Properties of polymer materials revealed by thermal analysis with optical observation

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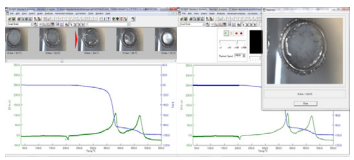
New thermal analyzers were developed that can observe samples during measurements. These systems can obtain optical images and collect thermal data including DSC, TG, DTA, DMA. Furthermore, the optical images are linked in the time-scale with thermal data, so we can properly correlate the phenomena occurring during thermal analysis.
We measured polyethylene terephthalate (PET) undergoing tensile stretching with this system. During glass transition, the observed physical transformation of PET was well correlated with changes in the DSC and DMA signal. Furthermore, we found that PET expanded unexpectedly during decomposition in air. When we used aluminum pans for measuring this decomposition, the aluminum pan was deformed by PET expansion, causing a dummy peak on the DTA signal. We report the results of various polymer samples analyzed by the new system.

Experimental

Material	PET			PE	Rubber (NBR)
System	TG/DTA	DSC	DMA (1 Hz oscillation)	TG/DTA	TG/DTA
Sample Detail	5 mg	10 mg	20 mm L x 10 mm W x 0.1 mm T	5 mg	5 mg
Heating Program	10˚C/min	10˚C/min	2˚C/min	20˚C/min(N_2) to 230˚C and hold at 230˚C	20˚C/min(N_2) , 10˚C/min(Air)
Purge Gas	Air or N_2	N_2	N_2	N_2→O_2 (change after temp. stability)	N_2→Air (change after drop to 300˚C)

Notes: In DSC and TG/DTA, PET sample is from a drink bottle. For DMA, PET film is a consumer product. PE sample is cut from a water pipe. NBR is a consumer product.

The USB-linked camera can be configured to take pictures based on various parameters (For example: every 1˚C temperature change, every second, over a range of times, etc.).
Furthermore, image data are linked to thermal analysis data, so data and images can be overlaid using the analysis software.



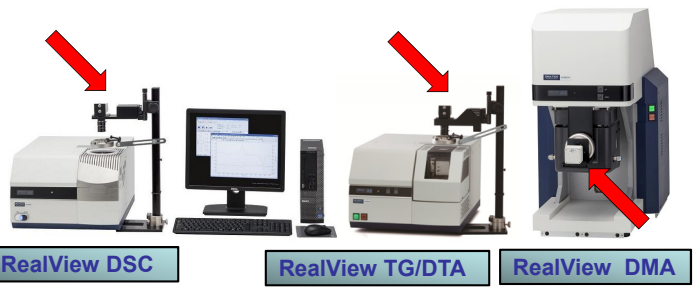
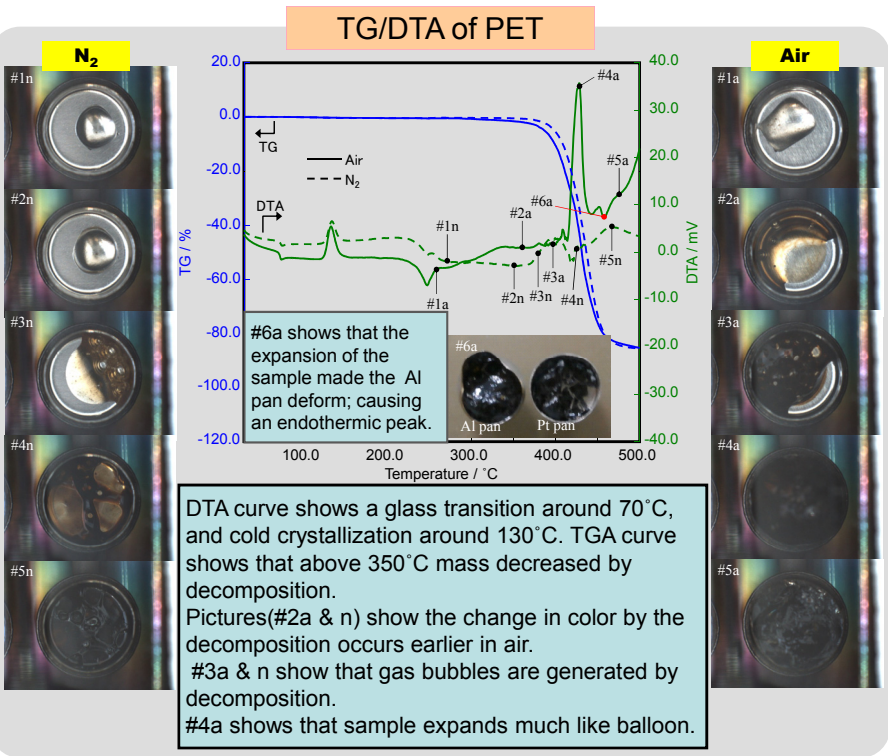


Fig.1 Thermal analyzers with optical observation units (red arrows) by Hitachi High-Tech Science Corp.

Results

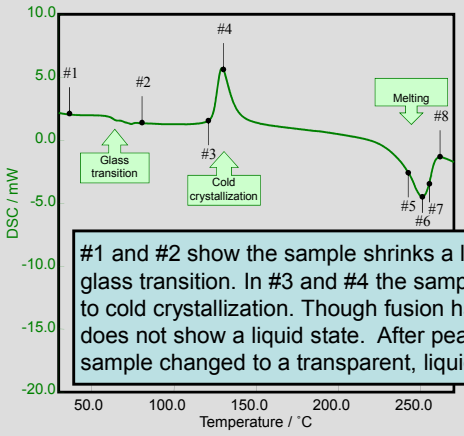
TG/DTA of PET



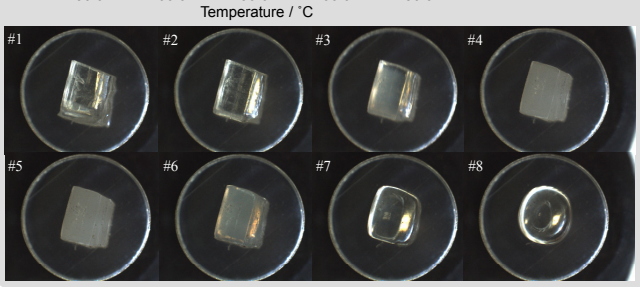
#6a shows that the expansion of the sample made the Al pan deform; causing an endothermic peak.

DTA curve shows a glass transition around 70˚C, and cold crystallization around 130˚C. TGA curve shows that above 350˚C mass decreased by decomposition.
Pictures(#2a & n) show the change in color by the decomposition occurs earlier in air.
#3a & n show that gas bubbles are generated by decomposition.
#4a shows that sample expands much like balloon.

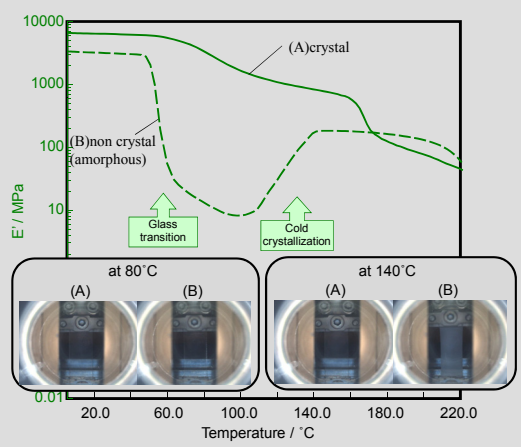
DSC of PET



#1 and #2 show the sample shrinks a little during glass transition. In #3 and #4 the sample is white due to cold crystallization. Though fusion has started, #5 does not show a liquid state. After peak apex, the sample changed to a transparent, liquid state (#7-8).

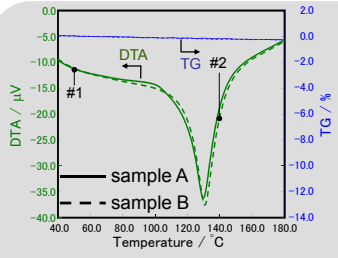


DMA of PET

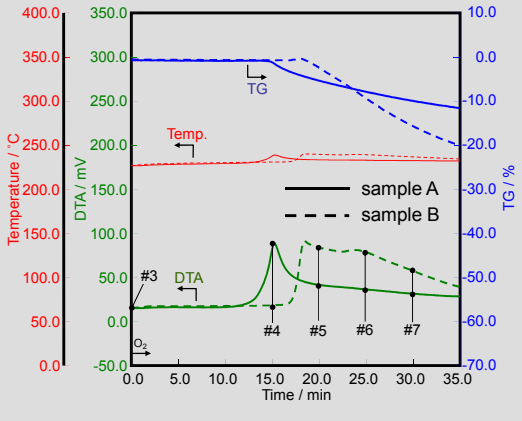


Comparing amorphous to crystalline PET shows that E' drops clearly during glass transition and rises during cold crystallization.
Both materials show the same transparency at 80 ˚C. However, at 140˚C, because amorphous PET crystallizes, it becomes translucent white.

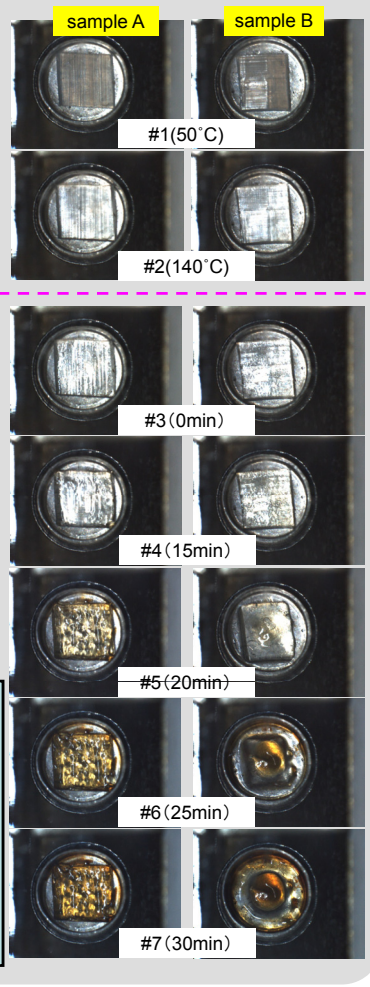
OIT measurement of PE



Both samples were white before melting (#1). At 140˚C (#2), they become transparent but keep their shape as if they are still solid.

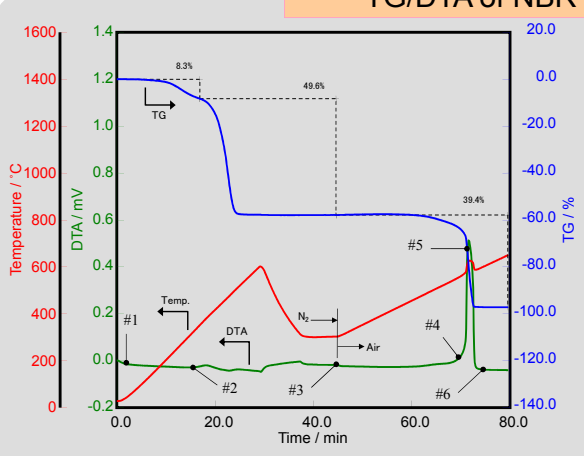


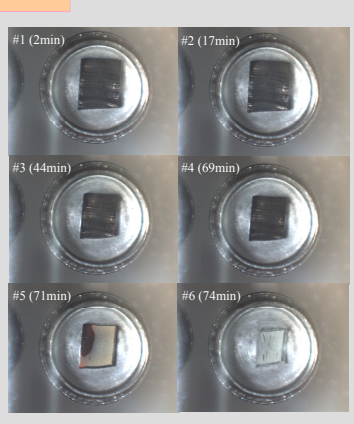
230˚C hold
Change to O_2



While sample A oxidation starts before sample B, the TGA curve indicates that sample A decreases less than sample B. This result means the decomposition reaction of sample B is more drastic. In pictures #4 to #7, we can see sample B collapses and flows widely, while sample A is stable.
So, from the TG/DTA curve and pictures, we can determine that sample B had a more drastic decomposition reaction than sample A.

TG/DTA of NBR





#2 and #3 show that the volume of rubber became smaller through decomposition.
In #5 oxidative degradation caused a decrease in carbon, and the color changes to white.
Finally, #6 shows that the overall change in sample size.

Conclusion

Using thermal instruments with optical observation, we can collect much more information about sample behavior during analysis.

This can help explain both the expected phenomena polymers undergo as well as anomalous or unexpected behaviors. This technology could be an important tool in education, failure analysis, and experiment design, to name a few.