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Dedicated to Professor Bernhard Wunderlich on the occasion of his 65th birthday

EVALUATION OF FOUR ABS RESINS BY THERMAL ANALYSIS

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Abstract

Four new commercial grades of rubber toughened ABS (acrylonitrile-butadienestyrene) terpolymers were characterized by differential scanning calorimetry (DSC), mechanical analysis and gel permeation chromatography (GPC). These rubber toughened ABS molding compounds were manufactured by a new "blended technology" to yield resins which offer a broad range of flow properties and levels of toughness. Based upon DSC estimates of the level of rubber included, the four ABS compounds can be divided into two groups; the first has about 11 wt.% butadiene and the second near 18 wt.%. In addition, two styrene-acrylonitrile copolymers with different average molecular weights were found blended within each ABS group. By this blending process four resins are produced with impact strengths ranging from below three to near seven ft–lb in^{-1}. These analytical results show that a resin's impact strength is enhanced not only by increasing the level of rubber particles in a given ABS compound but also by raising the molecular weight of the SAN which is blended into the terpolymer.

Keywords: acrylonitrile-butadiene-styrene (ABS) terpolymers, glass transition temperature, impact strength, modulus, mold lubricant, styrene monomer, thermoanalytical measurements

Introduction

AT&T telephone sets have an enviable reputation of being so tough that they can be dropped or strongly impacted without breaking. This toughness of the telephone's plastic shell results from the rubber toughened ABS (acrylonitrile-butadiene-styrene) molding compound used to produce the telephone housing. ABS resins are composed essentially of a mixture of poly (styrene-co-acrylonitrile) (SAN) and SAN copolymer grafted onto polybutadiene (BD) [1–3]. Typically bulk ABS forms a heterogeneous system of submicron size rubber particles (T_g ~–85°C) covered by a layer of graft SAN, embedded in a continuous SAN matrix (T_g ~ 100°C) [4–6].

A commercial ABS resin should have not only excellent impact strength and hardness but also good flow characteristics to facilitate molding complicated

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shapes. The source of these desirable properties is a complex matter which relates to the method of synthesis, BD content, BD cross-link density and domain size, levels of SAN grafting, the S to AN ratio, physical blending conditions and the additives used in the compound [7].

In the early nineties a new group of ABS compounds called the Cycolac® G series were introduced. These resins were manufactured by a blend process. In this investigation we characterize the composition of four of these new ABS compounds for effective rubber content, SAN molecular weight, impact strength and moduli.

Experimental

Four (natural) grades of Cycolac® G series ABS materials were received from the General Electric Co. which we designated as compounds A, B, C and D, respectively. These materials, in the form of pellets, were dried for a minimum of 4 h at 160°F prior to molding. Flexural (1/8×1/2×5 inches) specimens were molded on an Arburg injection molding machine with a 2 ounce shot size. The mold temperature was maintained at approximately 140°F while the stock (or melt) temperature was maintained at 425°F. Test specimens molded under a given set of molding conditions were collected only after the molding machine reached equilibrium.

Specimens, after molding, were conditioned for a minimum of 40 h at 73.4°F and 50% relative humidity, per ASTM D-618, procedure A. Testing was conducted under the same conditions, except for low temperature Izod Impact Tests.

Izod impact resistance

To obtain 2.5 inch Izod impact bars, the ends of flexural bars were removed and the center was notched using a 10 mil notching cutter. Impact measurements were made at 23°C. Specimens were allowed to condition for a minimum of five minutes before testing. The ASTM test method D256-78 was used to evaluate the impact strength of the ABS Cycolac G series compounds.

Thermal and modulus properties

The glass transition temperature, T_g, is taken at the temperature of half-vitrification ($1/2\Delta C_p$) [8]. The glass transition temperatures and the magnitude of change in specific heat (ΔC_p) at each T_g were measured at a heating rate of 15°C min^{-1} on a Perkin-Elmer Differential Scanning Calorimeter (DSC-7).

The amorphous and crystalline phases in the immiscible ABS phases can be identified by the position of T_g and the melting temperature, T_m, respectively [5, 6, 9]. The fraction x_a of an amorphous component in the ABS resin or polyblend is the ratio of the observed change in C_p for a particular component in the polyblend ΔC_p^{blend} to the known increase in C_p of the pure parent of this component ΔC_p^{parent} :

$$x_a = \Delta C_p^{blend}/\Delta C_p^{parent} \tag{1}$$

Likewise, the fraction of a crystalline component x_c can be computed from the ratio of the observed heat of fusion for a particular component in the polyblend ΔQ_f^{blend} to the known apparent heat of fusion of the pure parent of this component $\Delta Q_f^{*parent}$:

$$x_c = \Delta Q_f^{blend}/\Delta Q_f^{*parent} \tag{2}$$

Equations (1) and (2) assume that the polyblend components are completely phase separated.

The flexural modulus at 1 Hz and 0.05 percent strain was determined from –160 to 110°C at a heating rate of 6°C min^{-1} in a three point bending fixture on a Perkin-Elmer Dynamic Mechanical Analyzer (DMA-7). Above 110°C the storage modulus was evaluated using a parallel plate fixture at 1 Hz. Samples cut from the flexural specimens for the three point bending apparatus measured about 1.0×3.0×18mm in height, width and length, respectively. The sample for the parallel plate measurement was cut in disc form with a 5 mm diameter and 2.0 mm height.

Results and discussion

The specific heat, C_p, behavior of compound A is shown in Fig. 1 and it is typical of each of these ABS molding compounds in that it shows two discontinuities in specific heat, ΔC_p, near –86 and 99°C. The T_g's are due to the BD and SAN phases of the rubber toughened composite [5, 6]. ΔC_p values of 0.061 and 0.338 J g^{-1} $°C^{-1}$ were determined for the rubber and matrix, respectively. A small reversible melting transition occurred between 115 and 130°C with a heat of transition, ΔQ_f^{blend} equal to 0.7 J g^{-1}. The melt is due to an amide type of mold lubricant (*ML*) found in each ABS resin. $\Delta Q_f^{*parent}$ equals 98 J g^{-1}. Hence, there is 0.7 wt.% *ML* in compound A. The remaining ABS resins contain this same level of amide lubricant.

Note that the slope of C_p *vs.* T from above 130°C and into the melt must be established and extrapolated to below T_g in order to make a more accurate estimate of ΔC_p due to small physical aging peak at 108 and the *ML* peak at 126°C (Fig. 2). In addition, the latter figure establishes the extrapolated onset, T_1, and end, T_2, of SAN's glass transition at 94 and 104°C, respectively. The breadth of T_g for the SAN found in the remaining ABS compounds is also ten degrees for each of these resins.

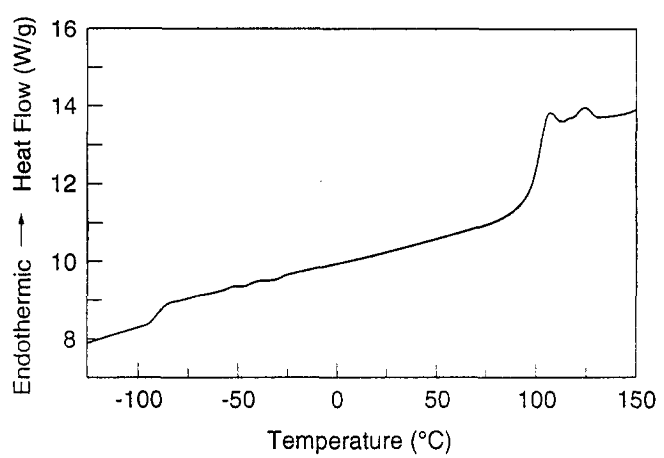

Fig. 1 DSC scan of Cycolac® G series ABS compound A from –125 to 160°C at 15°C $\min^{-1}$

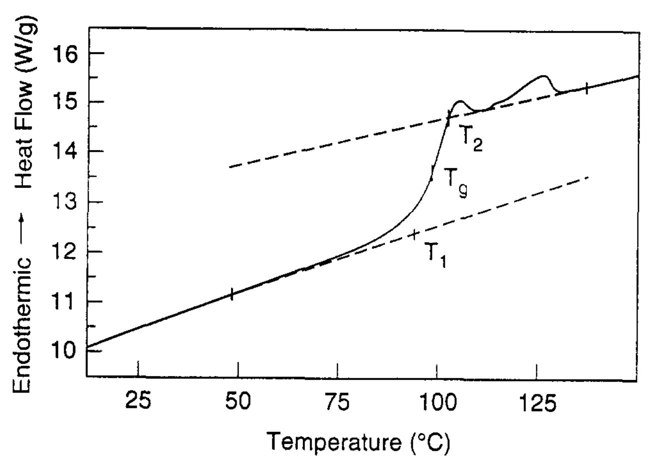

Fig. 2 Construction of C_p slopes before and after the glass transition temperature for the calculation of ΔC_p of the SAN in compound A

Previous DSC studies by Bair *et al.* have found that the magnitude of ΔC_p at T_g for the BD phase of an ABS resin decreased non-linearly as the ratio of SAN grafted to BD was increased [10]. The reduction of ΔC_p with increasing graft levels appears to be caused by the reduced number of configurational changes that can occur in the grafted BD molecules at T_g [11]. Hence, at high graft levels calorimetric determination of the rubber content using ΔC_p of an ABS resin does not give an absolute measure of the total BD content, but it does indicate the concentration of rubber that is effective in modifying the deformational behavior of the SAN matrix. Similar arguments can be made about determining the effective amount of SAN based on ΔC_p measurements. However, Table 1 shows the total fraction of glassy and crystalline components in the ABS compounds used in this study is close to 1.00 which indicates the amount of grafting is low enough that the calorimetric estimates of SAN and BD are absolute and accurate to within a few percent.

The four commercial Cycolac GPM compounds evaluated by DSC are listed in Table 1 along with data for the location and magnitude of the glass transition temperature for BD and SAN in each. Based on the amount of rubber found, the four ABS resins can be divided into two groups; the first has about 11 wt.% BD and the second near 18 wt.% (Fig. 3). In addition, Izod impact resistance at 23°C was measured for each grade and is listed also in Table 1.

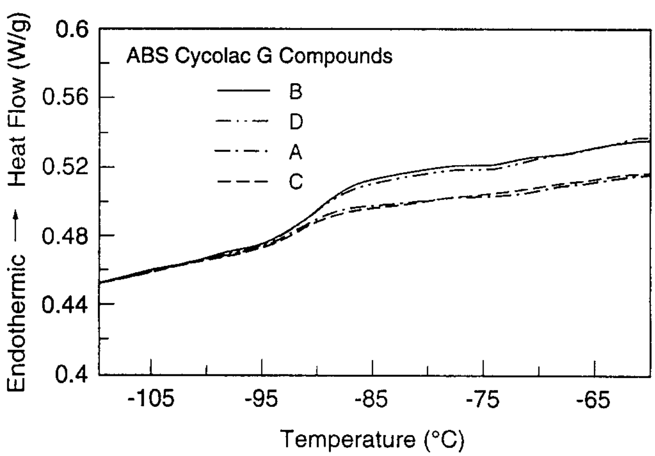

Fig. 3 Comparison of DSC scans of four grades of ABS from –110 to –60°C at 15°C min^{-1}

About two decades ago, the amount of monomeric styrene in commercial ABS was found to be about 1 wt.% [12]. Styrene has the highest boiling point (146°C) of the three monomers used in the production of ABS and is the most difficult to remove. Thermal chromatography, which is a technique employing gas chromatography and mass spectrometry, was used to volatilize, separate and identify chemical species when a sample of the ABS compound B was heated at 10°C min^{-1} from 23 to 240°C. Under these conditions, the ABS resin lost 1.1 wt.%. Two major volatile species were found: styrene and α-methylstyrene. The latter monomer may be an impurity in the reactants or it could be added to the reactants to increase T_g of the rigid phase [13]. The level of styrene is about 0.2 wt.% in compound B.

The five-fold reduction in the amount of styrene in the current Cycolac series as compared to older ABS resins results in the former resins' T_g being about 8°C higher than that of the resins manufactured 20 years ago [14].

A tensile bar of compound B was cooled to –196°C and broken. Examination of this fracture surface by scanning electron microscopy revealed numerous

Table 1 Thermal properties and impact strength values for Cycolac® G compounds

ABS Cycolac sample	BD[a] T_g /°C	ΔC_p/ J °C^{-1} g^{-1}	BD[b]/ wt.%	Impact strength/ ft.–lb.in.$^{-1}$	SAN T_g^*/°C	ΔC_p/ J °C^{-1} g^{-1}	SAN[c]/ wt.%	ML[d]/ wt.%	Total phases/ wt.%
A	–86	0.061	12	2.8	99	0.34	88	0.7	100.7
B	–83	0.094	19	5.6	100	0.31	80	0.7	99.7
C	–86	0.057	11	3.8	102	0.32	83	0.7	94.7
D	–86	0.090	18	6.8	101	0.29	76	0.8	94.8

[a] *The glass transition temperature was determined at 1/2 ΔC_p at a heating rate of 15°C min^{-1}.*

[b] Based on $\Delta C_p^{\mathrm{parent}}$ equal to 0.50 J °C^{-1} g^{-1} for polybutadiene.

[c] Based on $\Delta C_p^{\mathrm{parent}}$ equal to 0.39 J °C^{-1} g^{-1} for SAN copolymer.

[d] Based on $\Delta Q_f^{*\mathrm{parent}}$ equal to 98 J g^{-1} for polyamide mold lubricant.

spherical cavities measuring about 0.2 μm in diameter. The rubbery, discontinuous phase of this ABS resin is believed to be composed of these kinds of submicron domains.

For molecular weight determination the four ABS grades were dissolved in tetrahydrofuran, filtered to remove the rubber particles, and run on a Waters Chromatograph at 40°C. The average molecular weight calculations (relative to polystyrene standards) are summarized in Table 2. Note that compounds A and C which have a relatively low concentration of rubber (~11 wt.%) have SAN copolymer blended in them with average molecular weights of 81 000 and 89 000, respectively. This 10% increase in M_w of the SAN blended in C over the molecular weight of the free SAN found in A is accompanied by about a 30% increase in impact strength from 2.8 for A to 3.8 ft–lb in^{-1} for C. Conversely, the melt flow index was lowered from 3.4 to 1.7 g 10^{-1} min^{-1} as the molecular weight of the SAN blended in C was increased over that found in A.

Table 2 Average molecular weight

ABS Cycolac sample	M_n×10^{-3}	M_w×10^{-3}	M_z×10^{-3}	Dispersity	Flow rate* g 10^{-1} min^{-1}
A	28.3	81.4	157	2.88	3.4
B	28.6	78.5	149	2.74	2.0
C	33.1	89.8	169	2.72	1.7
D	29.7	84.7	159	2.85	–

*GE data

Compounds B and D which have the high concentration of effective rubber (about 18 wt.%) also show the same trend: the extracted SAN polymers have M_W values of 78 500 and 84 700, and impact strengths of 5.6 and 6.8 ft–lb in^{-1}, respectively.

It is therefore apparent that the manufacturer has blended two different molecular weight SAN copolymers into two master batches of ABS, each having a different concentration of rubber to produce four grades of ABS with different impact strengths and flow properties.

Further insight into the mechanical performance of these ABS resins was obtained by measuring the dynamic mechanical behavior as a function of temperature at 1 Hz. A plot of storage moduli and tan delta values for a sample of B is shown in Fig. 4. Two maxima in tan delta are noted near –84 and 108°C, the T_g 's of the BD elastomer and the SAN copolymer, respectively.

In the temperature range in which the low temperature loss tangent maximum occurs, the storage modulus decreased by about 30%. As the temperature rises modulus values drop slightly until the second loss maximum, i.e., the T_g of the SAN matrix, is attained. Then, a nearly three decade drop in modulus occurs from 2×10^9 to about 3×10^6 Pa.

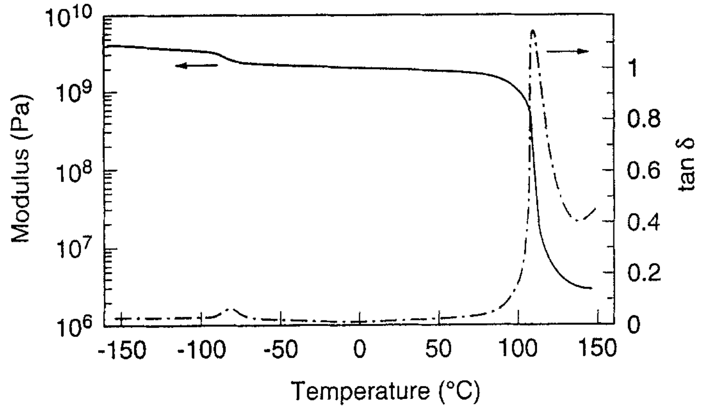

Fig. 4 Moduli and tan delta values *vs.* temperature for compound B at 1 Hz from –170 to 150°C

In Fig. 5 the respective moduli of A, B. C and D are plotted against temperature from –160 to 100°C. The curves are similar and absolute values at any temperature are found to fall within about a 10 percent range. Between –75 and 75°C A was found to have the highest modulus followed by C, D and B. These modulus values do not scale directly with effective amount of BD or SAN. Nevertheless, if we divide the four materials into two groups, first A and C and second B and D, the first has more SAN and higher moduli whereas the second has more BD and lower moduli values. The variations within a group may depend upon molecular weight differences and the nature of the graft or the difficulty in resolving modulus values at this level. Insight into additional details of these ABS structures requires further work. Our next goal is to study the morphology of these materials.

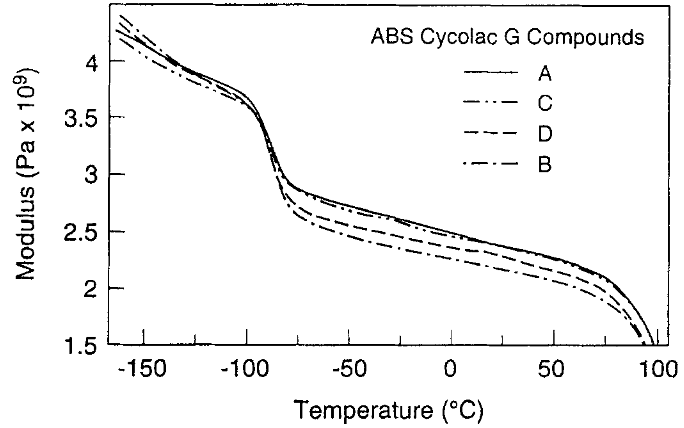

Fig. 5 Comparative modulus *vs.* temperature plots for A, B, C and D from –160 to 100°C

Conclusion

Calorimetric, GPC, mass spectrometry and mechanical analysis of four grades of Cycolac® ABS molding compounds reveals:

- the effective amount of rubber (BD) in these molding compounds varies from about 11 wt.% in compounds A and C to near 18 wt.% in compounds B and D;
- the two sets of samples with high and low concentrations of rubber are blended apparently with two different molecular weight SAN copolymers to yield four ABS compounds with significant differences in impact strength and flow behavior;
- a five-fold reduction in the amount of monomeric styrene to a level of 0.2 wt.% in these current Cycolac® G resins as compared to older ABS compounds results in the current terpolymers' T_gs being about 8°C higher than that of commercial ABSs manufactured 20 years ago;
- the modulus of each ABS resin at a given temperature increases in the order: B, D, C and A. Therefore modulus is not strictly correlated with SAN content but also depends upon other factors.

* * *

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