

Ageing Mechanisms of Advanced Polymer Matrix Composites

Meili Guo, Xinyu Fan and Fang Yang
College of Materials Science and Engineering,
Beijing University of Aeronautics and Astronautics, Beijing, China(100083)

Keywords: thermal age, hygrothermal age, carbon fiber reinforced composites, mechanisms, weight loss, dynamic mechanical properties

Introduction

For predicting the ageing life of a material based on the results obtained from accelerated ageing, it is necessary first of all to ensure that the accelerated ageing conditions selected meet the following two conditions at least: one is that they should have an accelerating effect on the ageing rate of the material, the other is that they should essentially keep the ageing mechanisms occurring in the accelerated ageing same as those occurring in the true ageing conditions. This work is intended to study systematically the ageing mechanisms at different ageing conditions of two types of composites to be used in aircrafts in order to properly predict their ageing lives, which is very important for the sake of flight reliability and durability.

2 Experimental

2.1 Materials

Composite laminates involved in this study were T300/P54 and T300/E39 with the layup style of $[0^\circ, \pm 45^\circ, 0^\circ]_{2s}$, in which P54 is a kind of polybismaleimide resin and E39 an epoxy resin.

2.2 Ageing conditions:

- 1) Thermal ageing: Composite specimens were held in a circulation oven at different constant temperatures in the range from 60°C to 180°C for various periods.
- 2) Hygrothermal ageing: Specimens, cast resins or composites, were immersed in distilled water at 80°C for various periods

2.3 Property measurements:

- 1) Weight change: The weight of a specimen aged or unaged was weighed by using an electronic balance (Mettler AE-260) and the weight loss or weight gain, ΔW , was calculated according to the following equation:

$$\Delta W = \frac{W_{aged} - W_{unaged}}{W_{unaged}} \quad (1)$$

- 2) Dynamic mechanical thermal analysis (DMTA): The profiles of dynamic properties, such as storage modulus, E' , and loss modulus, E'' , versus temperature of specimens (48mm×8mm×2mm) aged and unaged were measured using a DMTA IV (Rheometric Scientific Lt.,

USA), with the deformation mode being 3 point bending, heating rate 5°C/min and frequency 1Hz, taking the peak temperature on the E'' -T curve as the glass transition temperature, Tg.
 3) Infrared analysis: IR analyses were carried out on a Nicolet 560 with cast resin specimens in the form of thin film.
 4) SEM observation: Surface appearance of specimens aged or unaged were observed using a scanning electron microscope (JSM 5800, Japan).

3 Results and Discussion

3.1 Thermal ageing

Weight measurements show that for both T300/P54 and T300/E39, when thermally aged at temperatures not over 100°C, the weight of each specimen changed little even after the specimen had been aged for a period as long as several thousands hours except of a small amount of weight loss within an initial stage of less than 100hr which might result from the evaporation of residual moisture existing in the specimen, while at ageing temperatures above 100°C, especially above 150°C, the weight loss of a specimen increased continuously with ageing time as can be seen in Fig.1. At 180°C, up to 2800hrs, specimens of both composites had a weight loss around 1.2%. Apparently, such a significant weight loss could not be simply attributed to the evaporation of the residual moisture. Therefore, it was thought that degradation and then the escaping of small molecular components thus produced must have happened at temperatures over 100°C, with the heat stability of T300/E39 being inferior to that of T300/P54.

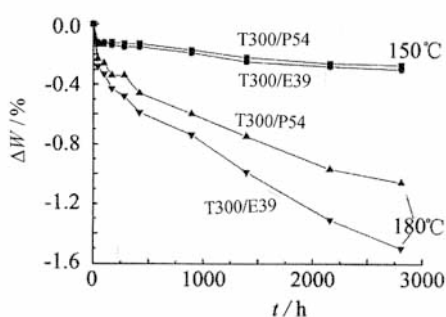


Fig 1 The weight loss of composites during thermal ageing

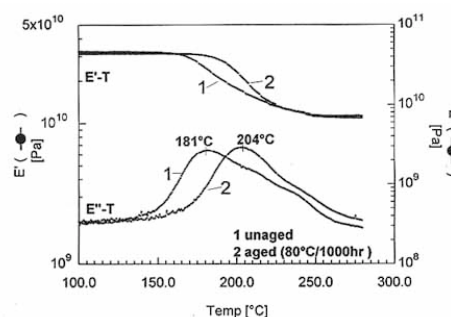


Fig 2 DMA-T profiles of specimens of T300/P54 before and after thermally aged

Fig 2 is a diagram of E' -T profiles of T300/P54 specimens before and after thermal ageing, from which the effects of thermal ageing can be seen clearly. Some main parameters extracted from all the DMTA results for unaged and thermally aged specimens of T300/P54 and T300/E39 at different conditions were summarized in Table 1, from which the following facts can be seen: 1) The Tg of each composite was continuously increased, with a maximum increment of approximately 30°C, but at very high ageing temperatures such as 180°C and after long ageing periods such as over 3500hr, the Tg dropped; 2) The storage moduli in glassy state (for instance, at room temperature) and in “rubbery state” (for instance at 260°C) of each composite aged at temperatures not over 100°C essentially kept constant whereas at higher ageing temperatures, they were significantly increased

For a same type of thermoset resin, the following rules are well known^[1-3]: 1) Its Tg mainly

Table 2 Dynamic property changes of composites with thermally ageing time

Ageig conditions	T300/P54			T300/E39			
	E' , GPa		Tg, °C	E' , GPa		Tg, °C	
	RT	260°C		RT	260°C		
T °C	time hr						
	unaged	31.4	10.8	181.4	25.5	5.1	182.7
60	1000	29.7	9.9	199.6	24.1	4.9	199.8
	2000	28.5	9.6	202.4	27.1	4.4	199.8
	5500	25.0	10	206.0	27.1	3.5	203.9
80	1000	25.4	9.4	203.3	25.2	5.2	197.8
	2000	30.7	11.3	206.1	25.2	5.1	198.8
	5500	31.2	14.7	208.7	20.6	4.3	202.7
100	1000	26.4	9.3	204.2	21.7	4.9	200.5
	2000	31.3	11.7	206.4	30.2	6.6	201.3
	5500	29.7	11.3	211.9	25.5	8.5	205.5
150	500	36.5	19.5	205.1	30.3	7.5	191.7
	3500	36.1	17.0	207.6	20.1	8.4	197.2
	5000	34.9	17.4	211.7	20.2	11.7	199.3
	6500	36.1	20.2	211.7	21.5	10.9	197.9
180	264	39.0	23.3	216.6	31.8	10.0	211.9
	500	38.4	23.7	221.2	29.4	10.8	215.4
	1000	40.7	22.5	212.2	31.7	12.0	208.3
	3500	37.3	23.8	216.0	25.3	10.7	196.4
	5000	36.0	24.4	223.0	22.7	11.0	195.9
	6500	36.3	20.2	211.7	23.8	11.5	186.6

depends on three factors: a)the degree of crosslinkage, ρ_c (or referred as to curing degree): the higher the ρ_c , the higher the Tg; b)the free volumn involved in the material, V_{free} : the less the V_{free} , the higher the Tg and c)the small molecular components in spite of incorporated in or produced in situ: the more the small molecular components, the lower the Tg; 2)Its stiffness in glassy state varies with the V_{free} in it: the larger the V_{free} , the lower the stiffness and it could hardly be influenced by the small molecular components if the quantity of the latter is not much enough; and 3)Its stiffness in “rebbery state” is greatly dependent upon the curing degree: the higer the curing degree, the higher the stiffness.

Based on the experimental results and the theoretical considerations described above, it was inferred that for T300/P54 and T300/E39, the ageing mechanisms during their thermal ageing included both physical and chemical events. The main physical events might be free volumn contraction and evaporation of residuel moisture and the chemical events might be postcuring

and degradation. However, the relative contribution of each event varied with ageing temperature. At ageing temperatures below 100°C, that is, the temperatures far below their T_gs, the chemical mechanisms and the free volume contraction could hardly play any roles. That is why their stiffnesses in glassy state and in “rubbery state” did not change much even after a long ageing period for the two composites. The only difference between aged and unaged specimens was the increase in T_g, which, as suggested previously, may be due to the evaporation of residual moisture. This has been further confirmed in a study of the sensitivity of T_g to the moisture content^[4]. However, at higher ageing temperatures, the ageing mechanisms included all the chemical and physical events mentioned above, such as postcuring, degradation, evaporation of small molecular components and free volume contraction. It was the postcuring that led to the increases in T_g and the stiffness in “rubbery” state; It was the volume contraction that caused the increases in T_g and the stiffness in glassy state but it did not have any contribution to the increase in stiffness in “rubbery” state because physical ageing would be completely eliminated at temperatures over T_g; and it was the degradation accompanied by the escaping of small molecules components that resulted in the continuous weight loss and the decrease in T_g with ageing time at high temperatures.

Taking account of the conditions encountered by the composite structures used in aircrafts during its storage, it was considered that the accelerated ageing temperature should not be over 100°C, and more conservatively, not over 80°C in order to properly predict the ageing life of the composite structures, otherwise the ageing mechanisms in accelerated ageing will not be the same as those occurring in the true storage conditions and the data obtained from the accelerated ageing will misleading the life prediction. Therefore, the temperature selected for studying the hygrothermal ageing behavior of the composites was 80°C.

3.2 Hygrothermal ageing

For the cast resin films of P54 or E39, IR analyses show that no any differences could be found between the IR spectrums of aged and unaged specimens of each resin even the ageing period was as long as 6 months, indicating that no any chemical events happened at all during hygrothermal ageing at 80°C.

Fig.3 gives a typical set of IR spectrums of a E39 film before ageing, after aged for 2 months and after aged for 6 months and then redried.

However, the water absorption behaviors revealed that though for a cast resin specimen of P54 or E39, the relationship between the weight gain, i.e, the water absorbed by the specimen, and the root of ageing time was typical Fickian^[5], while for a composite specimen of T300/P54 or T300/E39, the corresponding relationship was non-Fickian, manifested by a further rapid weight gain following the first platform in the $\Delta W - \sqrt{t}$ curve. Based on the water gain at the first platform and the volume fraction of carbon fibers in each composite, it was found that at that time the water content had approached to the saturated value for the cast resin. Consequently, it was thought that the extra water gain in the composite specimen after that must be accommodated in elsewhere rather than in the resin matrix, for example, in the flaws

or microcracks originally existing in the composite or produced during hygrothermal ageing. It is known that the moisture expansion coefficients between the matrix and carbon fibers are greatly different^[6]. Such a mismatch would result in considerable stress at the interface of carbon fiber/resin matrix and produce flaws and microcracks, particularly after long time hygrothermal ageing^[6-11].

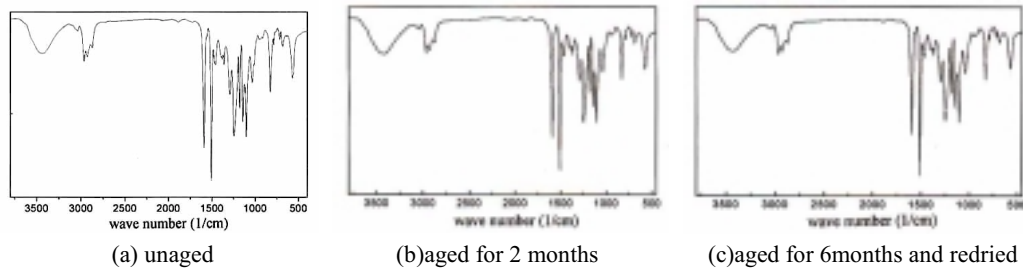


Fig 3 IR spectrums of E39 films

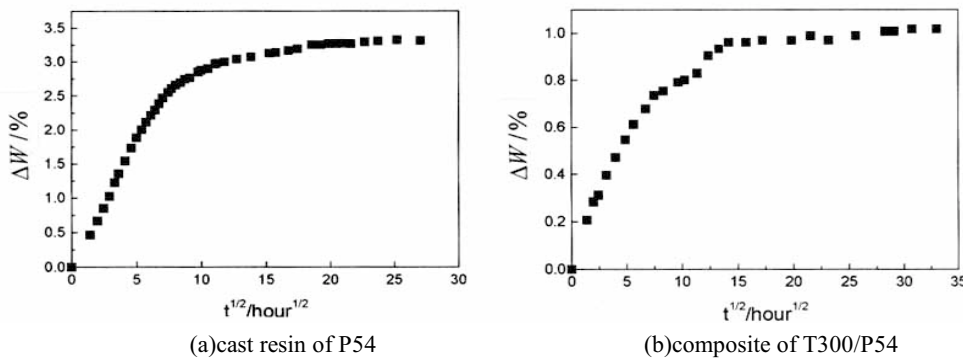


Fig 4 water absorption kinetics of resin P54 and composite T300/P54

SEM observation provided a direct proof for the above inference: The naked areas on the surface from where small pieces of resin had dropped off (Fig 5(a)), microcracks inside a lamina(Fig 5(b)) were more easily be observed in aged composites than in unaged ones. The phenomenon that some swollen resin dropped off the surfaces of aged composite specimens suggested one more mechanism occurring in hygrothermal ageing in addition to those mentioned above, which had been confirmed by the fact that when an aged specimen was redried in a vacuum oven below 80°C, its weight became less than its original value before ageing.

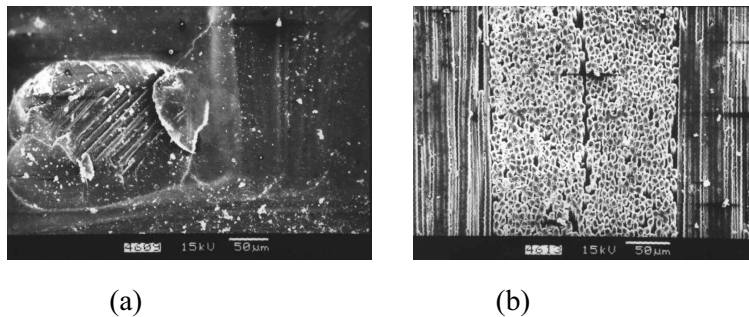


Fig 5 SEM graphs observed from aged composite specimen surfaces, showing an area from where a small piece resin had dropped off(a) and the microcracks in a lamina(b).

Needless to say, the water absorbed by the composites and the defects produced during the hygrothermal ageing would definitely influence the mechanical properties of the composites. Fig6 gives a typical digram including the E' -T and E'' -T profiles of specimens of T300/P54 before ageing and after hygrothermally aged. It can be seen from this figure that before ageing the specime exhibited only a single peak in the E'' -T plot, which corresponded to the Tg of the composite, whereas for an aged specimen a new peak at a relatively low temperatue, such as 164°C and 148°C, which can be denoted as Tg', occured. The lower Tg' reflected the plastisization effect caused by the absorbed moisture on the resin, thereby the composite, and the longer the ageing time the lower the Tg', mainly depending on the moisture content in the specimen and gradually approaching to a constant value as the moisture absorbed reached a saturated value. It can also be seen from this figure that the hygrothermal ageing had no obvious effect on the stiffnesses in glassy state and in “rubbery state”, indicating that the free volumn contraction and postcuring were not important under the present hygrothermal conditions, much less the degradation. It was also found that the dynamic property-temperature profiles of specimens hygrothermally aged and then redried were nearly the same as those of unaged specimens, further indicating that unrecoverable chemical events were negligible.

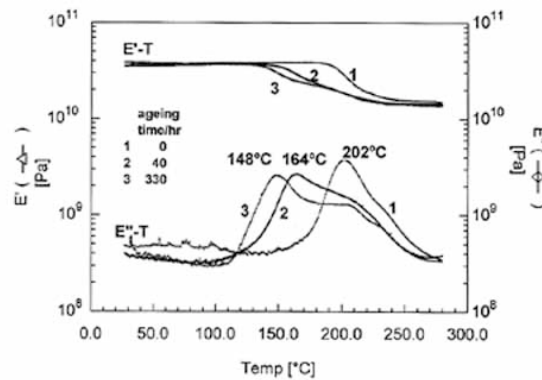


Fig 6 Dynamic property-temperature profiles of T300/P54 hydrothermally aged for different periods

Summery up the descriptions above, it can be concludcd that the ageing mechanisms of the composites during the hygrothermal ageing at temperatures not over 80°C are plastisizing and cracking resulting from the absorbed water and the mismatch in the moisture expansion coefficients between carbon fibers and matrix, and they are more physical than chemical. Plastisizing and cracking had no obvious effect on the stiffness of the composites but might have greater influence on their strength properties Mechanical tests such as compression, bending and short beam shear tests, have proved this inference and the results will be published.

4 Conclusion

For the two types of composites, T300/P54 and T300/E39, studied in this work, the ageing mechanisms involved are as follows:

- 1) During thermal ageing the main ageing mechanism is the evaporation of residual moisture at temperatures below 100°C while postcuring, free volume contraction and degradation are possibly occur at higher temperatures.
- 2) During hygrothermal ageing, the main ageing mechanisms are plastisizing and micro-

cracking.

3) To properly predicting the ageing life of those composites, it is suggested that the temperatures selected for accelerated thermal ageing or hygrothermal ageing should be below 100°C even not over 80°C.

Reference

[1] R J Morgan, Aging Of Polymer Matrix Fibrous Composites, International Encyclopedia Of Composites, Edited by Stuart M Lee, VCH Publishers, Inc. New York, Vol.1, 1990:15-26

[2] Lan liwen etc (editors), Polymer Physics, Northwest Technical University Publisher, 1993: Chapter 3 (in Chinese)

[3] L C E Struik, Physical Aging In Amorphous Polymers And Other Materials, Elsevier, Amsterdam, 1978, Chapter 1,2

[4] Guo meili, Glass Transition and Ageing, In preparing

[5] G S Springer, Editor, Environmental Effects On Composite Materials, Vol.1,2 and 3, Technomic Publishing Co. Westport, CT, 1981, 1984, 1988

[6] Ernest G Wolff, Polymer Matrix Composites: Moisture Effects And Dimensional Stability, International Encyclopedia Of Composites, Edited by Stuart. Lee, VCH Publishers, Inc. New York, Vol.2, 1990:279-323

[7] W L Bradley, T S Grant, The Effect Of The Moisture Absorption On The Interfacial Strength Of Polymeric Matrix Composites, J.Mat.Sci., Vol.30, 1995: 5537-5542

[8] W P Paplham, R A Brown, I M Salin and J C Seferis, Absorption of Water In Polyimide Resins and Composites, J, Appl. Polym. Sci., Vol 57, 1995:133-137

[9] J Zhou and J P Lucas, The Effects Of A Water Environment On Anomalous Absorption Behavior In Graphite/Epoxy Composites, Composites Science and Technology, Vol.53, 1995:57-64

[10] A Chateauinois, B Chabert, J P Soulier and L Vincent, Dynamic Mechanical Analysis of Epoxy Composites Plasticized By Water: Artifact and Reality, Polymer composites, August, No.4, 1995: 288-296

[11] W L Bradley, T S Grant, The Effect Of The Moisture Absorption On The Interfacial Strength Of Polymeric Matrix Composites, J.Mat.Sci., Vol.30, 1995: 5537-5542