# Study of the Effect of Poly(acrylonitrile-*co*-butadiene-*co*-styrene) on the Mechanical Properties of an Epoxy System

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**ABSTRACT:** The mechanical properties of an epoxy system containing a diglycidyl ether of bisphenol A and 1,3-bis(aminomethylcyclohexane) modified with different amounts of poly(acrylonitrile-*co*-butadiene-*co*-styrene) (ABS) were studied. Properties examined include tensile stress, percentage strain, tensile modulus, and tensile toughness determined in tensile tests, Rockwell hardness, and energy and maximum force to break a specimen in Charpy impact tests. The effect of the modification produced with the ABS was also studied using statistical methods including analysis of variance and multiple comparisons. The obtained data showed a significant effect of the modification produced with the ABS on the mechanical properties of this epoxy system, especially with the amount of 5 ABS per hundred parts of resin on the tensile properties and on the hardness. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 461–467, 2004

**Key words:** ABS; epoxy resins; hardness; impact tests; tensile properties

## INTRODUCTION

Crosslinked epoxy resins are important thermosets frequently used for structural applications. One more drawback of epoxy resins is their poor resistance to impact and, consequently, the aim of many investigations is the improvement of the fracture toughness of these materials, while maintaining other desirable properties, such as modulus, tensile stress, hardness, and glass-transition temperature, for example.[1]

The addition of a second-phase polymeric material, such as liquid rubbers or thermoplastics, is one frequently used approach to toughen crosslinked epoxy resins.[2–5] In this work the aim was to modify and mechanically characterize an epoxy system obtained by reaction of a diglycidyl ether of bisphenol A and a cycloaliphatic diamine hardener by using different amounts of poly(acrylonitrile-*co*-butadiene-*co*-styrene) (ABS) thermoplastic terpolymer. Previous studies have established the brittle character of the unmodified system,[6] the kinetics,[7] and the morphology of the epoxy–ABS blends.[8]

Three types of mechanical tests were used in this work to characterize the modified epoxy systems: tensile tests, hardness tests, and instrumented impact tests.

Using statistical methods including analysis of variance (ANOVA) and multiple comparisons, the effect of the modification produced with ABS on the epoxy system was studied for the three types of mechanical tests used.

Tensile properties such as tensile stress ($\sigma$) and percentage strain ($\epsilon$), both at break point and at yield point; tensile modulus ($E$); and tensile toughness, calculated as the area under the stress–strain curve and representing the tensile energy absorption were determined from stress–strain tests.

Hardness measurements have a practical importance, although these measurements do not represent a fundamental property of these materials. There are several methods to measure the hardness. Rockwell hardness measurements were made in this work.

With an instrumented impact pendulum, Charpy impact tests were carried out and from typical load–time or load–displacement curves were determined the work or energy ($W$) and the maximum force ($F_m$) to break a specimen by using dedicated impact data analysis software.[9]

## EXPERIMENTAL

### Materials and preparation of samples

The epoxy resin used in this study was a commercial diglycidyl ether of bisphenol A (DGEBA), Araldite GY 260 (Ciba-Geigy, Summit, NJ), with weight per epoxy equivalent of 205.1 g/eq as determined in our labora-

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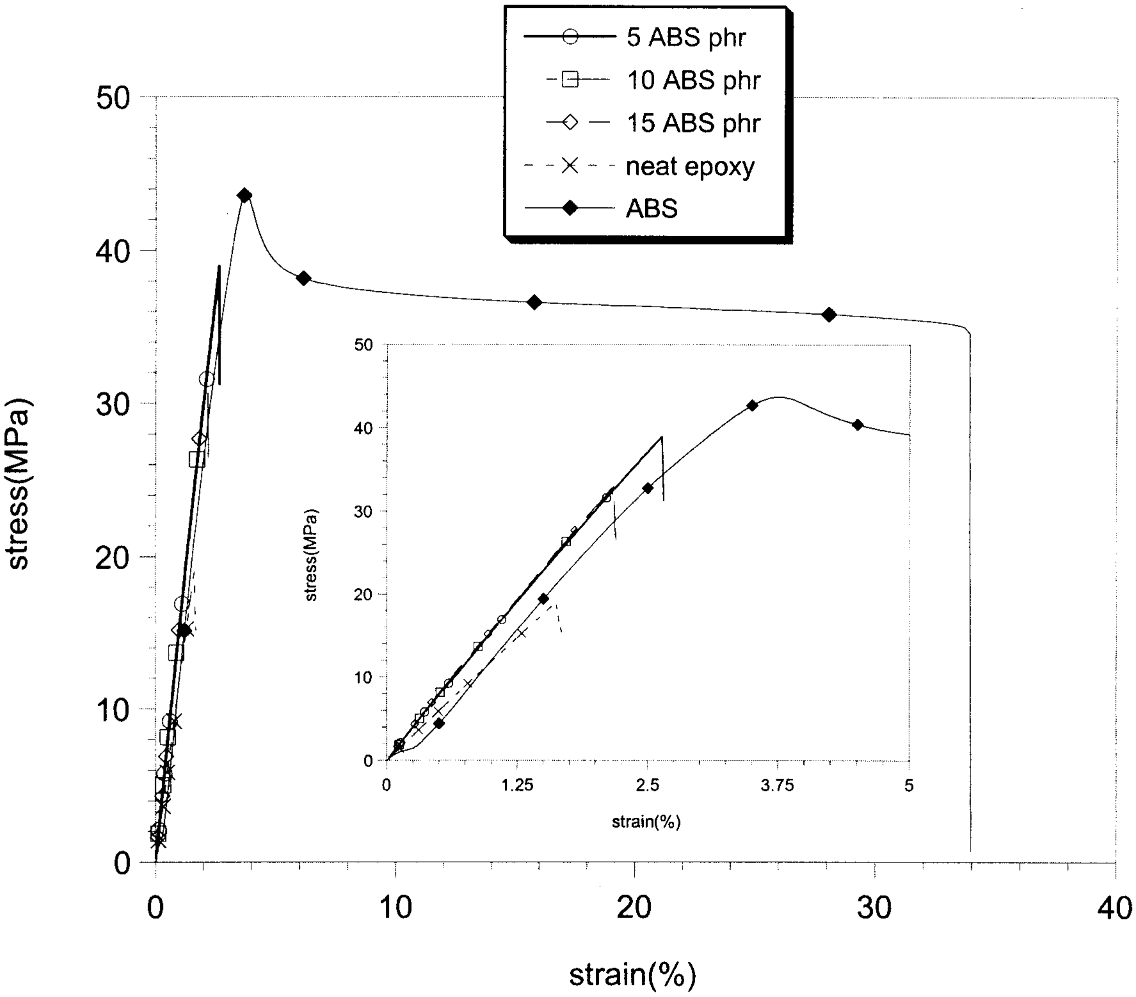


**Figure 1** Stress–strain curves. The zoom shows the initial part of the curves.

tory by hydrochlorination.[10] The neat epoxy resin and its blends with ABS, QI-300 with weight-average molecular weight $M_w$ = 163,500 and $M_w/M_n$ = 2.59 (manufactured by Polidux/Repsol) were cured with a cycloaliphatic diamine hardener, 1,3-bis(aminomethyl) cyclohexane (1,3-BAC; Aldrich Chemicals, Milwaukee, WI) with a molecular weight of 142.25 g $mol^{-1}$ and purity of >99% according to the supplier. All components were commercial products and were used without further purification.

For neat epoxy and all mixtures the epoxy/amine ratio was held constant and equal to 100/17 w/w. To prepare epoxy resin/ABS mixtures with 5, 10, and 15 ABS per hundred parts of resin (phr), the corresponding amount of dried ABS was dissolved in dichloromethane and mixed with the epoxy resin at room temperature. The resulting solution was then heated at 80–90°C and stirred in an oil bath to remove most of the solvent. When the solvent was less than 0.1% w/w the binary mixture was cooled at room temperature

**TABLE I**
**Data on Tensile Parameters**

| ABS (phr) | $\sigma_B$ (MPa) | $\varepsilon_B$(%) | $F$ (MPa) | Toughness (MPa) |
|---|---|---|---|---|
| 0 | 44.7 ± 8.7 | 2.8 ± 0.6 | 1695.4 ± 33.0 | 0.66 ± 0.24 |
| 5 | 56.8 ± 7.9 | 3.9 ± 0.6 | 1616.1 ± 38.4 | 1.20 ± 0.36 |
| 10 | 52.2 ± 5.8 | 3.5 ± 0.5 | 1649.5 ± 29.4 | 0.96 ± 0.23 |
| 15 | 38.2 ± 2.7 | 2.5 ± 0.1 | 1662.2 ± 35.5 | 0.49 ± 0.05 |
| Neat ABS | 34.3 ± 0.4 | 36.9 ± 3.2 | 1524.8 ± 20.2 | 12.46 ± 1.11 |

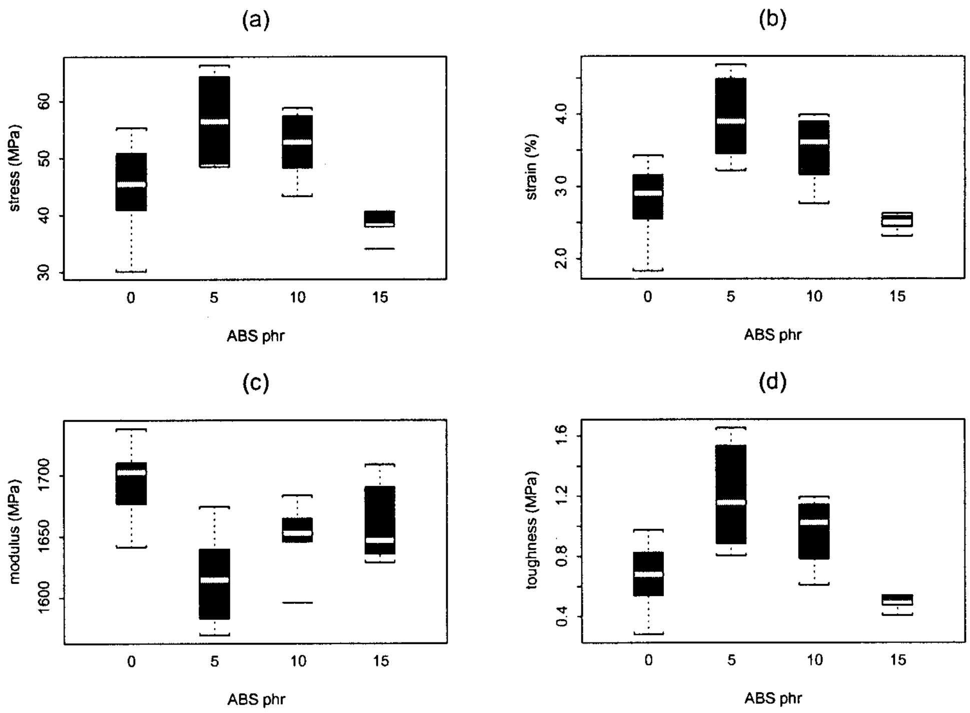


**Figure 2** Box plots for (a) stress, (b) strain, (c) modulus, and (d) toughness.

**TABLE II**
**ANOVA Tables for (a) Stress, (b) Strain, (c) Modulus, and (d) Logarithm of Toughness[a]**

| (a) | | | | | (b) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | *df* | ms | *F* | *p*-value | | *df* | ms | *F* | *p*-value |
| ABS phr | 3 | 370.011 | 7.844 | $1.3 \times 10^{-3}$ | ABS phr | 3 | 2.445 | 9.970 | $4 \times 10^{-4}$ |
| Error | 19 | 46.870 | | | Error | 19 | 0.245 | | |
| **(c)** | | | | | **(d)** | | | | |
| | *df* | ms | *F* | *p*-value | | *df* | ms | *F* | *p*-value |
| ABS phr | 3 | 6431.28 | 5.511 | $6.8\times10^{-3}$ | ABS phr | 3 | 0.851 | 8.765 | $7 \times 10^{-4}$ |
| Error | 19 | 1166.97 | | | Error | 19 | 0.097 | | |

[a] *df,* degrees of freedom; ms, mean square.

**TABLE III**
**95% Confidence Intervals for Difference of Means Between Pairs of Treatments for the Tensile Parameters[a]**

| | 95% confidence interval | | | |
|---|---|---|---|---|
| Comparison | Stress | Strain | Modulus | Log toughness |
| 0–5 | [−23.22, −0.99]* | [−1.95, −0.34]* | [23.82, 134.75]* | [−1.13, −0.12]* |
| 0–10 | [−18.63, 3.60] | [−1.51, 0.10] | [−9.61, 101.31] | [−0.92, 0.09] |
| 0–15 | [−5.19, 18.12] | [−0.54, 1.15] | [−24.95, 91.39] | [−0.29, 0.77] |
| 5–10 | [−6.53, 15.71] | [−0.37, 1.24] | [−88.90, 22.03] | [−0.30, 0.71] |
| 5–15 | [6.91, 30.23]* | [0.61, 2.29]* | [−104.23, 12.11] | [0.33, 1.39]* |
| 10–15 | [2.32, 25.64]* | [0.17, 1.86]* | [−70.80, 45.54] | [0.13, 1.19]* |

[a] Asterisks mark the intervals that exclude zero.

TABLE IV
Rockwell Hardness M Data

| ABS phr | Sheet 1 | Sheet 2 |
|---|---|---|
| 0 | 88.3 ± 0.28 | 88.8 ± 1.89 |
| 5 | 86.9 ± 0.85 | 87.7 ± 0.36 |
| 10 | 75.7 ± 0.43 | 76.9 ± 0.74 |
| 15 | 66.2 ± 1.55 | 68.1 ± 2.33 |

TABLE V
ANOVA Table for Rockwell Hardness M

| | *df* | ms | *F* | *p*-value |
|---|---|---|---|---|
| ABS phr | 3 | 536.956 | 631.899 | $1.1 \times 10^{-16}$ |
| Error | 16 | 0.850 | | |

and the 1,3-BAC hardener was added and continuously stirred for a few minutes. The mixture was poured into a vertical U-shaped glass mold and cured in an air-circulating oven. The time and temperatures scheduled in the cure were: 2 h at room temperature, 5 h at 40°C, and 8 h at 60°C. Plates of 4 mm thickness were obtained at the end of the curing process.

## Techniques

### Tensile tests

Tensile tests were conducted at room temperature with an Instron 5566 universal testing machine (Instron, Canton, MA) according to ASTM D638M for the tests of the neat epoxy and its blends with ABS, and according to ISO 527 for the tests of ABS. The specimens of ABS were obtained by injection molding according to ISO 3167:1993(E). The crosshead speed used was 1 mm/min. Average values were obtained from at least five successful determinations.

### Hardness tests

Rockwell hardness measurements were made at room temperature using an Instron–Wolpert hardness testing machine DIA-TESTOR 722 following ASTM D785. Rockwell numbers are directly related to the indentation hardness of a material, where the higher the reading, the harder the material. ASTM D785 procedure M, with fully specified time scales, was selected because control of the time scale (e.g., rate of loading and time after loading at which the reading is taken) is essential because of the viscoelastic response of these materials.

### Instrumented impact test

Unnotched specimens were fractured in an instrumented impact pendulum Instron–Wolpert PW5 of nominal energy of 7.5 J and velocity of impact of 3.85 m/s. The instrumented tup used had a maximum nominal force of 2 kN.

All samples used in the Charpy impact tests had dimensions of $80 \times 10 \times 4$ mm$^3$ as in ISO 179. The specimens of neat epoxy and epoxy/ABS blends were machine-milled from rectangular plates and the ABS specimens were obtained directly by injection molding. The tests were conducted at room temperature. Six specimens of every composition were tested.

### Statistical methods

The effect of the amount of ABS on the mechanical properties was studied using a completely randomized experimental design.

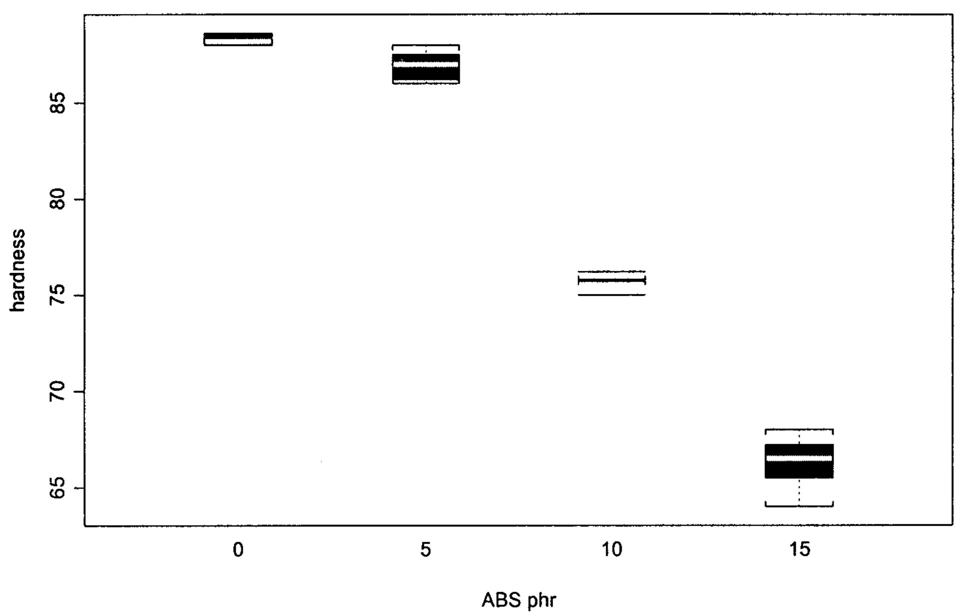


**Figure 3** Box plot for the Rockwell hardness.

**TABLE VI**
**95% Confidence Intervals for the Difference of Means Between Pairs of Treatments for the Hardness[a]**

| Comparison | 95% confidence interval |
|---|---|
| 0–5 | [−0.35, 2.99] |
| 0–10 | [10.89, 14.23]* |
| 0–15 | [20.35, 23.69]* |
| 5–10 | [9.57, 12.91]* |
| 5–15 | [19.03, 22.37]* |
| 10–15 | [7.79, 11.13]* |

[a] Asterisks mark the intervals that exclude zero.

The results were analyzed by a one-way analysis of variance (ANOVA). The amount of ABS was considered as a fixed-effects factor. Before the ANOVA the hypothesis of homoscedasticity was tested using the Fligner–Killeen test.[11] When the test was statistically significant it was considered a data transformation. The homoscedasticity and the normality of the data were graphically checked by residual analysis.

In cases in which the *F*-test of the ANOVA was significant, multiple comparisons were carried out between all the pairs of treatments, constructing simultaneous confidence intervals by the Tukey method.[12]

Throughout this work it was considered that the result of a hypothesis test was significant if its *p*-value was less than 0.05.

## RESULTS AND DISCUSSION

### Tensile tests

Figure 1 shows the stress–strain curves for one specimen of each tested material. For neat epoxy and all mixtures, brittle behavior was observed. For ABS the ductile behavior was observed with a clear yield point.

Table I presents the average values with the corresponding standard deviations of the tensile parameters measured for the different materials. The highest values of the mixtures were obtained with an amount of 5 ABS phr.

The data of the blends for the tensile parameters are graphically shown in Figure 2 using box plots. There is no evidence of heteroscedasticity for tensile stress, percentage strain, and tensile modulus values (*p*-values of Fligner–Killeen test are, respectively, 0.088, 0.054, and 0.789). The hypothesis of homogeneity of the variances for the toughness values cannot be accepted, although the test is only marginally significant (*p*-value = 0.023). A logarithmic transformation was effective in stabilizing the variance (*p*-value = 0.177).

Table II displays the ANOVA for each parameter. The data show a slight imbalance because of a missing value up to the standard of 15 ABS phr. From the analysis of this table it was deduced that the effect of the amount of ABS on the parameters was very significant.

**TABLE VII**
**Instrumented Impact Data**

| ABS phr | $W$ (J) | $F_m$ (kN) |
|---|---|---|
| 0 | 0.32 ± 0.12 | 0.28 ± 0.08 |
| 5 | 0.55 ± 0.22 | 0.30 ± 0.14 |
| 10 | 0.25 ± 0.09 | 0.20 ± 0.05 |
| Neat ABS | 1.95 ± 0.35 | 0.30 ± 0.01 |

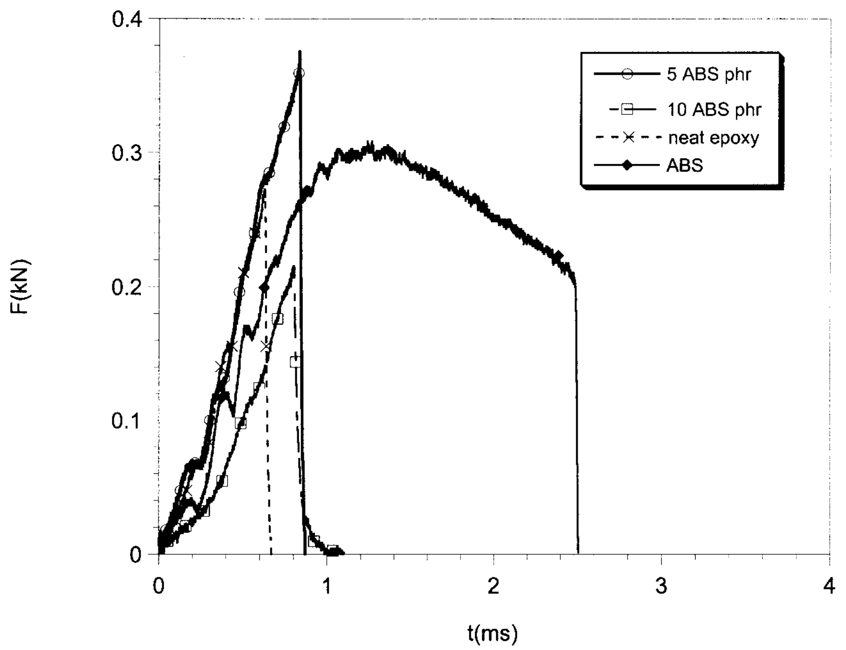


**Figure 4** Instrumented impact curves (force versus time).

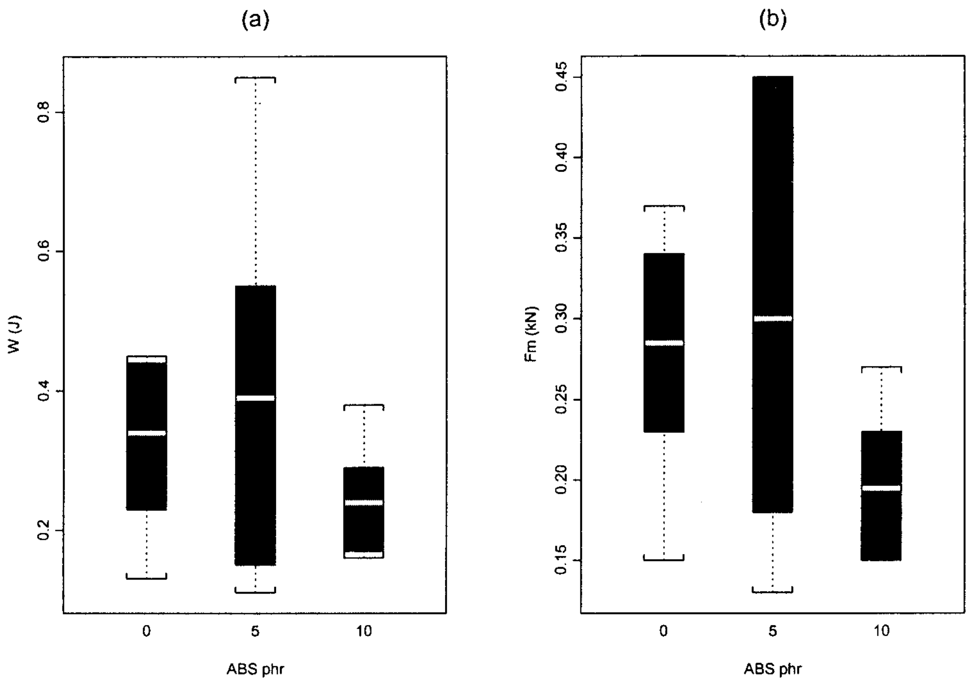


**Figure 5** Box plots for (a) energy and (b) maximum force.

Table III shows the 95% confidence intervals for the difference of means of all pairs of treatments. These intervals are indicative of differences between the means for the neat epoxy and the 5 ABS phr specimens for the four parameters. Except in the case of tensile modulus, there also were significant differences among the mean of 15 ABS phr specimens and the means of 5 and 10 ABS phr specimens. This fact suggests an improvement of the tensile properties when the amount of ABS is 5 ABS phr. A decrease in this improvement was observed if the amount of ABS was >5 ABS phr.

## Hardness tests

Table IV shows the Rockwell hardness M values for the different materials. The values were determined from two different sheets of the same material. There is good agreement between the two measurements. Also, there is a very small standard deviation for all blends studied.

The hardness values obtained of the neat epoxy, 5 ABS phr specimens, and even for 10 ABS phr specimens were very similar to the values of epoxy resins based in bisphenol A.[13]

The statistical analysis of hardness was carried out with the data of sheet 1. The box plot of Figure 3 displays the hardness data. There is no sufficient evidence against the homoscedasticity for this parameter ($p$-value = 0.082).

Table V shows the ANOVA for the hardness. It is evident that the amount of ABS on the hardness exerts a very significant effect.

The 95% confidence intervals (Table VI) suggest that the mean hardness for the neat epoxy and the 5 ABS phr specimens could be the same; however, a significant decrease of the hardness is produced when the amount of ABS is >5 ABS phr.

## Instrumented impact tests

Figure 4 displays the curve force versus time obtained during instrumented impact tests of one specimen of the studied materials.

The amplitudes of superimposed oscillations in the curve $F(t)$ were diminished by damping the tup with

**TABLE VIII**
**ANOVA Tables for (a) Energy and (b) Maximum Force**

| (a) | | | | | (b) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | *df* | ms | *F* | *p*-value | | *df* | ms | *F* | *p*-value |
| ABS phr | 2 | 0.146 | 0.434 | 0.656 | ABS phr | 2 | 0.219 | 1.527 | 0.249 |
| Error | 15 | 0.337 | | | Error | 15 | 0.144 | | |

a strip of rubber and the noise in the signal was filtered using an electronic filter of 10 kHz.

The shape of the curve $F(t)$ of unnotched specimens is very different from that for neat epoxy, in which the load increases linearly until a maximum where unstable crack propagation starts and for ABS in which unstable crack propagation starts after $F$ has passed the maximum. The curve of neat epoxy is typical of a brittle material and the curve of ABS, of a ductile material.

The total impact time (from $F = 0$ at $t = 0$ to $F = 0$ after impact) is of the order of milliseconds and is greater for the ABS than for neat epoxy.

Table VII shows the mean values of the energy absorbed ($W$) and the maximum force ($F_m$) for all materials.

The data of the blends are graphically presented in Figure 5 using box plots. There is clear evidence against the hypothesis of the homogeneity of the variances for the $W$ value ($p$-value = 0.005) and for the $F_m$ value ($p$-value = 0.0168).

The logarithmic transformation was not completely effective in stabilizing the variance for $W$ ($p$-value = 0.042); however, the well-known robustness against the heteroscedasticity (and nonnormality) of the $F$-test for balanced designs[14] warranted the validity of the subsequent ANOVA. On the other hand, the logarithmic transformation was effective in stabilizing the variance for $F_m$ ($p$-value = 0.1316).

From the impact tests the presence of ABS seemed to improve the values of $W$ and $F_m$ for 5 ABS phr blends; however, this conclusion must be taken with caution because the data dispersion of unnotched specimens was relatively great, as indicated by standard deviation, and also because from the ANOVA it was deduced that these two parameters are not significantly modified with different amounts of ABS (Table VIII).

## CONCLUSIONS

A study of the effect of ABS on the mechanical properties of the DGEBA/1,3-BAC epoxy system was carried out. The data obtained from the tensile tests, hardness tests, and instrumented impact tests combined with the statistical analysis of these data show a significant effect of the modification produced with ABS on the mechanical properties of this epoxy system.

From the tensile tests an improvement of the tensile properties was produced when the amount of ABS was 5 ABS phr. The same conclusion can be obtained from the hardness tests; the best value was produced when the amount of ABS was 5 ABS phr. From the instrumented impact tests it was concluded that the energy and the maximum force to break a specimen seemed to improve when the amount of ABS was 5 ABS phr, although the subsequent ANOVA showed no significant modification for these parameters with different amounts of ABS.

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