Property Change of a Rice-hull-PE Composite Exposed to Weathering

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- **Annual production of paddy --- 2 $\times 10^8$ t**
- **Annual production of rice hull ---- 4$\times 10^7$ t**

1 What we have done

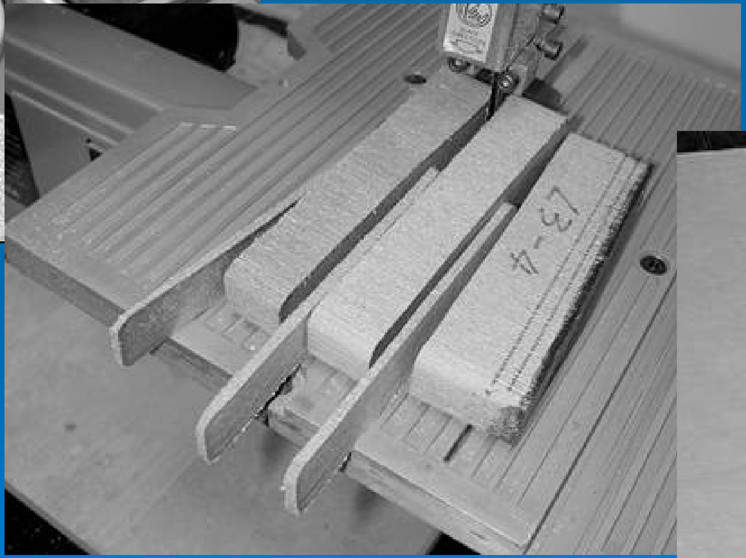
1.1 Water distribution in rice-hull-PE (RHPE) composite and effects of soaking on its mechanical properties

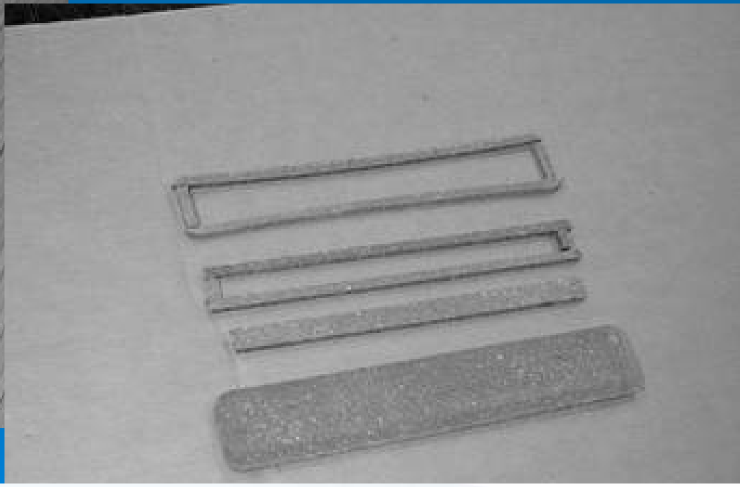
1.2 Effects of freeze-thaw cycling on the mechanical properties of RHPE composite

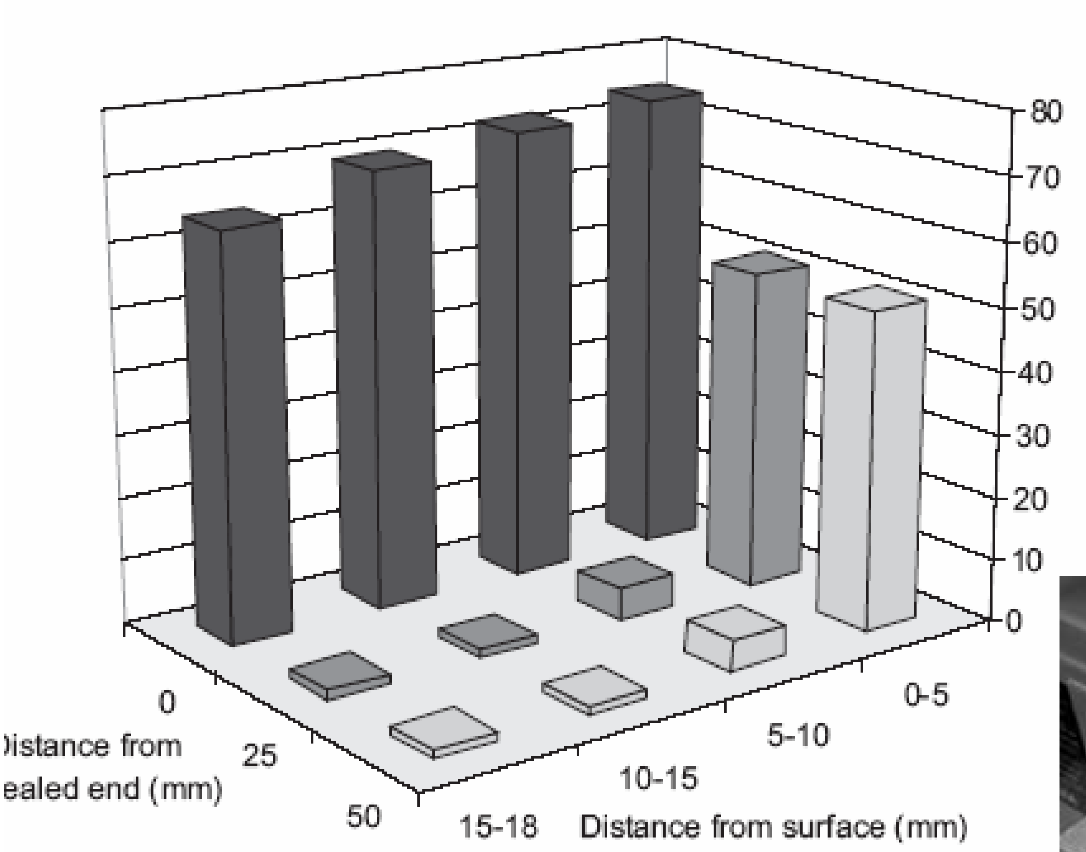
1.3 Effects of accelerate UV weathering on the surface conformation and mechanical properties of RHPE composite

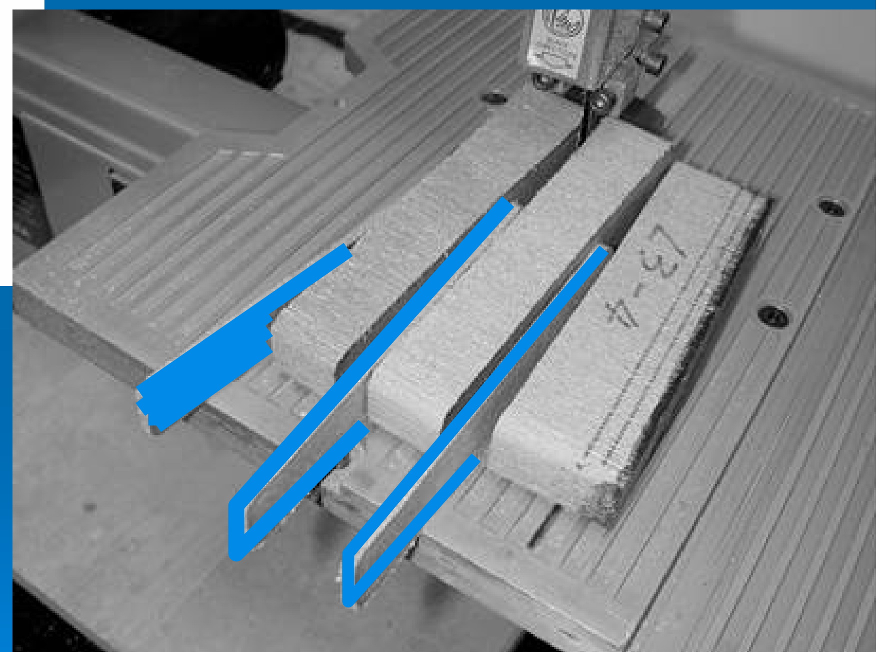
1.4 Natural weathering on RHPE composite

1.1 Water absorption



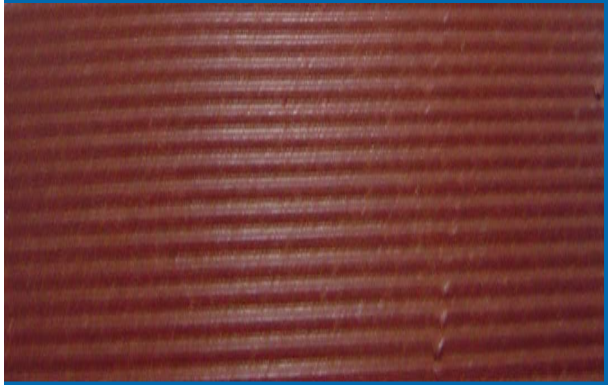






Water concentrated in surface of 5 mm thickness.

Effect of surface texture on water absorption ability



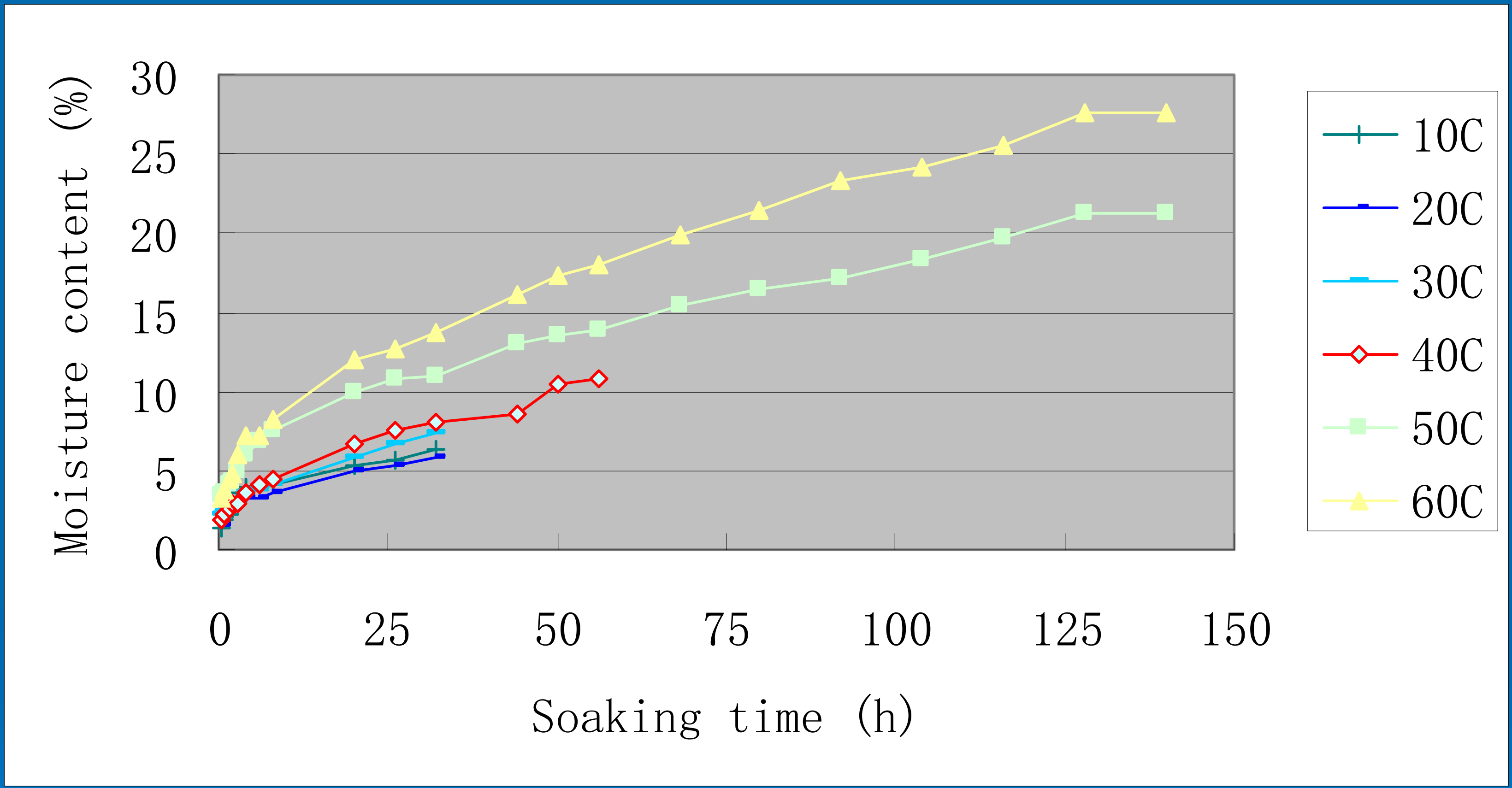
7.1%

9.3%

11.8%

MC of exposed surface in 5mm thickness, based on rice hull mass

Effect of soaking temperature on the moisture content of rice hull flour-PE composites



Soaking temperature above 40 ℃ results in a significant higher absorbing rate

Effects of soaking on MOR and MOE

	MOR/MPa	MOE/GPa
Control sample	13.64 (0.7)	1.61 (0.8)
Samples soaked at 25℃ for 60 h	12.89 (0.91)	0.94 (0.10)

For small size samples, it is MOE significantly decreased after soaking

1.2 Freeze-thaw cycling treatment

Method: Soaking at ambient for 2days, frozen at -29℃ for 2days, and thaw at ambient for 3days.

Effect freeze-thaw cycling treatment on MOR and MOE

Sample size （mm）	Cycling number	MOR （MPa）	MOE （GPa）
500*140*25	0	13.65	1.72
	3	14.87	1.87
	6	14.9	1.92
	9	14.65	1.8
	1 2	14.47	1.79
5*25*100	0	13.64	1.61
	1	12.19	0.87
	3	9.05	0.73

Big size and small size sample differ in the variation trend of flexural properties幻灯片 33

1.3 UV accelerate weathering

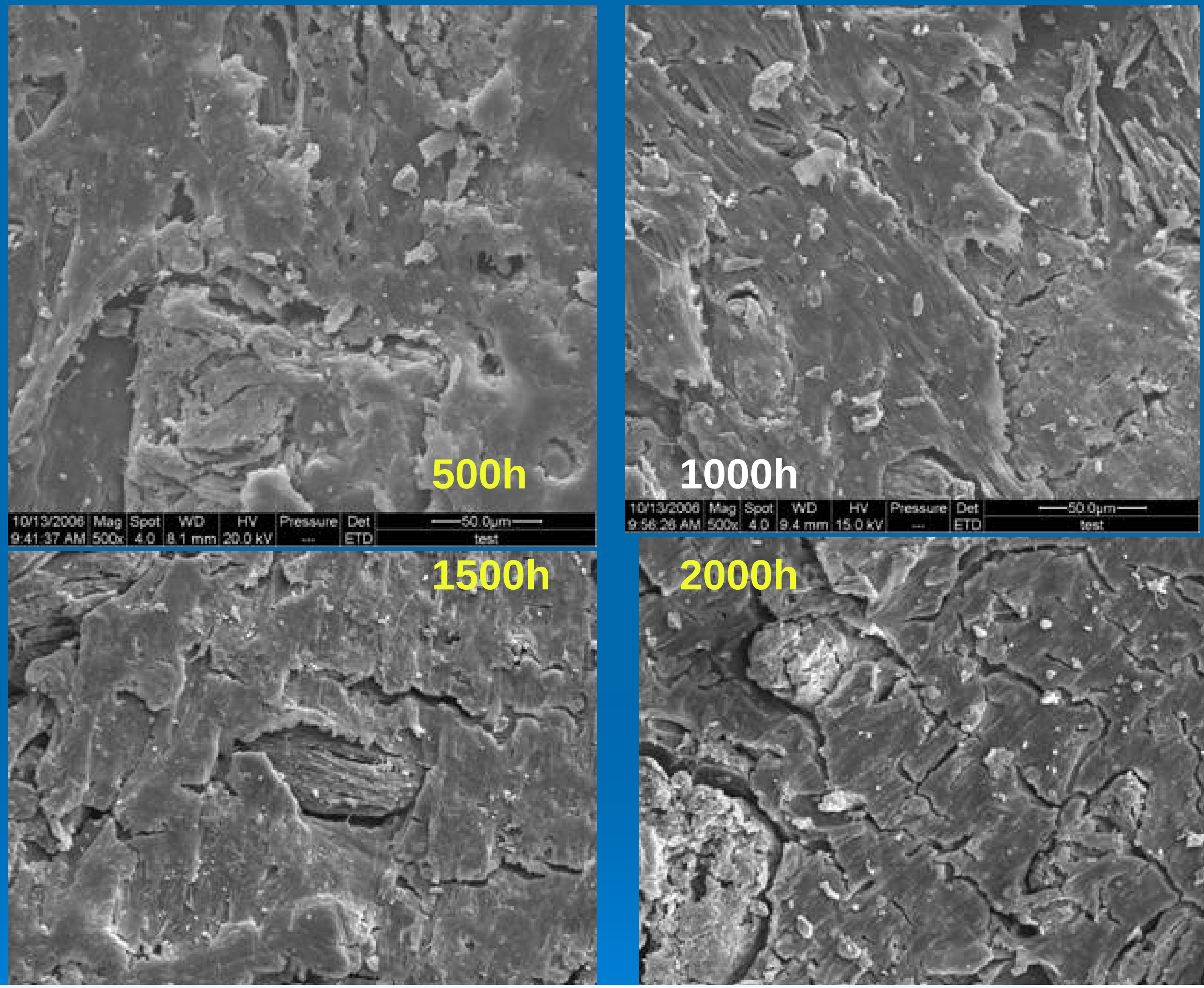
one cycle = 8h UV radiation + 4h dew

At least 6 replicates are tested after 500,1000,1500, and 2000h UV accelerate weathering，

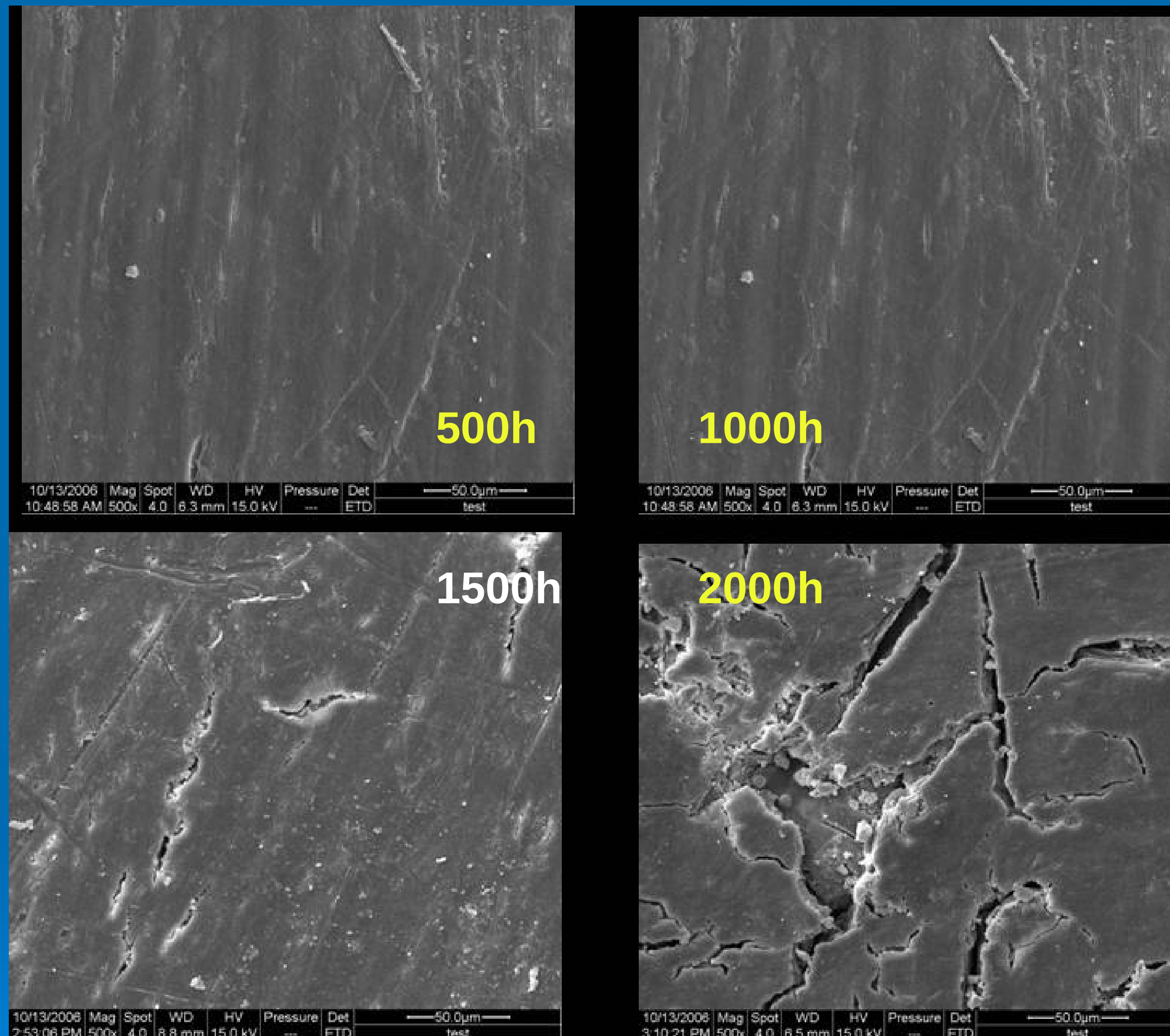
Effects of UV accelerate weathering on configuration

small size sample cut from surface of big sample may warp after UV accelerate weathering, which should be paid attention in service. Balance is necessary.

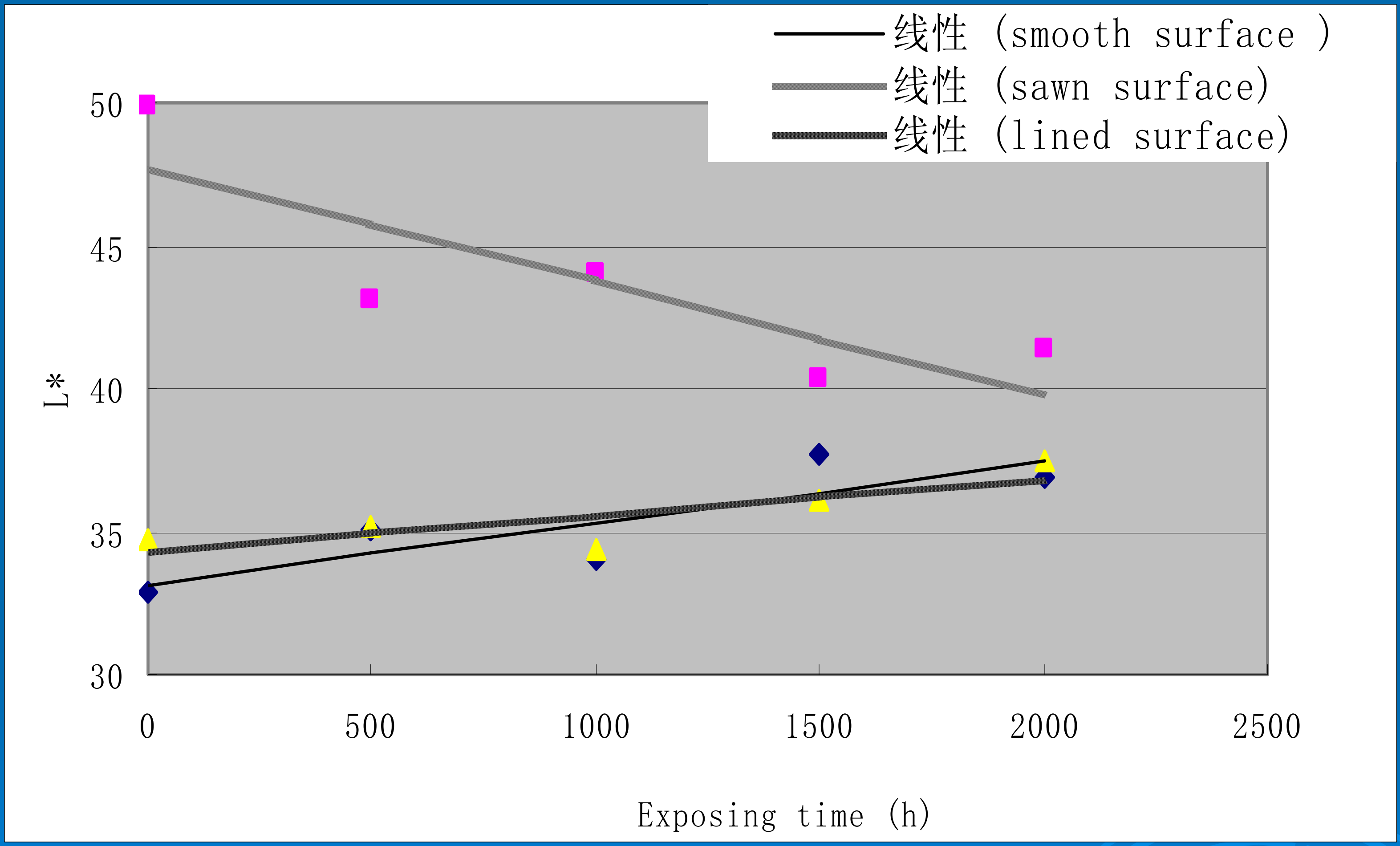
Sawn surface



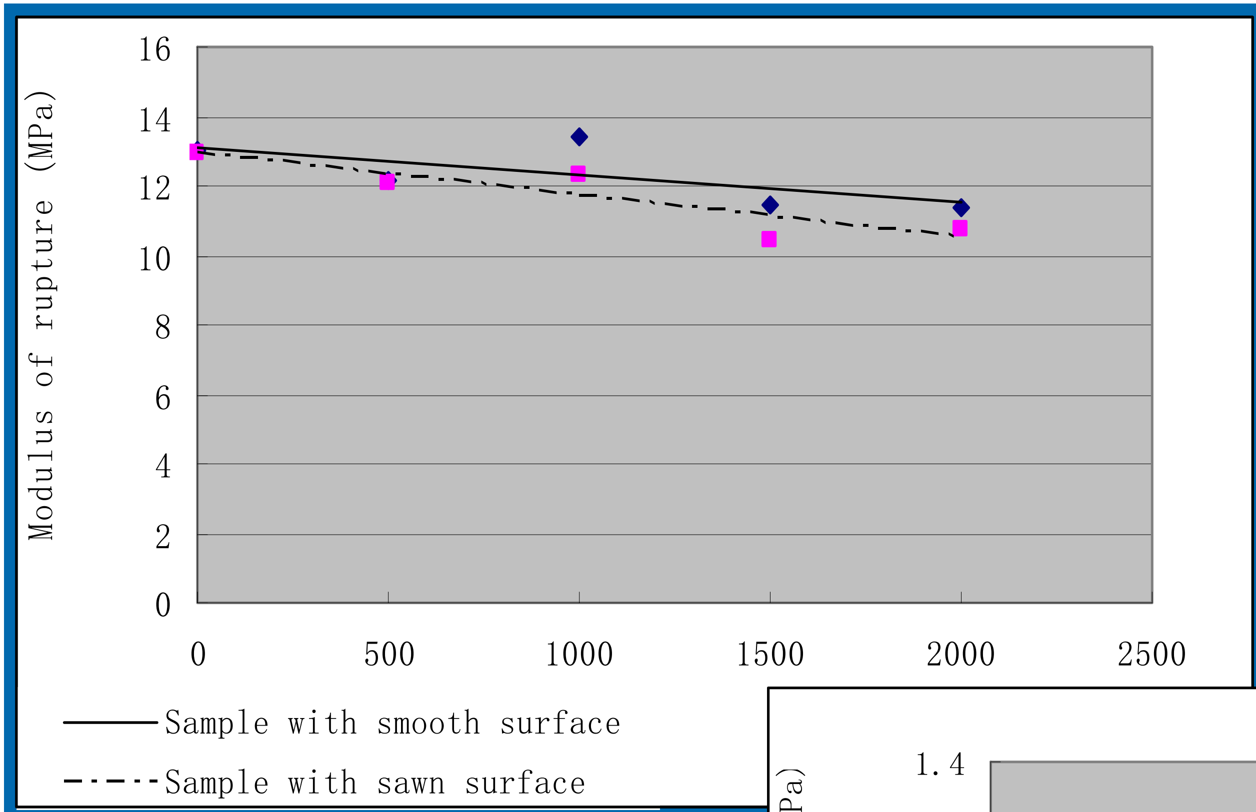
Smooth surface

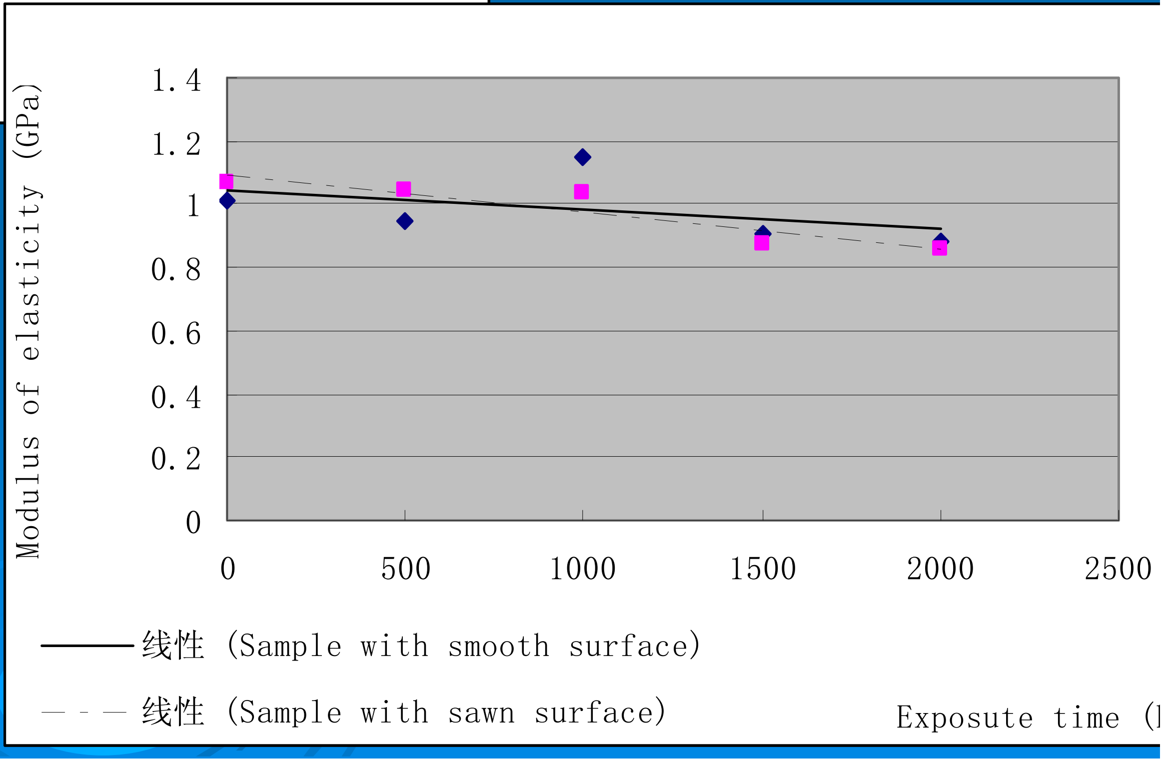


Effect of UV accelerate weathering on lightness



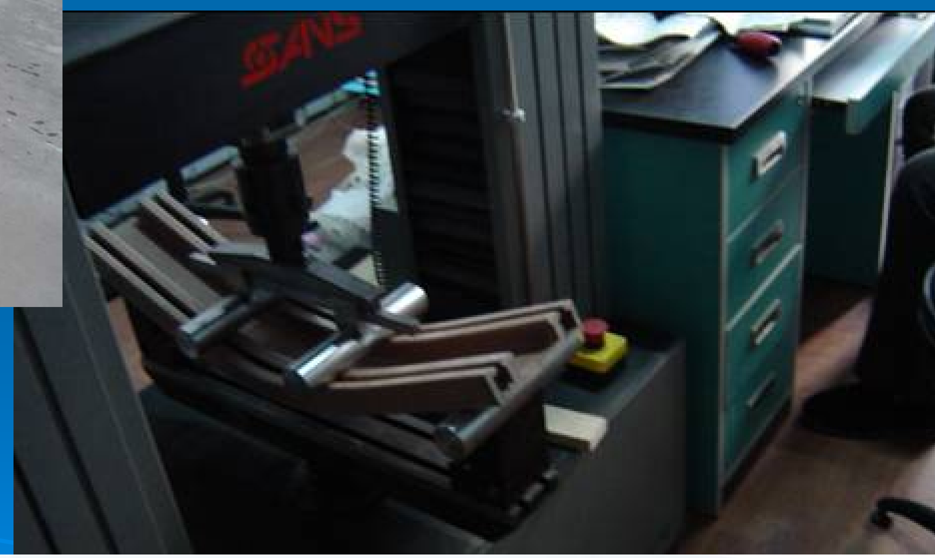
L* increased since 500h UV accelerate weathering, and continued increased during 2000h testing。Color lightened most in initial 500h

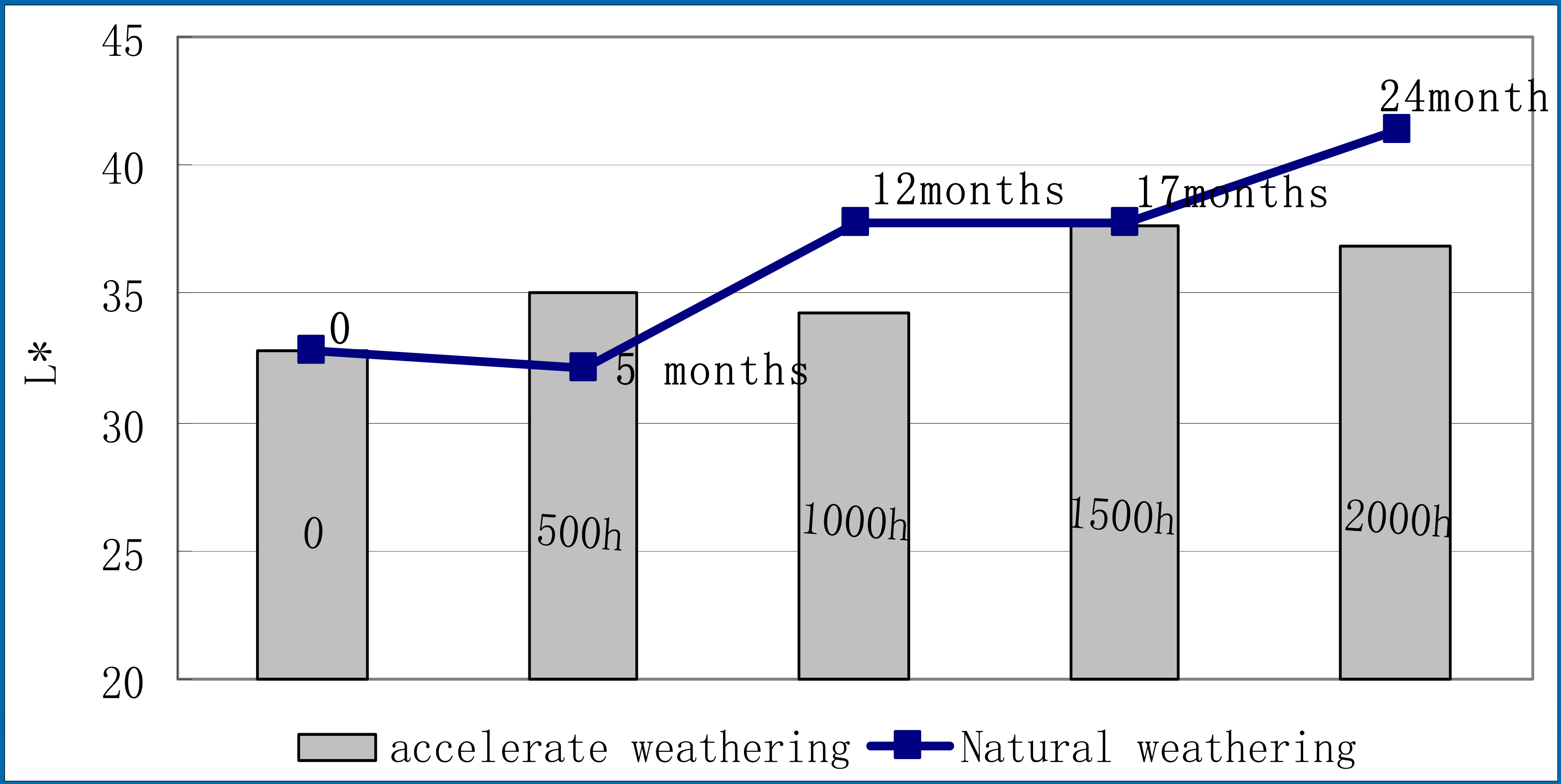




Both MOR and MOE of sawn surface decreased since 1500h UV accelerate weathering。

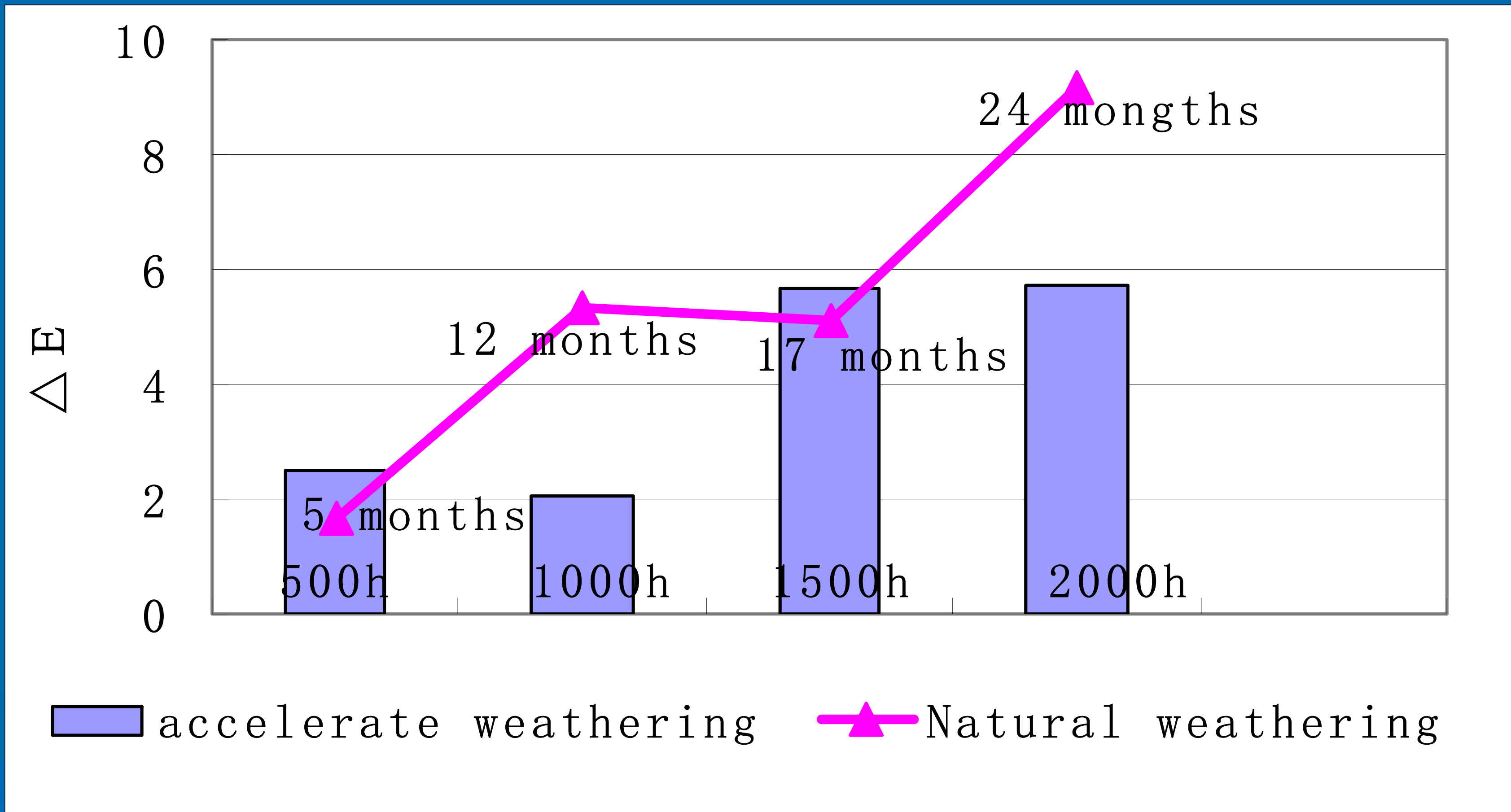
➢ 1.4 Natural weathering





△ L* $_{accelerate}$ = 12%

△ L* $_{natural}$ = 26%

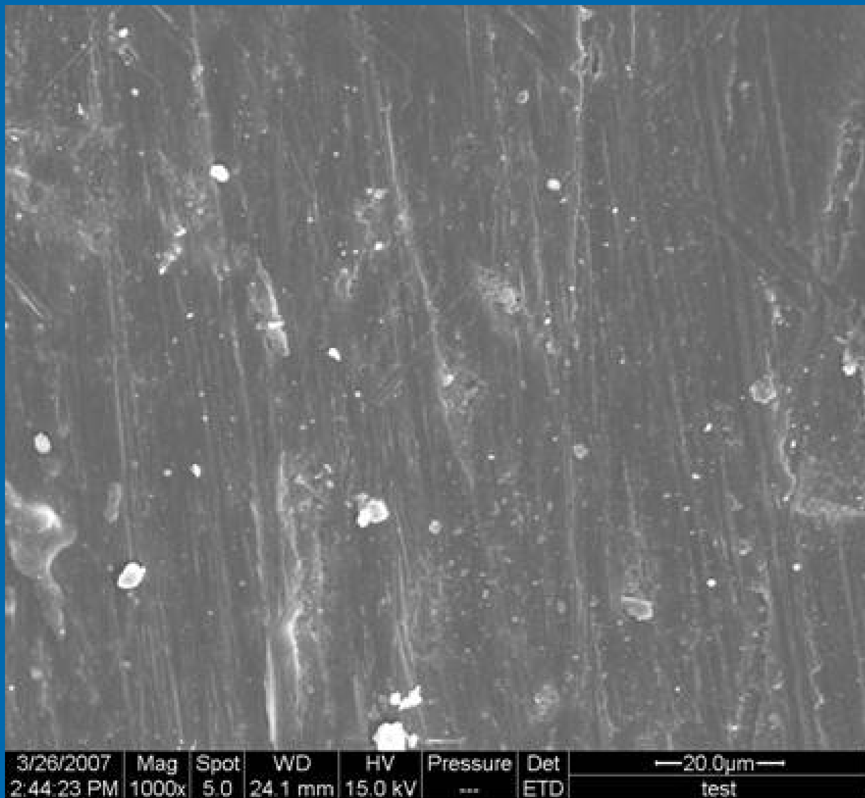


10
8
6
4
2
0
△E
24 mongths
12 months
17 months
5 months
500h
1000h
1500h
2000h
accelerate weathering
Natural weathering

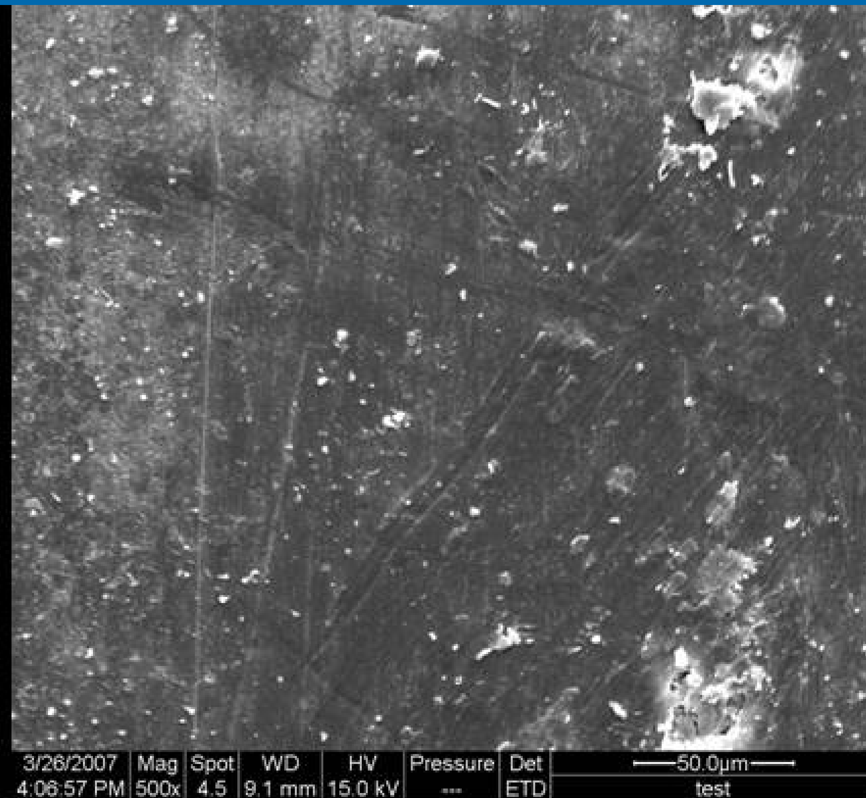
Effects of natural weathering on MOR and MOE

Natural weathering time	MOR (MPa）	MOE（GPa）
Unweathered	13.65	1.724
Natural weathered for 5 months	13.401	1.69
Natural weathered for 12 months	13.3	1.59
Natural weathered for 17 months	**13.89**	**1.69**

Unsignificant change

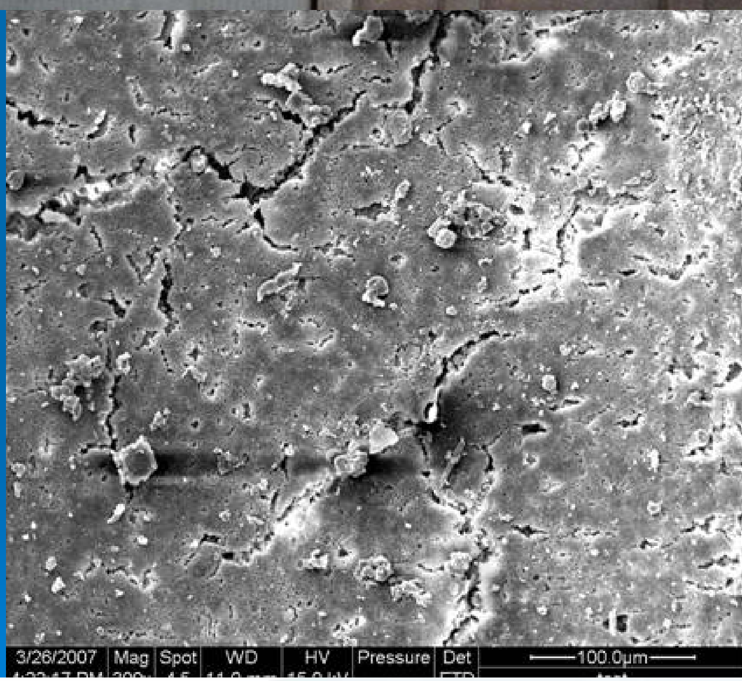


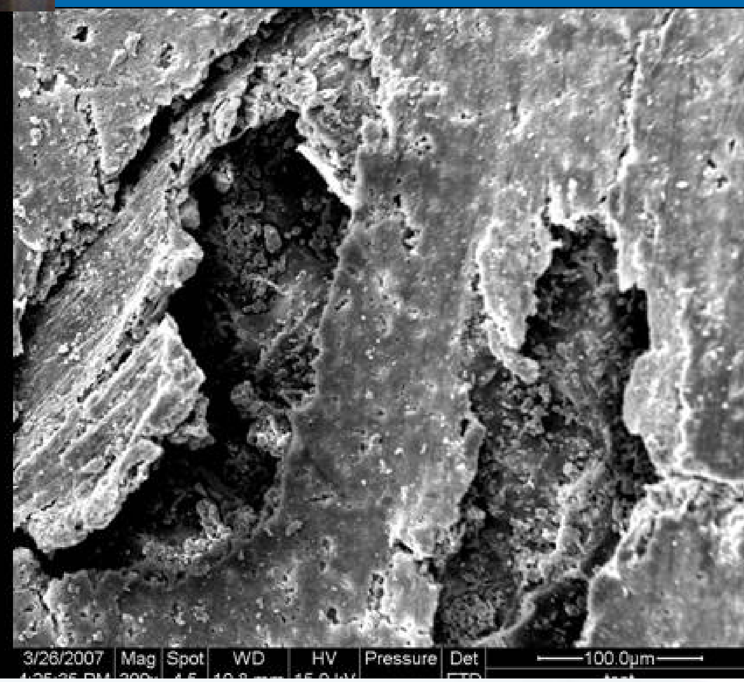
Natural weathered for 12 months

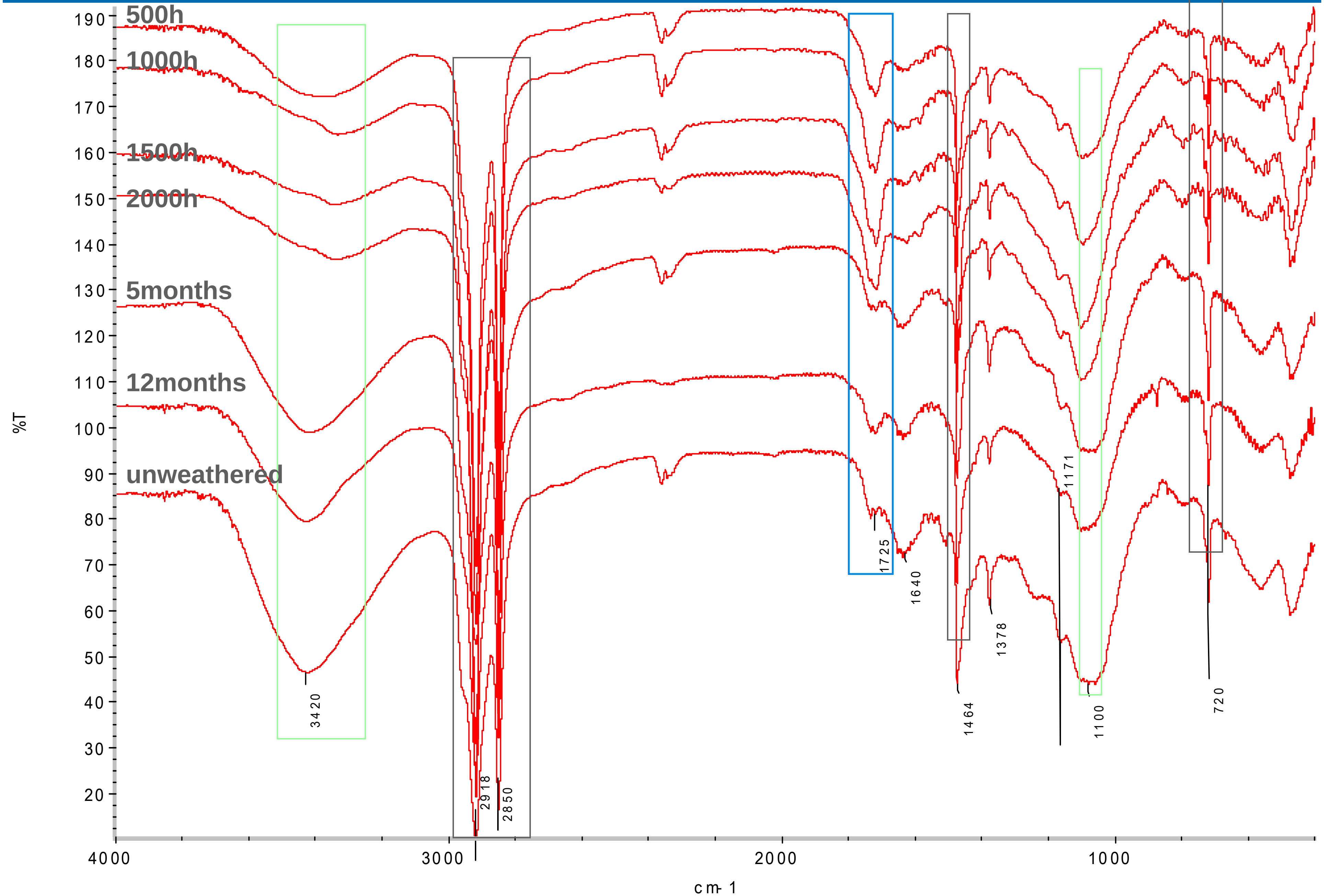


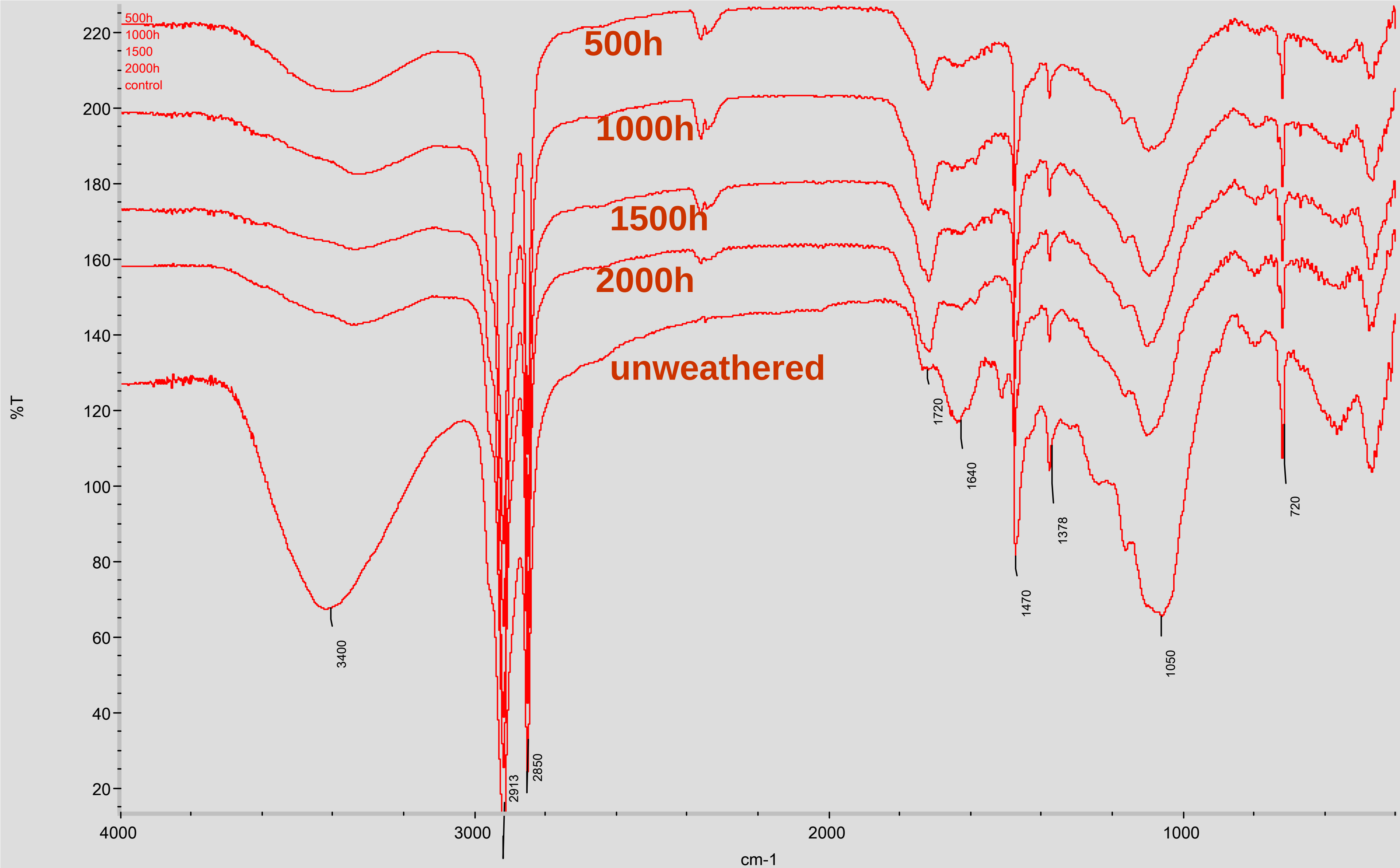
12 frozen-thaw cycling treatment

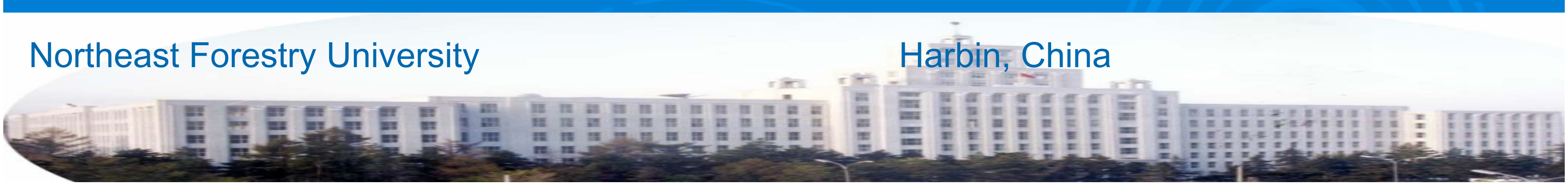
Placed outside for more than 2 years

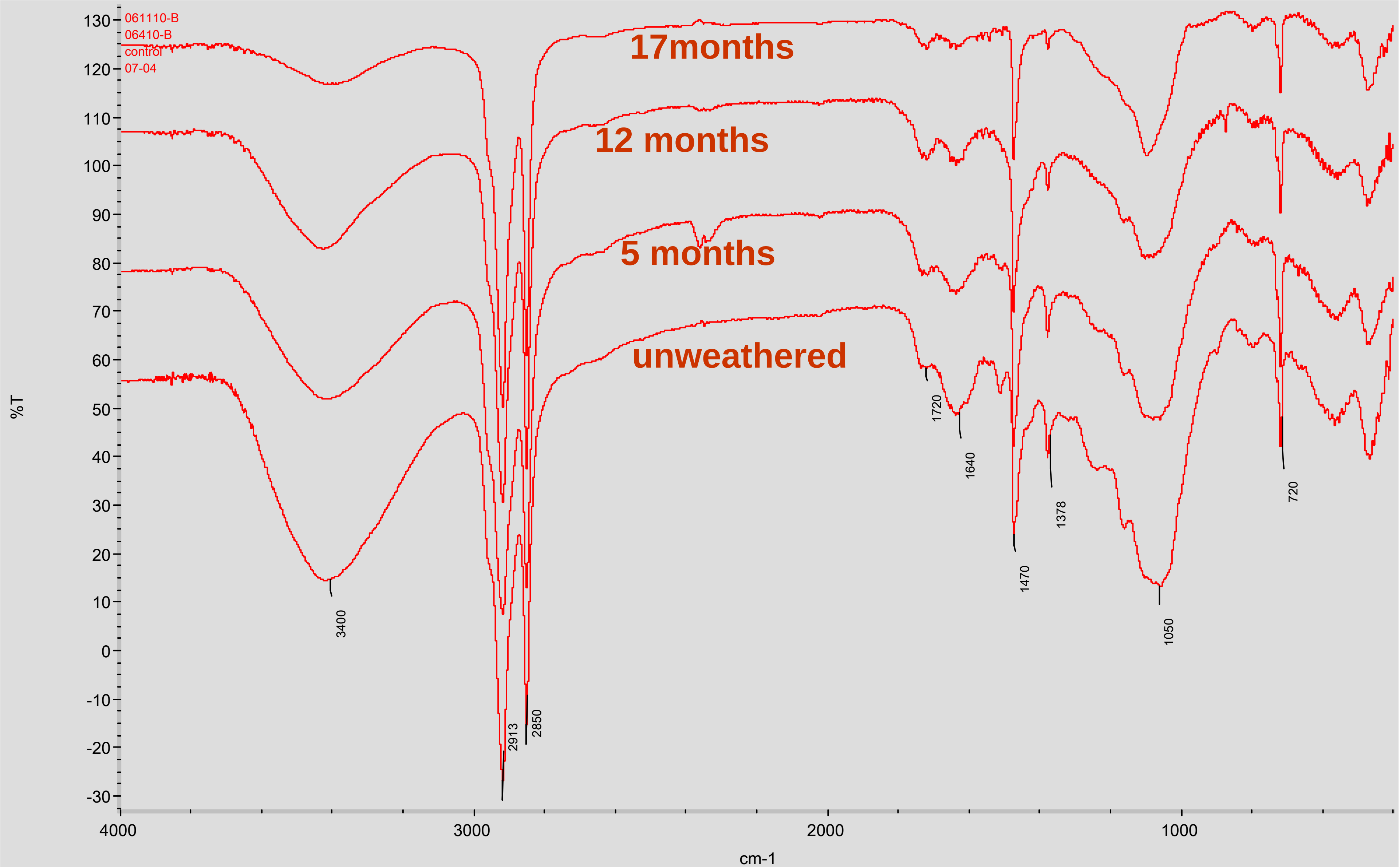





500h
1000h
1500h
2000h
5months
12months
unweathered
%T
cm-1
3420
2918
2850
1725
1640
1464
1378
1171
1100
720
4000
3000
2000
1000


500h
1000h
1500
2000h
control
500h
1000h
1500h
2000h
unweathered
%T
220
200
180
160
140
120
100
80
60
40
20
4000
3000
2000
1000
cm-1
3400
2913
2850
1720
1640
1470
1378
1050
720





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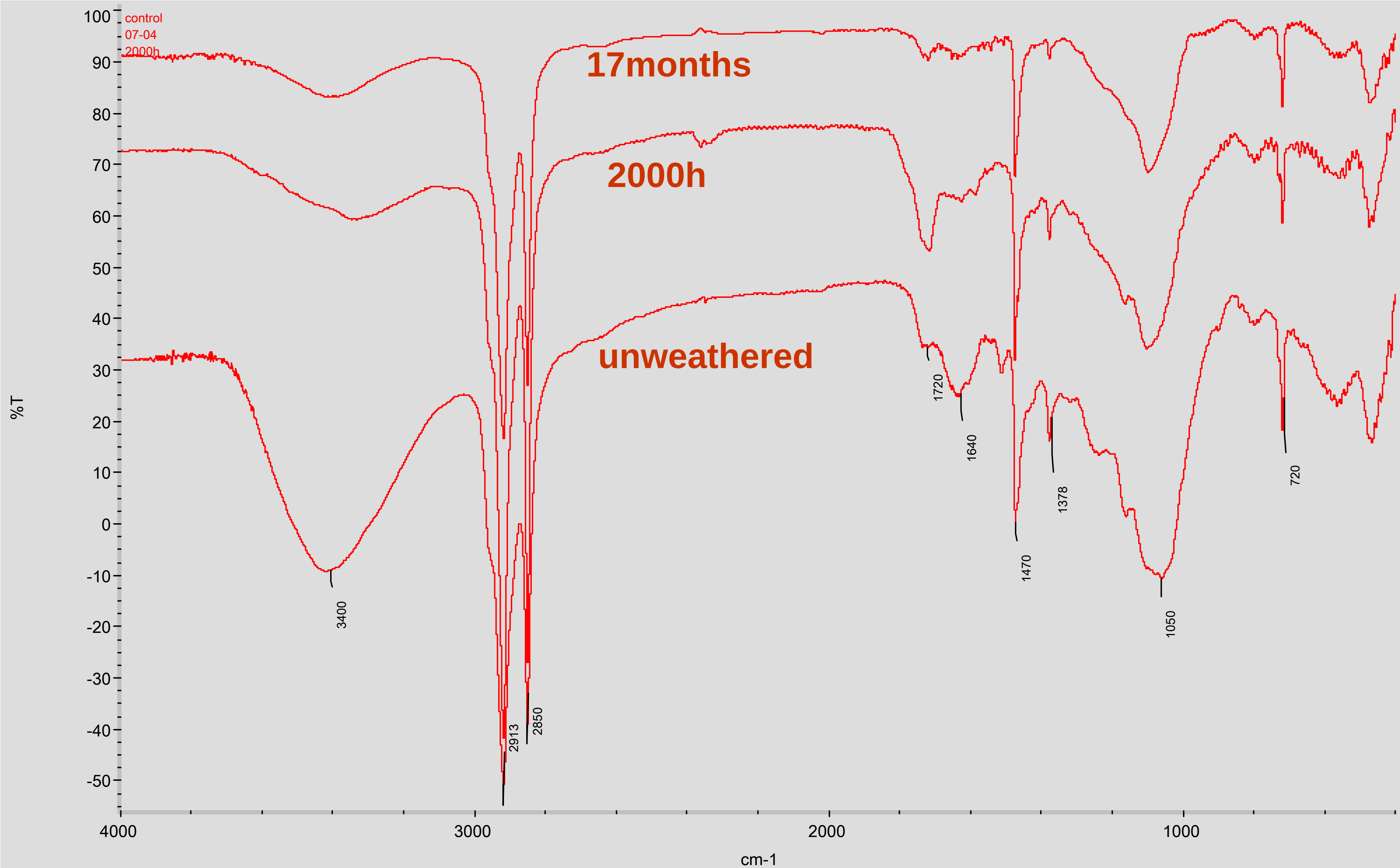
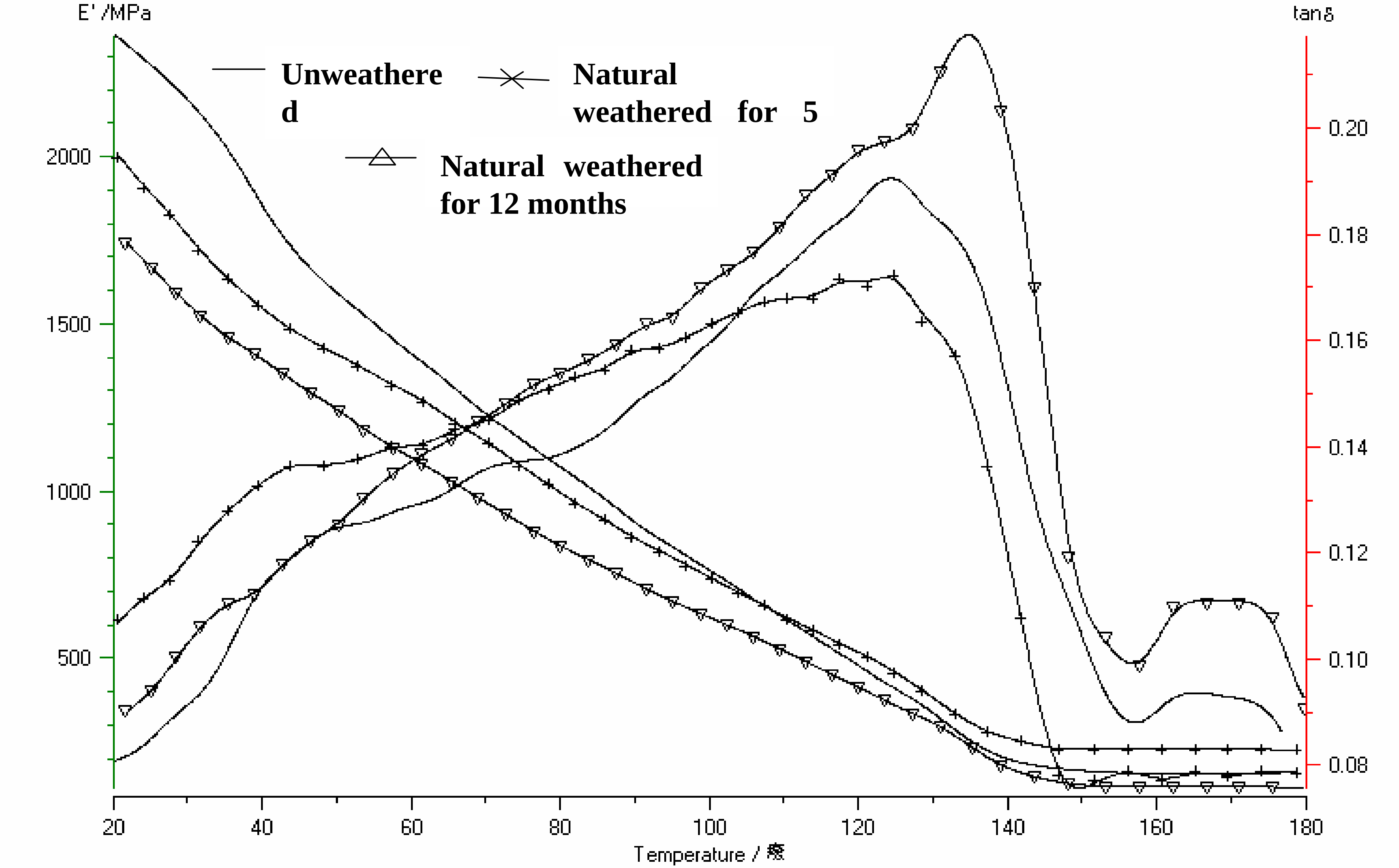

control
07-04
2000h
17months
2000h
unweathered
%T
cm-1
3400
2913
2850
1720
1640
1470
1378
1050
720
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
4000
3000
2000
1000

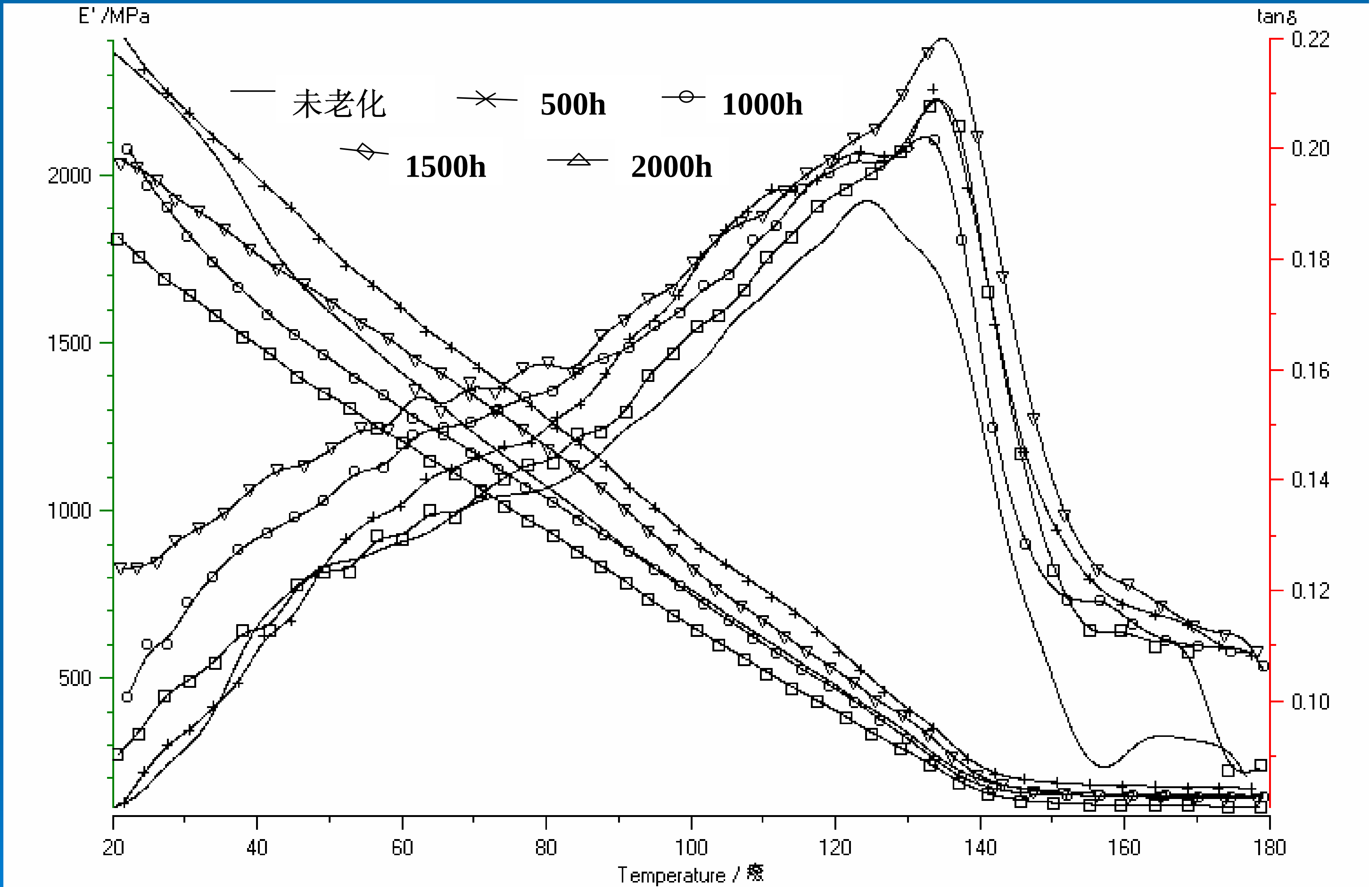
- 通常，位于**3230-3550 cm-1**的宽阔峰来自于分子间氢键缔合的伸缩振动，**1050 cm-1** 处的宽峰及其两侧的系列突起，都体现出纤维素的明显特征。而**2800-3000 cm-1**之间、**1470 cm-1**和**720 cm-1**则是聚乙烯的典型特征峰位置。
- 与未处理试件相比，老化试件在**3420 cm-1**和**1050 cm-1**两处的纤维特征峰明显减弱。加速老化试件在**500h**内即发生变化，以后则没有明显改变；而自然老化试件放置**12**个月的变化更为明显。一些研究者认为，木材的光降解源于纤维素、半纤维素、木质素和抽提物等组分的降解（**Dence, 1992**）。木质素以多种方式经历光降解，遭受破坏后生成水溶性产物并最终形成发色基团，如羧酸、醌、过氧羟基等，成为木材褪色的主要原因（**Heitner,1993**；**Hon**，**2000**）。稻壳也是由上述几种成分构成，老化使纤维信息减弱；同时，从图**3**还发现**1725 cm-1**位置峰有所增强，为羰基伸缩振动，加速老化比自然老化试件的增强幅度更大。由于米糠中纤维素特征峰的存在，掩盖了对**1100 cm-1**位置醚键变化的观察。老化试件羰基峰的增强很可能是木质成分和乙烯成分光氧化降解共同作用的结果。
- 与自然老化相比，加速老化**500h**后即可明显表现出各种化学特征的变化趋势，但在以后的**1500h**里化学特征没有再表现出明显变化。自然老化**5**个月后可看出化学特征变化，老化延长**12**个月时变化则更为显著。自然老化**12**个月时的颜色变化与加速老化**1500h**的基本相同，但加速老化试件表面化学特征变化发生得更早也更明显。

- 自然老化试件在气温较低和日照时间较短的前5个月内（冬季）颜色基本没有变化，经历盛夏之后，第12个月测量时颜色已发生显著变化，变化幅度与实验室加速老化1500h的结果相同。
- 与褪色结果相类似，人工加速老化试件在500h内ΔE已发生显著变化，说明色调变化明显。1000和1500h之间ΔE也有显著变化，1500h以后基本不变。自然老化试件在5个月内产生色调变化，但仍小于人工老化1000h的效果；12个月以后基本达到人工老化1500h的效果。
- 强烈的日光照射和雨水冲刷都应该是褪色及色调变化的原因。而在实验室UV加速老化过程中，凝露主要是模拟夜晚无光照、气温下降的状况，不能完全体现雨水作用结果。在本试验中，UV加速老化1500h基本可以反映室外老化一年时稻壳/聚乙烯复合材的颜色变化。板材在使用过程中是继续发生颜色变化，或类似于人工老化的1500-2000h基本不变，还有待于今后的跟踪分析。



E' /MPa
tanδ
Unweathered
Natural weathered for 5
Natural weathered for 12 months
2000
1500
1000
500
0.20
0.18
0.16
0.14
0.12
0.10
0.08
20
40
60
80
100
120
140
160
180
Temperature / 泵

- 复合材料的存储模量随自然老化的时间的延长而下降的趋势较明显；而损耗因子却表现出异常，在**100ºC**范围，损耗因子随老化时间的延长而增大，且自然老化**12**个月后其内耗明显增大。这表明材料在自然环境中相应的分子运动单元的活动性降低了，最为显著的是**160ºC**附近的内耗峰的变化，此处聚乙烯的α松弛。关于其说法，目前尚有争论。有人认为是晶区的分子运动引起，另外的学者则提出是晶片表面分子链回折部分的再取向运动所形成，倾向性的意见认为它是由两个不同活化能的松弛过程所组成的复合过程


E' /MPa
tanδ
未老化
500h
1000h
1500h
2000h
2000
1500
1000
500
0.22
0.20
0.18
0.16
0.14
0.12
0.10
20
40
60
80
100
120
140
160
180
Temperature / ℃

- 材料在经紫外加速老化**1000**小时和**1500**小时后的存储模量较未老化的明显下降，但在**140ºC**后其存储模量均趋于一致。从图中我们还可以看出在熔点以前紫外加速老化后的复合材料的损耗因子变化很大，随紫外老化时间的延长损耗因子越大，在峰值时，紫外老化**500**小时和**1500**小时的损耗因子相当，经紫外老化后的稻壳/聚乙烯木塑复合材料的内耗值均低于未老化的。这可能是因为在紫外线的高强度和反复的照射下，稻壳中的稻壳纤维和聚乙烯均发生了不同程度的光氧化，从而发生了复合材料在不同程度上使存储模量下降和内损耗增大。

4 What we think

- Sample size: big and small 幻灯片 10
- Main problem in weathering: lightening
- Safety in service: sudden break幻灯片 35
- Raw material: increase resources
- Surface decoration: protection from plastic matrix

thank you!