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Aging Effect in Different Aqueous Media on Thermal Stability of Epoxy Resin

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ABSTRACT

The present work deals with the influence of aging conditions on thermal stability of authentic epoxy resin exposed to different aqueous media. Thermogravimetric analysis (TGA) shows that epoxy samples cured at moderate temperatures are more stable in acidic media than the samples cured at higher temperatures. The complete decomposition temperature of the epoxy resin exceeds 400^0C for samples cured at 25^0C then decreased gradually for samples cured at 32 and 48^0C respectively.

تأثير التقادم في الأوساط المائية المختلفة على الاستقرارية الحرارية لراتنج الايبوكسي

الملخص

يهدف هذا البحث الى دراسة تأثير التقادم على الاستقرارية الحرارية لراتنج الايبوكسي المعالج في أوساط مائية متغيرة الحامضية وبدرجات حرارية وأزمان مختلفة. أشارت دراسة التحليل الحراري الوزني إلى أن النماذج الراتنجية المصلبة (المقساة) بدرجات حرارية منخفضة في الأوساط الحامضية هي أكثر ثباتاً من النماذج المصلبة في درجات حرارية عالية نسبياً. كما وجد أن درجة حرارة نهاية تفكك البوليمر تتجاوز 400^{o}م في الراتنج المصاب بدرجة 25^o م وتقل تدريجياً في النماذج المصلبة بدرجتي 32 و 48^{o}م على التوالي.

INTRODUCION

Epoxy resins are reactive monomers, which are commonly cured with amine to form thermosetting polymers. The importance of these materials for a varity of applications is well established (Chawla, 1998 and Feldman et al., 1996). Detailed characterization of such systems is needed for at least two reasons. First this enables the development of systems with specific predefined properties which has related to the processing procedures and the choice of the material composition and structure. The second reason is the need for understanding the role of the matrix in fiber-based composites (Bazylink et al., 2000). The curing reactions of epoxy resin involve opening of the epoxide ring by various curing agents like anhydride, amines, phenols, thiols (Lee and Neville, 1985). It can be opend catalytically in the presence of Lewis acids, triamines or photolytically in the presence photo-initiators. Later Schiff – base amino resin hardeners are used for production of conductive and/or semiconductive epoxy resins (Hadad and Adam, 2000). Because the behaviour of thermosetts is affected by the addition of fillers, it is important to investigate the changes that take place during thermal degradation of these materials. Such study is important because it can determine the upper temperature limit, the mechanism of the solid state process and life – time of the thermoset (Nunez et al., 2002).

The aim of this work is to investigate the thermal resistance of epoxy samples cured and aged in different aqueous media at variable periods and temperatures.

EXPEREMENTAL

Materials:

1. Commerical epoxy resin (Leyco-Pox 103) of low viscosity and 1.05 g/cm^3 density at 25^{0}C. The resin and its amino hardner are provided from Lycochem. Leyde, Cologne-Germany.
2. Hydrochloric acid (conc.), Reagent grade.
3. Sodium hydroxide (pel.), Reagent grade.

Preparation of samples:

Epoxy samples are prepared by mixing the resin with the hardner (4:1 vol. ratio). After fast homogenization films of 1 $\pm$ 0.1 mm thickness were prepared using flat dishes. After curing, the films were peeled from the dishes, divided with sharp cutter to small pieces (1 cm^2 area) and kept in a closed container.

Curing conditions:

The samples are cured (solidified) for two days in the following temperatures; group (A) at 25^{0}C, (B) at 32^{0}C and (C) at 48^{0}C.

Aging conditions

Epoxy samples were aged in aqueous media using the following conditions:

pH : 1, 7, 11

Temp. (^{0}C) : 0, 32, 59

Time (days): 7, 14, 21

After aging the samples washed with distilled water, dried and kept in closed container.

Thermogravimetric analysis (TGA)

TGA was performed using a thermal balance designed according to the reference “Laboratory Preparation for Macromolecular Chemistry” (McCaffery, 1970).

RESULTS AND DISCUSSION

Thermal stability of the cured epoxy resin in different conditions was investigated by dynamic thermogravimetric analysis in air. Three thermograms (selected from ninety) are shown in figure 1 (a, b, c). The results of thermal data from the ninety thermograms are shown in tables 1, 2 and 3. These data are the weight (%) at 100, 200, 300 and 400 ^{0}C; as well as, the temperature of complete decomposition (TCD). The analysis of the presented data leads to the following results:

1. The weight (%) was not seriously affected within the studied aging period (7-21 days) at the same pH. We think that expansion of the aging time (e.g. months) may give different results.
2. The transfer from acidic (pH, 1) to alkaline (pH, 11) medium at the same conditions, reveals no considerable effect on thermal stability.
3. The tables show that epoxy samples cured (hardend) at moderate temperatures (A) are more thermally stable than the samples cured at higher temperatures (B and C).
4. Table 1 shows that the temperature of complete pyrolysis (TCD) is higher for samples aged at 0^{0}C. The values of TCD exceed 400^{0}C (approximatly) for all (A) samples and decreased directly for samples cured and aged at higher temperatures (B and C in tables 2 and 3).

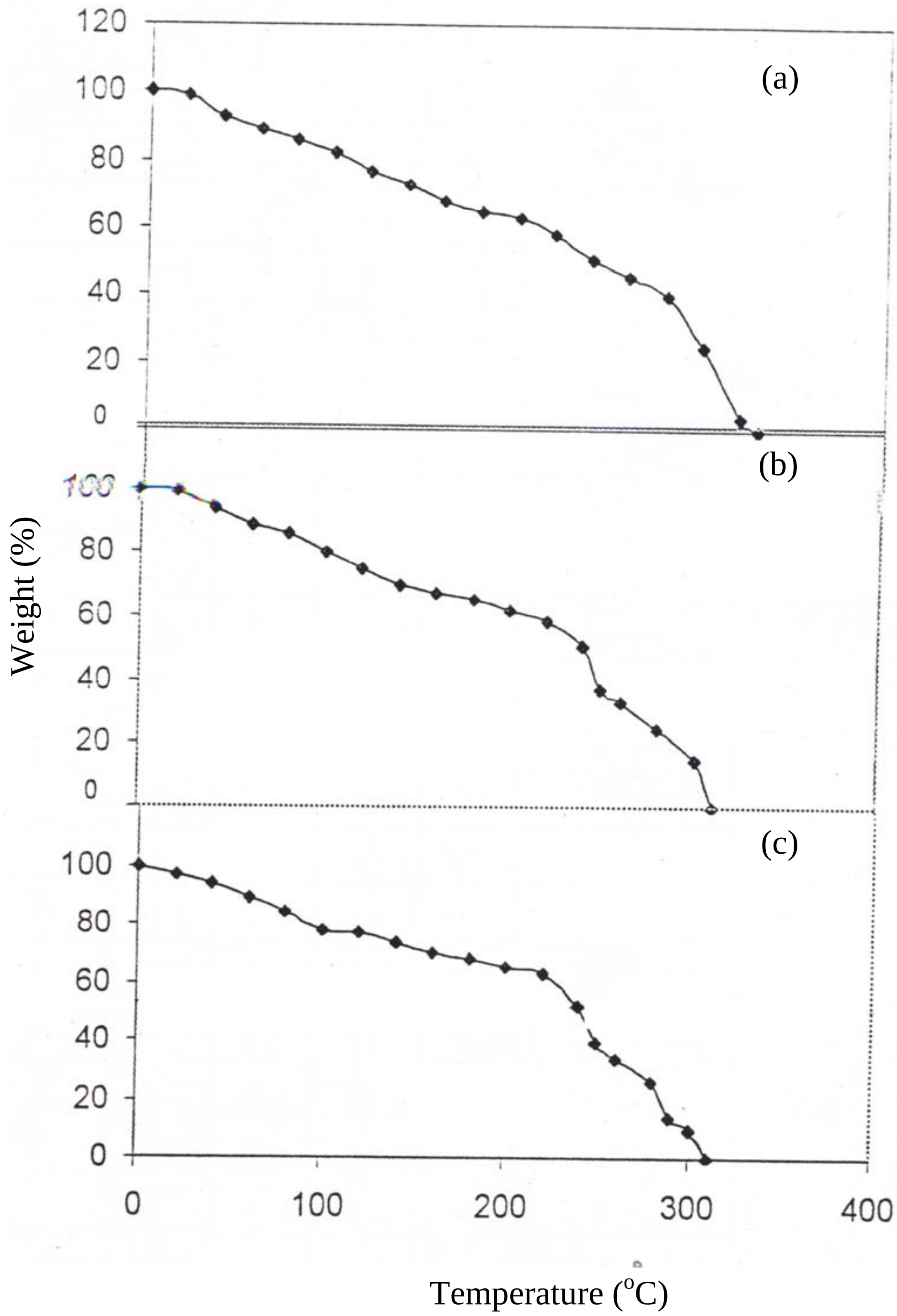

Fig. 1: TGA thermograms of epoxy samples (A) aged at 59^0C, pH = 1 for 7(a), 14(b) and 21(c) days.

Table 1: Thermogravimetric analysis of epoxy samples aged at 0^0C.

Sample	Time (day)	pH	Weight (%) at:				TCD (^0C)
			100	200	300	400	
A	7	1	95	85	55	7	407
		7	92	73	63	5	410
		11	90	65	54	3	400
	14	1	90	79	51	5	400
		7	92	85	72	10	412
		11	92	82	70	10	420
	21	1	94	82	70	10	430
		7	85	70	59	5	415
		11	85	70	60	-	390
B	7	1	86	65	40	-	380
		7	85	65	50	-	380
		11	87	66	50	-	360
	14	1	82	58	45	-	370
		7	80	58	42	-	370
		11	84	71	55	-	390
	21	1	80	62	45	-	370
		7	75	60	38	-	350
		11	82	65	45	-	360
C	7	1	84	70	35	-	340
		7	85	70	55	-	358
		11	70	50	20	-	320
	14	1	81	62	22	-	340
		7	84	64	35	-	360
		11	70	52	20	-	340
	21	1	85	66	40	-	350
		7	80	65	45	-	360
		11	85	70	55	-	375

Table 2: Thermogravimetric analysis of epoxy samples aged at 32^0C.

Sample	Time (day)	pH	Weight (%) at:				TCD (^{0}C)
			100	200	300	400	
A	7	1	87	75	42	-	370
		7	75	55	30	-	360
		11	62	35	15	-	330
	14	1	84	70	38	-	350
		7	70	50	25	-	360
		11	65	35	12	-	320
	21	1	73	60	35	-	340
		7	70	48	20	-	358
		11	60	30	14	-	350
B	7	1	88	80	68	-	370
		7	80	65	50	-	365
		11	86	75	60	-	380
	14	1	81	66	25	-	330
		7	84	67	18	-	340
		11	80	66	45	-	320
	21	1	75	47	20	-	330
		7	60	35	25	-	340
		11	77	56	20	-	330
C	7	1	70	43	15	-	320
		7	79	61	40	-	360
		11	65	45	15	-	310
	14	1	85	75	45	-	345
		7	82	60	20	-	310
		11	83	64	48	-	320
	21	1	65	45	10	-	305
		7	55	20	-	-	260
		11	74	48	25	-	320

Table 3: Thermogravimetric analysis of epoxy samples aged at 59^0C.

Sample	Time (day)	pH	Weight (%) at:				TCD (^{0}C)
			100	200	300	400	
A	7	1	82	63	25	-	330
		7	72	56	35	-	350
		11	71	55	20	-	360
	14	1	80	62	15	-	310
		7	75	50	35	-	350
		11	68	52	28	-	340
	21	1	78	65	10	-	310
		7	75	51	38	-	342
		11	65	50	25	-	335
B	7	1	80	64	23	-	340
		7	85	65	40	-	330
		11	84	62	48	-	360
	14	1	80	63	10	-	305
		7	85	70	30	-	360
		11	87	78	50	-	360
	21	1	75	60	10	-	330
		7	78	54	35	-	350
		11	70	55	40	-	330
C	7	1	80	72	20	-	345
		7	85	64	20	-	330
		11	75	50	30	-	320
	14	1	82	65	20	-	340
		7	83	67	35	-	350
		11	79	55	20	-	330
	21	1	75	54	-	-	270
		7	77	62	30	-	350
		11	80	60	25	-	340

The conclusion from the previous results is that thermal stability of samples cured at 25^0C is better than samples cured at 32 and 48^0C. this result is consistent with the results of mechanical resistance of the same epoxy resin exposed to the same conditions (Abd Al-Hameed, 2002). According to the same reference, heating of epoxy samples aged in the same aqueous media (pH = 1, 7 and 11) leads to 10-20% weight loss at

100^{0}C. Whilst the maximum water uptake ascertained by these samples not exceeds 7%. Morgan, Pryde and Appicella have reported that absorbed water in an epoxy can lower the glass-transition point Tg (by as much as 20^{0}C) and elastic modulus (Nunez et al., 1999). This reduction in Tg was attributed to the increase in segmantal motion resulted when H-bonds between the free hydroxyl groups and water were demolished. Such rupture increase intermolecular motion. This hint may explain the decrease in polymer weight at moderate temperatures. The increase in segmantal motion with temperature transform it to a molecular motion. The final result of this effect is more collisions and disruption in resin molecules. This explanation may be reliable in the case of epoxy samples aged in nuteral or alkaline media where the hydroxyl groups are still free in both cases. In acidic medium, the weak bonding resulted between H-ions and the free hydroxyl groups increases mechanical resistance of the polymer (Abd Al-Hameed, 2002). Accordingly, thermal resistance of the resin raised to certain extent. At higher temperatures, the weak H-bonding breaks - down and the eleberated H-ions behave like free-radicals causing depolymerization of the resin molecules.

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