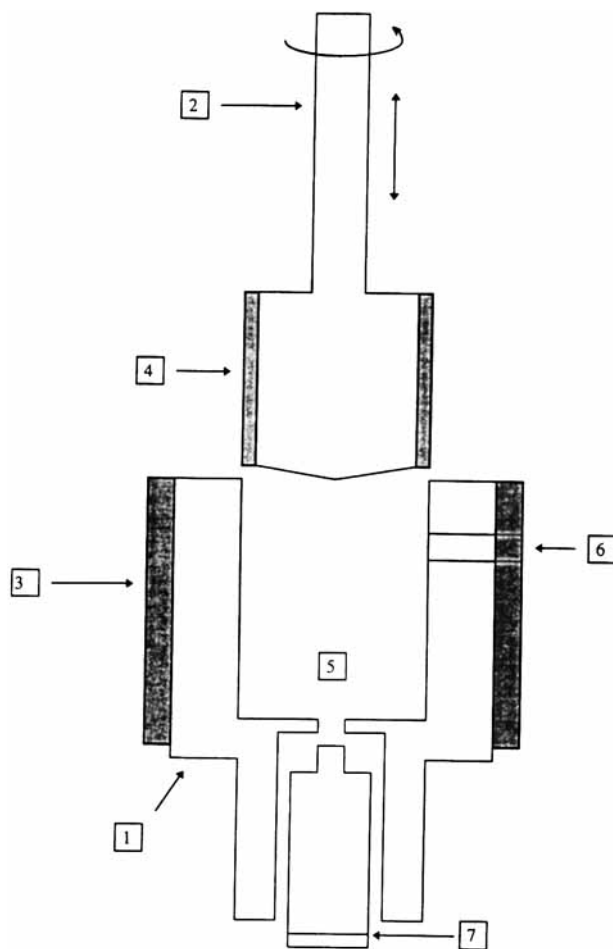accumulating 64 and 20,000–50,000 scans for ^1H and

Figure 1 Thermostated mixer: (1) stainless-steel ther-
mostated container; (2) rotating shaft; (3) heating ele-
ment for container; (4) heating element for shaft; (5)
place for material to be mixed; (6) inert gas inlet valve;
(7) extruding valve.

^{13}C, respectively, at 65–70°C. Proton–carbon decou-
pling was used for the ^{13}C spectra.

Thermal Analysis

For differential scanning calorimeter (DSC) mea-
surements, a TA Instrument DSC 10 was employed
coupled with a 2100 controller. The samples in pow-
der form were heated under nitrogen from 10 to
230°C at a rate of 15°C/min with an isothermal pe-
riod of 5 min at the start. Each sample was tested
at least in duplicate with no significant differences
observed between experiments.

Thermogravimetric analysis (TGA) measure-
ments were performed in duplicate with a TA In-
struments, Model 2050, TGA analyzer for samples
of about 10 mg using a thermal procedure which
simulates the thermal conditions in the extruder,

**Table I Reaction Conditions of PVOH with Epoxides in the Molten Phase**

Reaction Product	Epoxide/Mol Percent Used	Catalyst	Temperature	Reaction Time (s)	Appearance of End Product
PVOH	—	—	190	300	Off-white
E_{12}	C_{12}/5.0	—	190	300	"
E_{14}-1	C_{14}/5.0		190	300	"
E_{14}-2	C_{14}/5.0	H_3PO_4 (0.1 mol %)	190	300	"
E_{16}	C_{16}/5.0	—	190	300	"
E_{18}	C_{18}/5.0	—	190	300	"
E_{PGE}	PGE/5.0		190	240	Orange/yellow
E_{SO}	SO/5.0	—	190	240	"
E_{CHE}	CHE/5.0	—	190	240	Light yellow

specifically: (1) an isothermal period of 5 min at 40°C, (2) heating to 220°C at a rate of 50°C/min, and (3) an isothermal run of 15 min. Finally, the samples were heated at a rate of 20°C/min to 300°C. Both the balance chamber and the oven were purged with nitrogen throughout the course of the thermal experiments. The processing of data and calculation of thermal transitions were performed using the software programs provided by TA Instruments.

RESULTS AND DISCUSSION

### Synthesis

From commercially available epoxides (C_6–C_{18}) that have been tested, only those with a high boiling point were used for the modification of the structure of PVOH. The reaction was conducted at high temperatures in the melt and, therefore, low boiling point epoxides were difficult to handle in the reactor described above since they partly evaporate during the experiment. The epoxides employed were the long aliphatic chain epoxides (C_{12}, C_{14}, C_{16}, C_{18}), the aromatic epoxides SO and PGE, and also a cycloaliphatic epoxide, CHE. The aromatic and cycloaliphatic epoxides were expected to be more reactive than were the aliphatics[12] and the general reaction scheme is shown below:
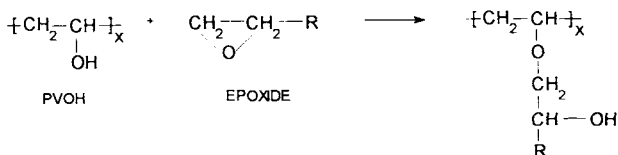
R = $CH_3(CH_2)_9$—, dodecyl epoxide (C_{12}); CH_3 $(CH_2)_{11}$—, tetradecyl epoxide (C_{14}); $CH_3(CH_2)_{13}$—, hexadecyl epoxide (C_{16}); $CH_3(CH_2)_{15}$—, octadecyl

epoxide (C_{18}); $PhOCH_2$—, phenyl glycidyl ether (PGE); and Ph—, styrene oxide (SO).

The reaction with cyclohexene oxide (CHE) is as follows:
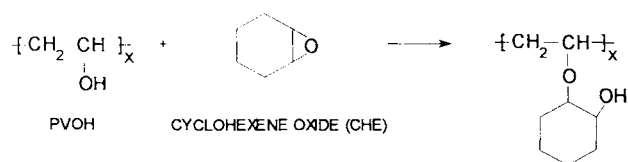
The reaction conditions of the experiments are summarized in Table I. For comparison and to simplify the treatment of the results, the reaction conditions as well as purification procedures were kept the same in all the experiments.

NMR Characterization

Proton NMR spectroscopy of the modified polymers was employed for the quantitative determination of the amount of epoxide that has reacted with the hydroxyl group according to the general reaction. On the basis of the reported chemical shifts for PVOH,[15-19] the chemical shifts of protons and carbons of the modified resins were assigned. The percentage of epoxide introduction was determined from the intensities of the peaks for protons assigned to the side chains as tabulated in Table II. From our results, it is seen that with aliphatic epoxides the reaction is very sluggish since the incorporation is very small (<0.1 mol %). In fact, it cannot be determined with accuracy. Indicatively, phosphoric acid was used as a catalyst to enhance the reactivity of tetradecyl epoxide. The ^{1}H-NMR spectrum of the product (E_{14}-2) shows a single methylene resonance peak at 1.26 ppm assigned to the methylenes of the side chain and corresponding to an incorporation of

Table II ^{1}H-NMR Chemical Shifts of Minor Peaks, Molecular Percent of Incorporation of Side Chain, and ^{13}C-NMR Chemical Shifts of Modified PVOH Resins and Their Spectral Assignments

Modified Resin	^{1}H-NMR Chemical Shifts of Side Chain,[a] δ (ppm)			Molecular Percent of Side Chain in Polymer	^{13}C-NMR Chemical Shifts, δ (ppm)
	$-(CH_2)-$	CH_3-	Aromatic		
E_{12}	1.24 (w)[b]	0.85 (w)	—	< 0.1	23, 32 (w); $-(CH_2)_x-$
E_{14}-1	Not shown	0.86 (vw)	—	< 0.1	Not shown
E_{14}-2	1.26 (m)	—	—	0.80	23, 32; $-(CH_2)_x-$, 77 (w); $>CH-O-$
E_{16}	Not shown	0.85	—	< 0.1	79 (w); $>CH-O-$, 23 (w); $-CH_2-$
E_{18}	1.24 (w)	0.85	—	< 0.1	23 (w); $-CH_2-$
E_{CHE}	1.17 (m)	n/a	—	0.70	56; $>CH-O-(CH_2)_4$, 29, 33.5; $-(CH_2)-$
E_{SO}	—	—	7.30 (d)[c]	1.39	125, 126, 127; aromatic, 71 (d); $>CH-O-$
E_{PGE}	—	—	7.27 (t)	1.58	158.5 (w); $-CH(OH)-O-$, 114.5, 120;
			6.95 (d)		Aromatic, 76 (w); $>CH-O-$

[a] Chemical shifts with respect to DMSO-d_6 at 55°C.

[b] w, weak; vw, very weak; m, medium.

[c] d, doublet; t, triplet.

approximately 0.8 mol %. Concerning aromatic and cycloaliphatic epoxides, they are incorporated in larger amounts as shown from the resonance peak intensities at 1.17 ppm for E_{CHE}, 7.3 ppm for E_{SO}, and 7.27 and 6.95 ppm for E_{PGE}, corresponding to 0.7, 1.39, and 1.58 mol % incorporation of the epoxide, respectively.

In conclusion, the extent of the reaction of aliphatic epoxides with the hydroxyl group of PVOH is minimal according to NMR analysis, whereas, for the rest, the extent of the reaction is appreciable if we take into account the short time of mixing, the volatility of the epoxides, and the small quantities used.

Observed chemical shifts and proposed assignments for ^{13}C-NMR spectra are shown in Table II and seem to confirm ^{1}H-NMR results. Polymers modified with aliphatic epoxides show extremely weak, hardly detectable $-CH_2-$ and CH_3- resonance peaks. On the contrary, all the main resonances observed were in accordance with the NMR data of PVOH copolymers.[15-17] However, E_{16}-treated polymer shows two new very weak resonance peaks with respect to the parent polymer at 71 and 79 ppm which can be assigned to the two newly formed methine carbons, e.g., the methine carbon of the backbone previously bearing the hydroxyl group and the new one on the side chain bearing the hydroxyl

group. On the other hand, E_{CHE}, E_{SO}, E_{PGE}, and E_{14}-2 epoxide-modified polymers clearly show the expected characteristic resonance peaks (Table II).

Differential Scanning Calorimetry

DSC thermograms for parent and modified polymer are shown in Figure 2 and the thermal analysis data are displayed in Table III. All measurements refer to the first heating, since PVOH is not resistant to extensive thermal treatment above its T_m. On the other hand, glass transition temperatures cannot be reliable when determined on the first heating since they depend on the thermal history of the samples. The actual results show distinct, although broad, melting transitions for all polymers except for the aromatically modified ones which are amorphous as indicated by the absence of melting transitions. For the rest of polymers which remain mostly crystalline, a small decreasing trend of T_m is seen as one shifts to (a) longer-chain epoxides and (b) higher incorporation of side chain into the polymer backbone. Thus, the T_m of 197.4°C for the melt-processed parent polymer decreases to 195.8°C for E_{12}, 195.0°C for E_{14}-1, 194.7°C for E_{16}, and 194°C for E_{18}. This is expected from the structure of the modified polymers, i.e., the longer the pendant aliphatic chain, the higher the reduction in crystallinity and, con-

sequently, the lower the T_m. The decrease is, of course, minimal for these modified polymers because, as previously indicated, only small amounts of the epoxides have been introduced into the parent polymer. For E_{14}-2 and E_{CHE}, the lowering of T_m is stronger since there is an 8 and 5°C lowering of the melting range, respectively, and, furthermore, a complete absence of crystallinity for polymers E_{SO} and E_{PGE} is observed. For T_g values determined on the first heating, there is no obvious trend except of the general observation that the T_g is appreciably depressed with a reasonable extent of reaction. In one case (E_{14}-2), a T_g depression of 12°C was observed, while for E_{CHE} and E_{PGE}, the depression was 6°C, and for E_{SO}, it was substantially higher, i.e., 16°C. These results suggest that when the side chains are present in amounts of approximately 1 mol % or above, a change of the segmental motion of the polymer backbone and, consequently, an increase in free volume can occur, leading to a lowering of the glass transition.

Analysis of DSC results illustrates the effect that the modification reaction exerts on the polymer properties. In the first place, it is suggested that an incorporation of about 1.5 mol % of aromatic epoxide or aromatic epoxy ether is sufficient to intervene with the crystalline portion of the polymer, rendering it amorphous by breaking the hydrogen bonds

Table III Glass Transition (T_g), Melting Temperature (T_m), and Enthalpy of Melting (ΔH) of Modified PVOH Polymers as Determined by DSC

Modified Polymers	T_g (°C)	T_m (°C)	ΔH (J/g)
PVOH	69.5	197.4	36.2
E_{12}	68.9	195.8	35.9
E_{14}-1	68.3	195.4	35.4
E_{14}-2	57.5	189.3	33.18
E_{16}	66.9	194.7	36.8
E_{18}	67.1	194.0	38.8
E_{CHE}	63.4	192.6	37.1
E_{SO}	53.2	—	—
E_{PGE}	63.6	—	—

that are mostly responsible for the high crystallinity of the resins.[22] Second, long-chain aliphatic epoxides are not reactive enough, but even with a minimal incorporation of less than 0.1 mol %, a reduction of T_m was observed. However, such differences may also be attributed to the thermal history of the samples although we attempted to avoid this problem by keeping the experimental conditions the same. When the incorporation of tetradecyl epoxide was increased to 0.8 mol % with the use of catalyst (E14-
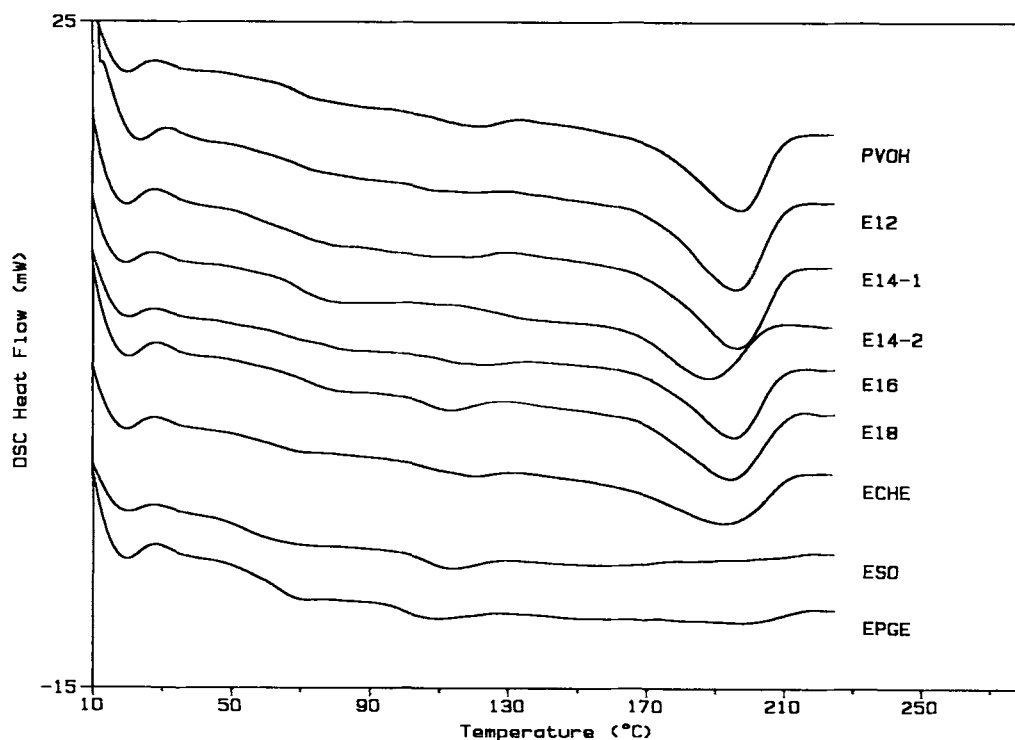

Figure 2 DSC traces of parent and modified PVOH polymers.

2), the result was more profound on the T_m and on ΔH. Cyclohexene oxide did not have a similar effect because of its shorter length.

Thermogravimetric Analysis

Thermal instability is known to be a disadvantage of PVOH polymers and its copolymers with vinyl acetate,[3,23] especially when one is faced with strenuous processing requirements. It is therefore necessary to facilitate melt processability along with improving thermal stability. Therefore, we attempted to simulate the thermal conditions encountered in the extruder where the processing of PVOH will take place. Thus, the temperature was increased at a rate of 50°C/min from 40 to 220°C, which is the processing temperature for this grade of PVOH; then, the sample was heated isothermally for 15 min, which is a reasonable time for the PVOH to mix in the extruder. Finally, the temperature was increased at a rate of 20°C/min up to 280°C. In Figures 3 and 4, all the thermogravimetric traces of the parent PVOH and modified polymers are shown with respect to time and temperature, respectively. The points of interest on the curves are (a) the total weight % loss during heating (W_{tot}), (b) the weight % loss near the start (W_{start}) and end (W_{end}) of the isothermal period, and (c) the weight loss difference

during the isothermal period (ΔW), which can be expressed as the difference between W_{end} and W_{start}. These values were obtained from the data points in the graphs and are tabulated in Table IV for all polymers under investigation.

By considering the curves in Figure 3 and the values in Table IV, it is obvious that there is an improvement in thermal stability for most modified polymers compared to the parent polymer. Higher stability is displayed by the polymers incorporating small amounts of the long aliphatic chain epoxides, the most stable being E_{16} and E_{18} followed by E_{14}-1. The E_{16} weight loss was 1.54% less than that of PVOH at the end of the heating period and 1.4% less at the end of the isothermal period. The group of these three polymers behave differently compared to the remaining polymers which, with the exception of E_{14}-2, fall into a second group. This second group of polymers which has incorporated a higher amount of epoxide exhibits a smaller difference (compared to previous polymers) in thermal stability. This group, however, shows a significant melting point depression and can therefore be processed at lower temperatures, avoiding thermal degradation. In the other case, the long-chain aliphatic epoxides behave better than does PVOH at similar processing temperatures. Explaining this behavior is not an easy task since many factors are involved. It seems that
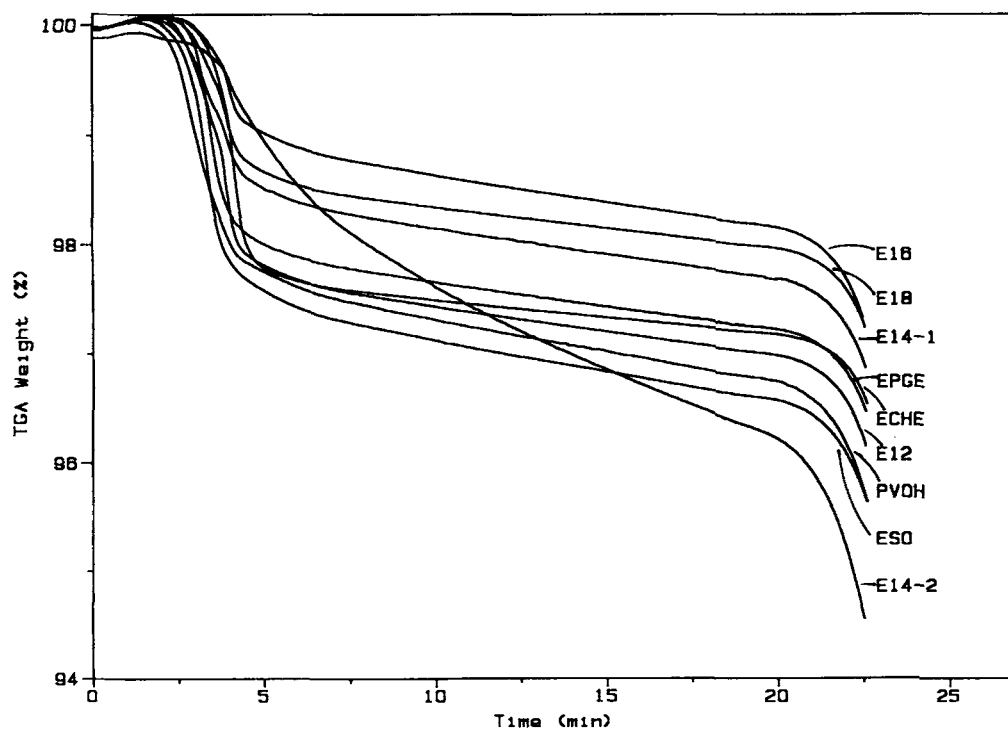

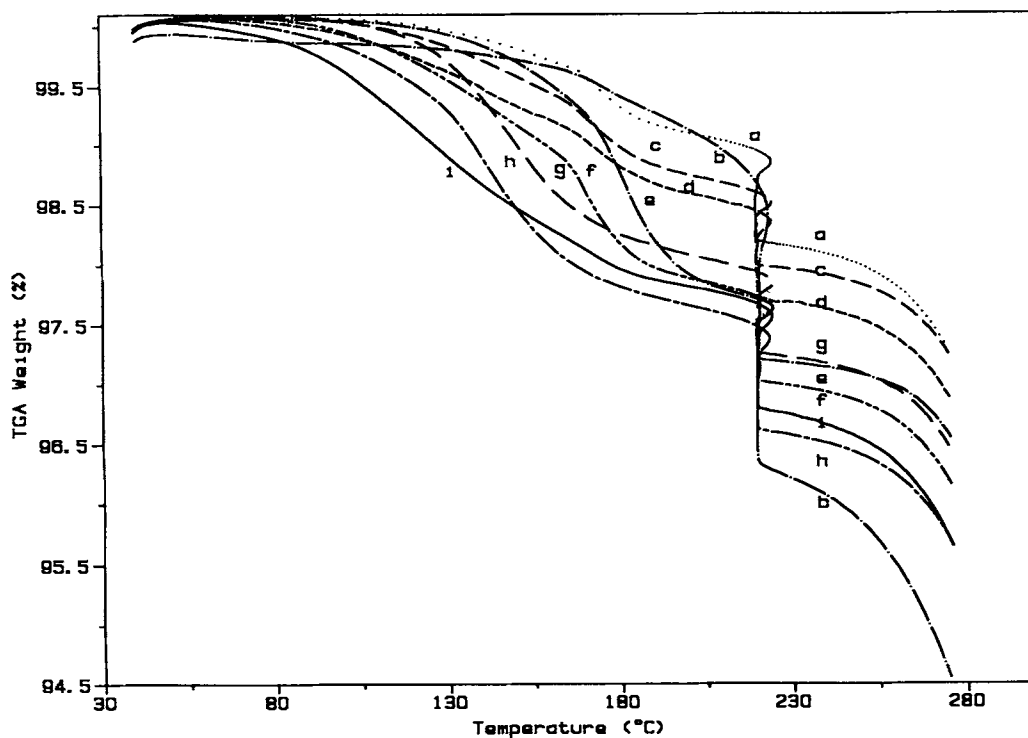**Figure 3** TGA curves of parent and modified PVOH polymers with respect to time.

Figure 4 TGA curves of parent and modified PVOH polymers with respect to temperature:
(a) E_{16}; (b) E_{14}-2; (c) E_{18}; (d) E_{14}-1; (e) E_{CHE}; (f) E_{12}; (g) E_{PGE}; (h) E_{SO}; (i) PVOH.

even small amounts of the long aliphatic chains that are present in E_{16} and E_{18} and less so in E_{14}-1 modify the crystalline morphology by intervening with the hydrogen bonding between hydroxyl groups. The decreasing stabilities of E_{14}-1 and much more of E_{12}

Table IV Weight Loss (%) at the Start (W_{start}) and End (W_{end}) of the Isothermal Period, Total Weight Loss (%) (W_{tot}), and Weight Loss (%) Difference (ΔW) for Modified PVOH Polymers

Modified Resin	W_{start}^a (%)	W_{end}^a (%)	W_{tot}^b (%)	ΔW^c (%)
PVOH	97.75	96.82	95.86	0.93
E_{12}	97.81	97.05	96.33	0.76
E_{14}-1	98.51	97.75	96.99	0.76
E_{14}-2	98.94	96.41	94.74	2.53
E_{16}	99.02	98.22	97.40	0.80
E_{18}	98.67	98.01	97.36	0.66
E_{CHE}	97.79	97.22	96.70	0.57
E_{SO}	97.58	96.65	95.83	0.93
E_{PGE}	98.01	97.28	96.59	0.73

[a] W_{start} taken at $t = 5$ min; W_{end} taken at $t = 18.5$ min.
[b] W_{tot} taken at $t = 22.4$ min.
[c] ΔW is obtained as ($W_{start} - W_{end}$).

seem to confirm this assumption. It seems that the chains are not long enough to interfere with the crystallization process.

The TGA trace of E_{CHE} deserves some comment because it has the smallest ΔW of all polymers in the isothermal region, which means that it is more stable than the rest at 220°C. It is proposed that the ring interferes effectively with the crystalline structure of the polymer chains, enhancing simultaneously polymer stability. A similar mechanism must be envisaged for E_{PGE} and E_{SO}, the small variations observed being attributed to their different chemical structure. Finally, we can speculate on the poor behavior of E_{14}-2 as originating from the traces of the acid catalyst remaining in the sample. For this purpose, further work is planned with other more appropriate catalysts. Summarizing, some of the modified polymers exhibit better thermal stability compared to PVOH which may be attributed to the interference of appropriate moieties within the matrices of basic polymeric material.

CONCLUSIONS

The extent of modification of PVOH by various epoxides was established with NMR spectroscopy, in-

dicating that the reaction proceeds faster with aromatic and cycloaliphatic epoxides compared to simple long-chain aliphatic epoxides. The reaction with epoxides and the effect on the properties of PVOH are summarized in the following: (a) Long-chain aliphatic epoxides were incorporated in minimal amounts and affected the T_m by only a few degrees, (b) the reaction can be catalyzed by phosphoric acid but the products are not thermally stable, and (c) the aromatic epoxides were the most reactive, transforming the previously crystalline polymer to amorphous. With respect to thermal stability, however, the situation appeared differently. Although the hydrophobically modified polymers exhibited small changes in thermal transitions, they showed the most improved thermal stability compared to PVOH. Polymers modified by the introduction of aromatic and cycloaliphatic moieties exhibited better thermal stability compared to PVOH. The polymer with the cycloaliphatic ring also displayed a better balance between processing temperature and thermal stability and it is therefore a more effective candidate for enhancing the processability of PVOH.

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