

## The determination of the composition of polymeric composites using TG–FTIR

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### Abstract

In this experiment, the determination of the percentages of butadiene and styrene in unknown samples of copolymers was attempted. In order to determine the percentage composition of the unknown samples, samples with known percentage composition had to be analyzed first. The five samples which were used as our standards were styrene latex, butadiene latex, styrene/butadiene in 70/30 ratio, styrene/butadiene 60/40 ratio, and styrene/butadiene in 50/50 ratio. The standards, along with the unknowns (Sample No. 4-7), were decomposed in a nitrogen atmosphere using the TG–FTIR system.

### INTRODUCTION

The percentages of styrene/butadiene cannot be determined directly from the TGA dynamic run because the decomposition of the two samples occurs simultaneously. Nor can the percentages be determined using the glass transition temperature because the glass transitions are linear for samples with greater than 40% styrene but non-linear for samples with less than 40% styrene. Measurement of the glass transition temperatures is also unsatisfactory because of the inaccuracy of this method; ASTM allows a temperature variation of 10°C. The percentages could not be determined directly from FTIR or NMR readings [1–4], because the copolymer would not dissolve in tetrahydrofuran (THF), dioxane, toluene or a 50/50 mixture of THF and dioxane, which are known to dissolve styrene latex and butadiene latex.

### EXPERIMENTAL

The samples were decomposed using a Du Pont 951 thermal gravimetric analyzer to determine weight loss. Nitrogen gas was used in this experi-

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ment. The flow rate was kept at  $50 \text{ ml min}^{-1}$  to prevent any gas build-up in the TGA cell. A sample weight of 5 mg was selected. Each sample was analyzed at least three times so that more accurate results could be obtained.

The composition of the stable gas decomposition products flowing out of the TGA were analyzed using a Perkin-Elmer 1650 fourier transform infrared spectrophotometer (FTIR). The TGA was coupled with the FTIR using an insulated teflon tube heated to a temperature of  $120^\circ\text{C}$  by a Powerstat variable autotransformer. The gas cell with the FTIR was heated using a Barnant thermocouple controller. The tubing and the gas cell are heated to prevent condensation within the tubing and the gas cell.

## RESULTS AND DISCUSSION

### TG curves

When styrene latex is pyrolyzed in a nitrogen atmosphere, only one DTG peak is observed at approximately  $434^\circ\text{C}$  (Fig. 1). Butadiene latex decomposed at a slightly higher temperature. The DTG peak for butadiene is observed at approximately  $482^\circ\text{C}$  (Fig. 2). When a styrene/butadiene

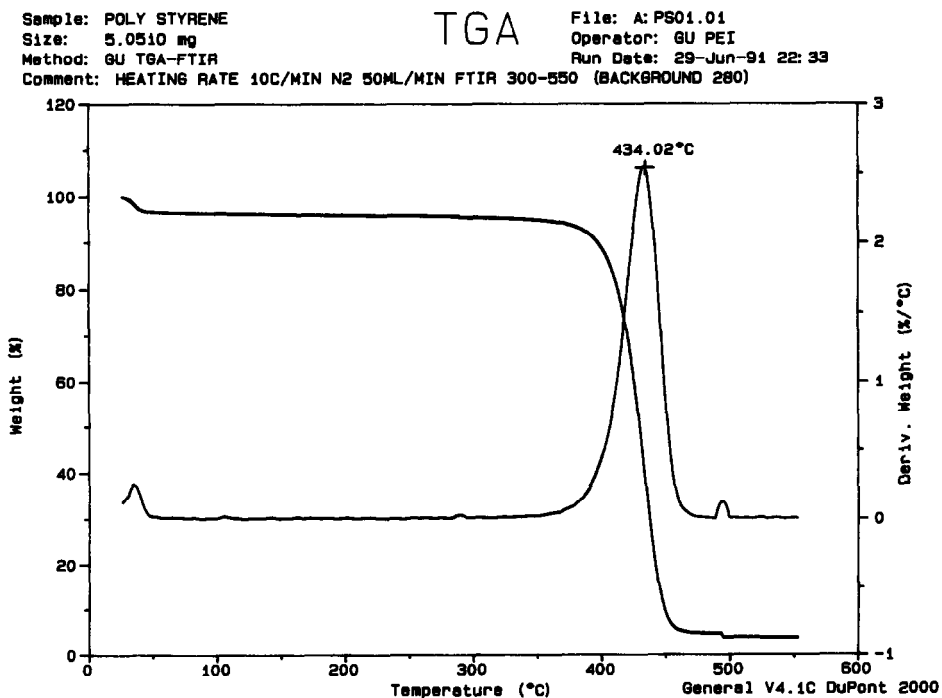


Fig. 1. TG/DTG plot of polystyrene.

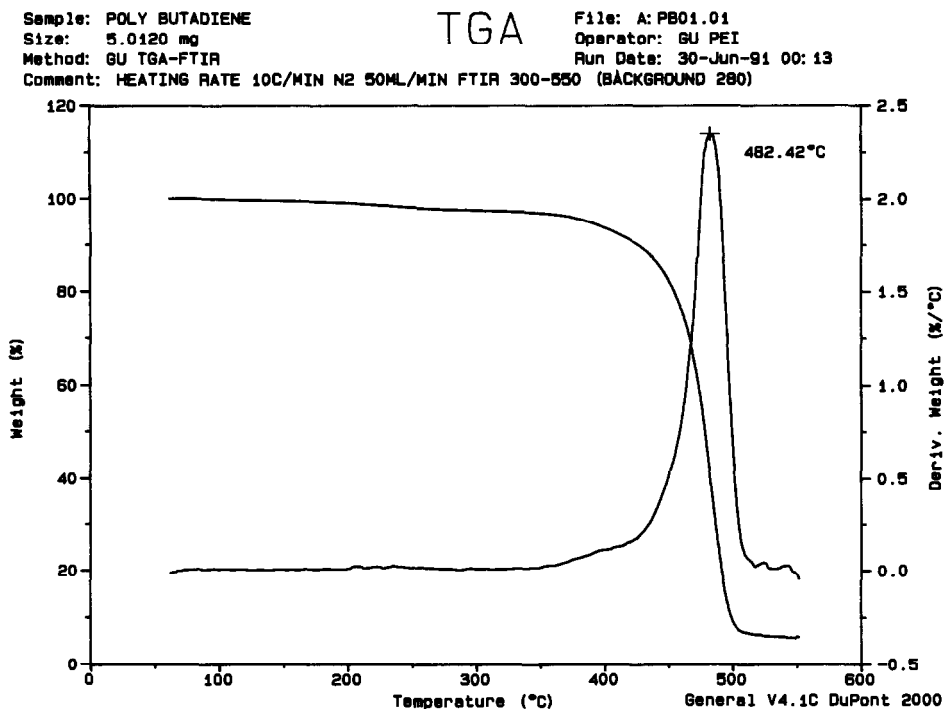


Fig. 2. TG/DTG plot of polybutadiene.

copolymer is pyrolyzed in a nitrogen atmosphere, two overlapping DTG peaks appear: the first at approximately 423°C (Fig. 3), was assumed to be primarily caused by the decomposition of the styrene in the copolymer; the second at about 435°C, was assumed to be primarily butadiene.

#### Gas analysis by FTIR

By measuring the height of the absorbance peak of the aromatic carbon–hydrogen stretch for styrene (corresponding to the aromatic ring in styrene at  $3075\text{ cm}^{-1}$ ), the relative concentrations of styrene can be calculated. Measuring the height of the absorbance peak of the aliphatic carbon–hydrogen stretch for butadiene (corresponding to the structure of butadiene at  $2936\text{ cm}^{-1}$ ), allows the percent concentration of butadiene to be determined.

Substituting the peak heights into Simpson's rule,  $10/3x(pt_1 + 4pt_2 + 2pt_3 + 4pt_4 + 2pt_5 + 4pt_6 + 2pt_7 + 4pt_8 + 2pt_9 + 4pt_{10} + pt_{11})$ , calculates the area under a curve by estimating the area under the parabolic sections of the curve [5,6]. A standard curve for polybutadiene was constructed by taking the mean value of the calculated areas at various concentrations (Fig. 4). The construction of the standard curve for polystyrene was much more complex than for polybutadiene. Figure 5 shows the plot of percent

Sample: STYRENE/BUTADIENE 60/40  
 Size: 5.0020 mg  
 Method: GU TGA-FTIR  
 Comment: HEATING RATE 10C/MIN N2 50ML/MIN FTIR 300-550 (BACKGROUND 280)

TGA

File: A: SB64.01  
 Operator: GU PEI  
 Run Date: 30-JUN-91 03: 22

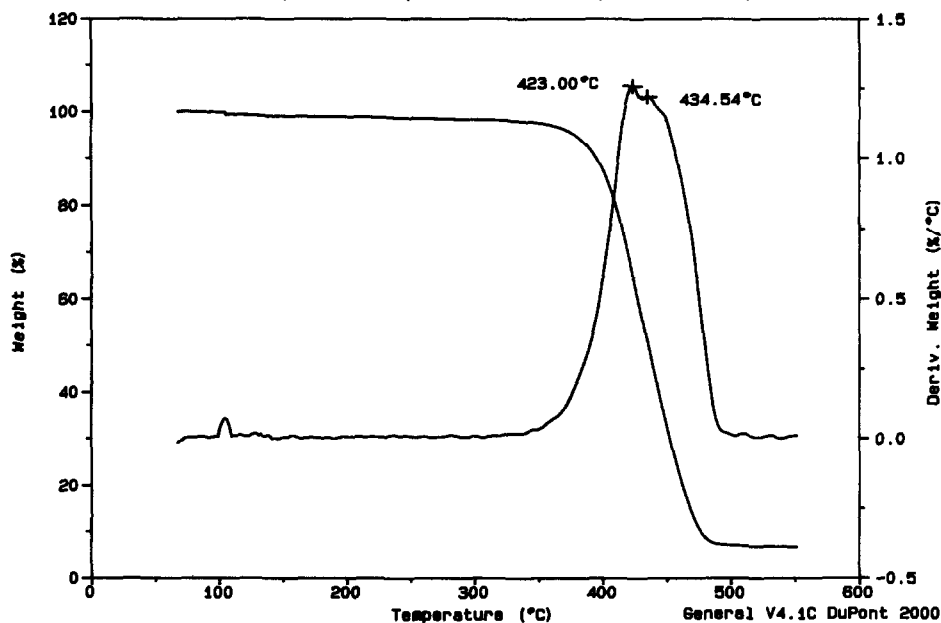


Fig. 3. TG/DTG plot of styrene/butadiene copolymer.

polystyrene versus the mean value of the calculated areas; this plot is neither linear nor logarithmic on an entire basis. For instance, the samples which contain between 40% and 80% styrene are linear, and the samples below 30% styrene and the sample which contained 100% styrene are also linear.

## POLY(BUTADIENE)

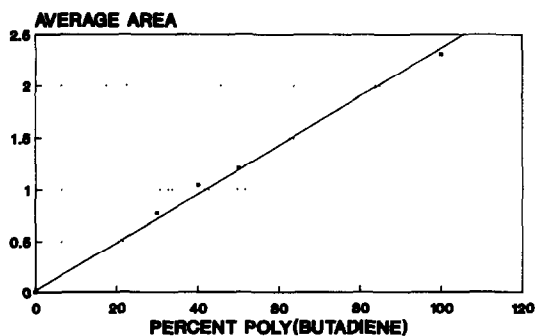


Fig. 4. Poly(butadiene) standard samples (average area under the curve vs. percent polybutadiene).

**POLY(STYRENE)  
ALL SAMPLES**

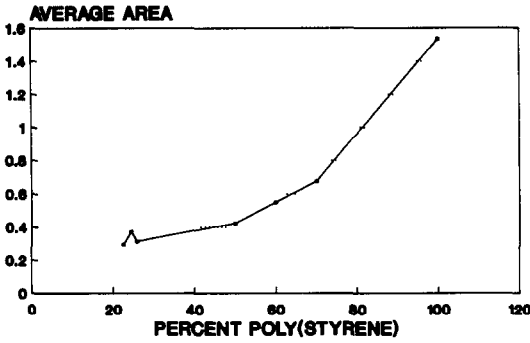


Fig. 5. Polystyrene standards and unknown samples (average area under the curve vs. percent polystyrene)).

The reason for the unusual graphical relationship of the variables can be understood by looking at the FTIR spectra of a copolymer of styrene/butadiene (Fig. 6) and sample 7 (Fig. 7). There is a substantial drift in the baseline of the styrene/butadiene copolymer (Fig. 6). Because the carbon–hydrogen stretching peak ( $3074\text{ cm}^{-1}$ ) for styrene lies well within the frequencies that are experiencing the drifting, the peak height of styrene is affected to a greater extent than that of butadiene ( $2935\text{ cm}^{-1}$ ).

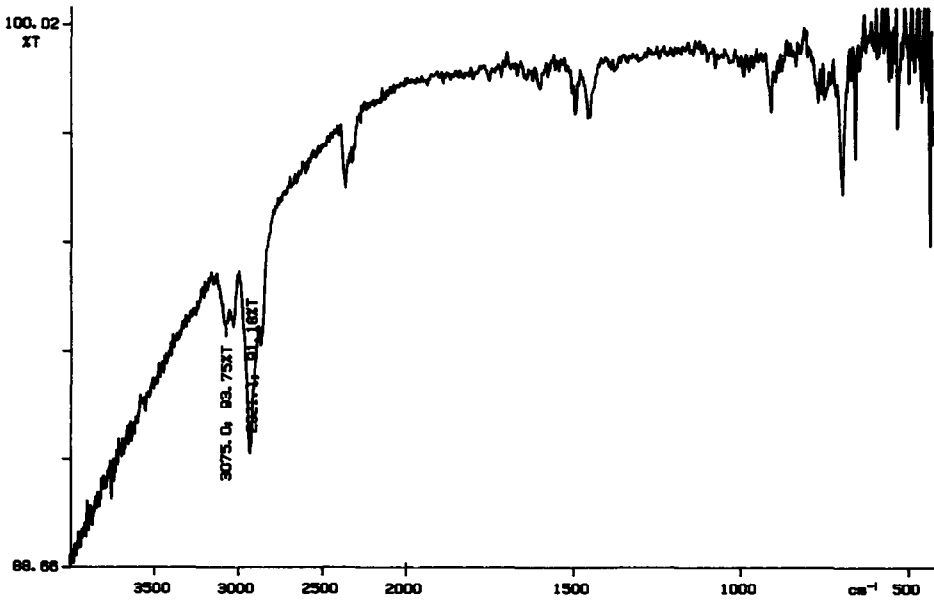


Fig. 6. FTIR spectra of polystyrene/polybutadiene (50/50).

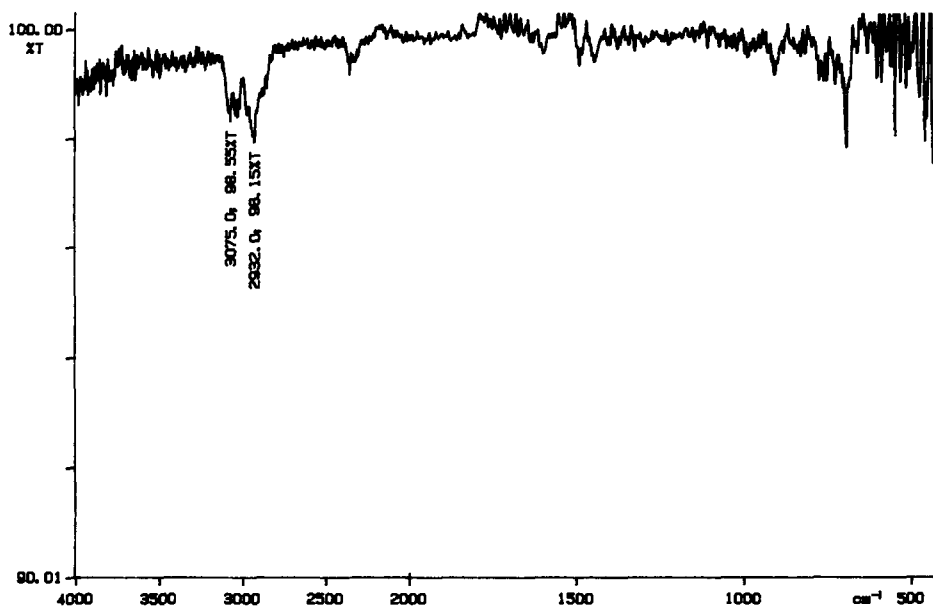


Fig. 7. FTIR spectra of sample 7.

In order to measure the peak height absorbance, a reference baseline must first be established. The lowest absorbance value to the right of the styrene peak was established as the reference. Because there was no drifting in the baseline of sample 7 (Fig. 7), which contained approximately 24.4% styrene, the results of the peak height calculations were slightly different than those of the samples which experienced the drifting. The samples which experienced drifting were the samples that contained high percentages of styrene in the copolymer ( $50\% < \text{styrene} < 70\%$ ). Samples which contained just styrene or low concentrations of styrene/butadiene experienced only nominal drifting.

Two standard curves were constructed for polystyrene. One curve is used for samples which experienced only nominal drifting, and another was established for samples which experienced major baseline drifting.

The percentage of butadiene and the percentage of styrene which were calculated from the standard curves are listed in Tables 1 and 2 respec-

TABLE 1  
Butadiene content (%) in samples

Sample no.	Experimental	Calculated	Difference
4	39.8	40.0	-0.2
5	17.7	15.0	2.7
6	15.2	12.8	2.4
7	17.8	17.0	0.8

TABLE 2  
Styrene content (%) in samples

Sample no.	Experimental	Calculated	Difference
4	60.7	60.0	-0.7
5	21.0	22.5	1.5
6	22.1	25.8	3.7
7	25.9	24.4	-1.5

tively, along with the percentage calculated by adding specific quantities of polystyrene and polybutadiene.

### CONCLUSIONS

TG-FTIR is an accurate way of calculating the butadiene/styrene content of samples; however, it is a very time-consuming method. Every styrene/butadiene sample analyzed will take approximately 6 h.

### ACKNOWLEDGEMENT

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