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Detection of degradation of ABS materials via DSC

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Abstract

ABS is a well-known and widely used rigid engineering polymer. The mechanical properties of ABS are critical to its proper functioning in a given application, such as a medical device. It is therefore important to retain those properties during processing, fabrication, and use. To that end, thermal analysis and mechanical testing were employed to understand the origin of observed mechanical property losses. Oxidation onset temperature (OOT) testing and differential scanning calorimetry (DSC) analysis indicate a slightly lower onset temperature and a higher glass transition temperature, respectively, for parts which demonstrate a reduction in mechanical properties. It is also demonstrated that degradation of the butadiene-phase of the ABS is responsible for the mechanical property reduction, and that this degradation only proceeds at an appreciable rate at elevated temperatures in the presence of oxygen.

Keywords: ABS; Degradation; DSC

1. Introduction

ABS (acrylonitrile/polybutadiene/styrene) graft copolymers are widely used in many industrial applications. Typically, ABS consists of a styrene/acrylonitrile continuous phase partially grafted to a dispersed butadiene phase. The latter acts as an impact modifier, and imparts excellent mechanical properties to the material. Preservation of the impact-modifying properties of ABS during melt-processing (e.g. extrusion, injection molding) and product use (e.g. stability towards UV light) center on protecting the polybutadiene phase from degradation. This phase is particularly susceptible to oxidation due to the presence of residual double bonds [1].

Various research papers have appeared addressing detection of degradation, such as color changes [2], impact testing, dynamic mechanical analysis and infrared spectroscopy [3], and derivative thermogravimety and differential scanning calorimetry [4], to mention several. This study correlates DSC, mechanical testing, and oxidation onset temperature analyses, and will be directed to understanding ABS degradation in a production setting.

2. Experimental

2.1. Injection molding

Commercial ABS and colorant master batch were gravimetrically fed into a hot-runner-equipped 80-t injection mold with a screw diameter of 25 mm and a 7 mm nozzle. Nominal injection molding parameters are summarized in Table 1.

2.2. Oxidation onset temperature

The onset of oxidative thermal degradation of the various resins and parts investigated in this study was determined on a TA Instruments/DuPont 910 Differential Scanning Calorimeter controlled by an Instrument Specialists control module and software. Samples (~5 mg) were placed in an open aluminum pan and heated in the presence of air (100 mL/min) from room temperature to 280 °C at a ramp rate of 20 °C/min. The onset temperatures were determined manually.

2.3. Differential scanning calorimetry

Thermal properties were measured with a TA Instruments® Q1000 Modulated DSC with auto-sampler and refrigerated cooling system. In the case of base resin and colorant master batch samples, test samples were taken as a slice from the center of the pellet. In the case of injection-molded parts, samples were taken

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Table 1
Injection molding conditions

Parameter	Setting
Barrel temperatures (°C)	200, 220, 230, 240
Block temperature (°C)	260
Nozzle temperature (°C)	280
Mold temperature (°C)	40
Packing pressure (bar)	1000

Table 2
Summary of OOT results

Hold time (min)	OOT (°C)
0	224
5	212
10	212
15	210
25	204

from the same location to ensure consistency and comparability. Samples, crimped in aluminum pans, were heated and cooled at 20 °C/min from 250 to −90 to 250 °C under a 50 mL/min N_2 flow. Sample sizes were 5–10 mg.

2.4. Impact testing

Impact testing of injection molded parts was performed on an MTS 810 Material Test System, at a speed of 1000 in./min, using a steel blade (blunt tip, thickness 0.05 in.) attached to a load cell.

3. Results and discussion

Injection molding equipment shutdowns, while undesirable, occur from time to time in any production setting. When this happens, molten polymer is trapped in the barrel of the molding machine, and thermal and oxidative degradation may accelerate and lead to severely degraded polymer and poor part properties. While short stoppages may not be an issue for some polymers (such as polyethylene), they are a concern for polymers containing residual unsaturation, like ABS. This is even more important when a hot-runner injection molding machine is employed.

In an effort to understand how to retain the excellent impact properties of ABS in a hot-runner injection molding production setting in the event of an equipment stoppage of moderate duration (up to 25 min), a study was developed in which a hot-runner injection molding machine making ABS parts was halted for varying lengths of time. Specifically, the injection molding parameters (barrel, hot runner, and melt-drop temperatures, injection speed and pressure, hold time and pressure, and mold temperature) were set to nominal operating conditions. Parts were made continuously under these parameters for 15 min. The machine was then stopped for a predetermined period (2, 5, 10, 15, or 25 min, *with the mold open*), after which time part production was resumed. The first five shots molded after the stoppage were collected in individual sample bags, which were labeled with the hold time and the shot. After these five shots had been collected, the machine was allowed to run for 15 min to completely purge the barrel, hot runners, and melt drops of material, and return the machine to a “steady-state” condition before the next hold time was run.

Oxidative onset temperatures (OOT) of parts from the first shot after a stoppage were determined under an airflow rate of 100 mL/min. The results, summarized in Table 2, indicate that as the hold time increased, the onset temperature decreased from about 225 to about 205 °C. Clearly, degradation has occurred in these parts.

A typical DSC DSC curve of the ABS resin used in this study is shown in Fig. 1. The rubber-phase glass transition is apparent at −58.1 °C, and the styrene–acrylonitrile glass transition occurred at 112.2 °C. Since the rubber (butadiene) phase of the ABS is most susceptible to oxidative degradation, leading to crosslink formation and decreased chain mobility, an increase in the glass transition temperature (T_g) is expected for degraded samples.

To that end, DSC curves were obtained for the injection molded parts at the various hold times. Typical DSC curves for parts taken from the first shot after the 2, 5, 15, and 25 min hold times are shown in Fig. 2. An increase in T_g is clearly discernible in these DSC curves as the hold time increased. It is also apparent from the DSC curves that as the T_g increases, the transition also become broader and less distinct.

The rubber phase T_g results of parts from the first shot molded after the hold time are shown in Fig. 3, in which T_g is plotted against molding machine hold time. The circles denote results obtained from samples taken from the first shot, the squares from the second shot, and the triangles from the fifth shot. It is clear from this figure that the glass transition temperature of parts from the first shot increased dramatically as the hold time increased. Surprisingly, however, the glass transition temperature of parts from the second shot were typical of parts made during normal production, except in the case of the 25 min hold time. In this case, T_g was between −45 and −50 °C. Parts from the fifth shot had normal T_g’s for all hold times.

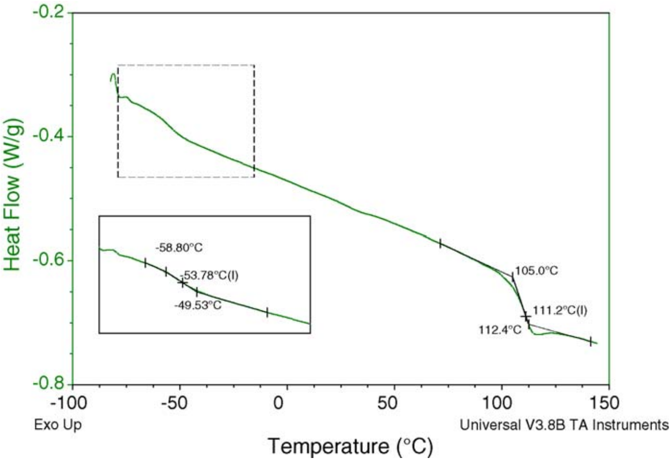

Fig. 1. Typical second-heat DSC curve of ABS.

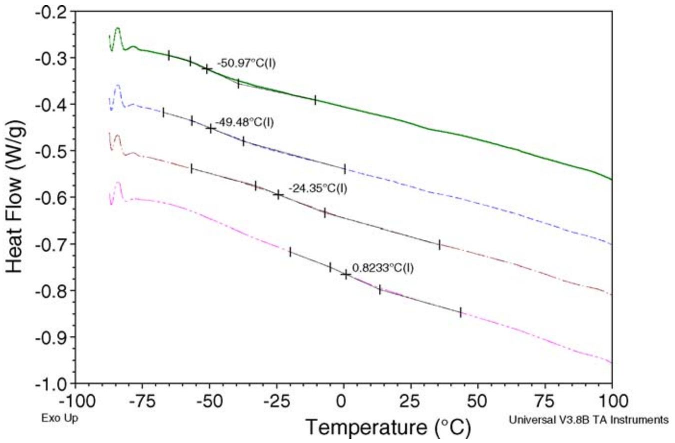

Fig. 2. Second-heat DSC curves of first-shot parts after hold times of 2, 5, 15, and 25 min.

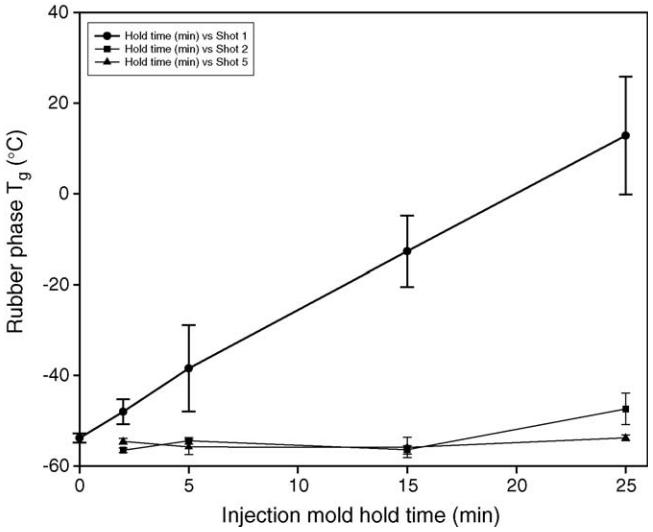

Fig. 3. Effect of injection molding hold time on rubber phase glass transition.

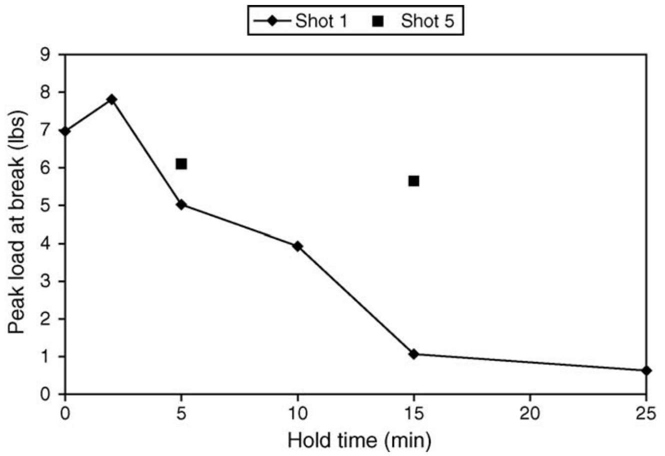

Fig. 4. Peak load at break as a function of hold time for first and fifth shot samples.

Impact testing was also performed on the injection molded parts. A portion of the part suitable for impact testing was struck at 0.42 m/s (1000 in./min), and the peak load was recorded. The results are summarized in Fig. 4. Peak load at break for samples from the first shot after the hold time (diamonds) show a marked decrease as a function of hold time. Parts from the fifth shot (squares) exhibited impact strengths only somewhat less than for samples produced under “steady-state” injection molding conditions.

Considering the data in Figs. 3 and 4 together, it is clear that degradation of the butadiene phase of ABS (as indicated by the shift to higher temperatures of the glass transition) led to losses in impact strength of injection molded parts. Extensive cross-linking of the butadiene during degradation renders the material almost useless, with peak loads at break as low at 1 lb.

The observation that only parts from the first shot after a mold stoppage are adversely affected in terms of rubber phase T_g and impact strength is important. The material for this first shot is in the melt-drop region of the injection molding press, which is the hottest zone in the process. However, volume calculations indicate that enough material for 3–5 shots reside in this melt-drop zone. If higher temperatures alone were sufficient to cause degradation, one might expect that parts from the first 3–5 shots would show significant degradation. The fact that only parts from the first shot undergo any significant degradation indicates the necessity of oxygen for the degradation process. Only the material at the melt-drop exit is exposed to oxygen, and thus only this material begins to degrade. Exposing ABS to the temperatures used in this study for up to 25 min, in the absence of oxygen, did not lead to measurable degradation. As the length of the hold time increases, the extent of degradation increases as oxygen is able to diffuse further into the melt-drop zone. Thus, material further back from the gate begins to degrade as well.

4. Conclusions

It has been shown that DSC is a sensitive and useful tool for monitoring the degradation of butadiene-containing polymers such as ABS. Correlation of the rubber phase T_g to mechanical properties was demonstrated. Furthermore, degradation of the ABS only proceeds at an appreciable rate at melt-processing temperatures in the presence of oxygen.

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