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Calibration for the composition of polymeric composites using TG/GC

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Abstract

In this study, we attempt to evaluate the calibration of a combined TG/GC system for determining the percentage composition of polymeric composites. For a poly(styrene–butadiene) latex film, the TG/GC system was calibrated using known percentages of poly(styrene):poly(butadiene) mixtures. The standards were evaluated under a nitrogen atmosphere for their usefulness in industrial applications.

INTRODUCTION

In a dynamic TG run, the percentages of styrene and butadiene in a poly(styrene–butadiene) latex film cannot be determined directly because the polymer components decompose simultaneously. Moreover, the percentages cannot be determined using glass transition temperatures, because the glass transitions are not linear if the samples contain less than 40% poly(styrene) or less than 40% poly(butadiene) [1]. Nor can direct NMR and FTIR techniques be used, because the samples do not dissolve in THF, dioxane, or toluene. Even when a 50/50 mixture of THF and dioxane was used, it did not dissolve the latex film, although this mixture is known to dissolve the styrene and butadiene polymers separately [1–4].

Two projects were undertaken to investigate these difficulties. In the first project the percentages of styrene and butadiene in the polymer latex film were determined using TG/FTIR to within two percent of either component [5]. In the second project, TG/GC technique was evaluated to either confirm and/or strengthen the TG/FTIR results.

In the basic theory for both projects, the gases evolved from a sample as

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it proceeds throughout a single TG run develop a bell-shaped curve when the arbitrary peak heights of each sampling point are plotted against the respective sampling temperatures. This means that as the sample decomposes, the peak height is a direct reflection of the amount of gases evolved for a specific temperature. Therefore, for this project, the area under a curve for a given sample was taken to represent its percentage and a calibration curve of percentage versus average peak height was then obtained.

EXPERIMENTAL

The calibration was studied using a full Shimadzu TG/GC system (Fig. 1). A Shimadzu TGA-50 was set to decompose the latex film and pass it on to a Shimadzu GC-8A (with an OV-17 column) for evolved gas analysis through a Valvco 10 port valve that can be controlled through a Shimadzu PRG-102A relay programmer and an upgraded Shimadzu Chromatopac 3A under a set time program. The gas was passed to the GC in an insulated stainless steel line at 200°C at a complete flow rate of 60 ml min^{-1} to prevent any sample slagging or condensing in the transfer line. The TG sample weight was 40 mg while the GC sample volume was 2 μl. The sample weight and volume were set to make sure that enough sample was being analyzed, and that the repeatability between runs could be duplicated.

As mentioned above, the system was controlled by a Shimadzu 3A under a time program. The time program was set with many specified repeated

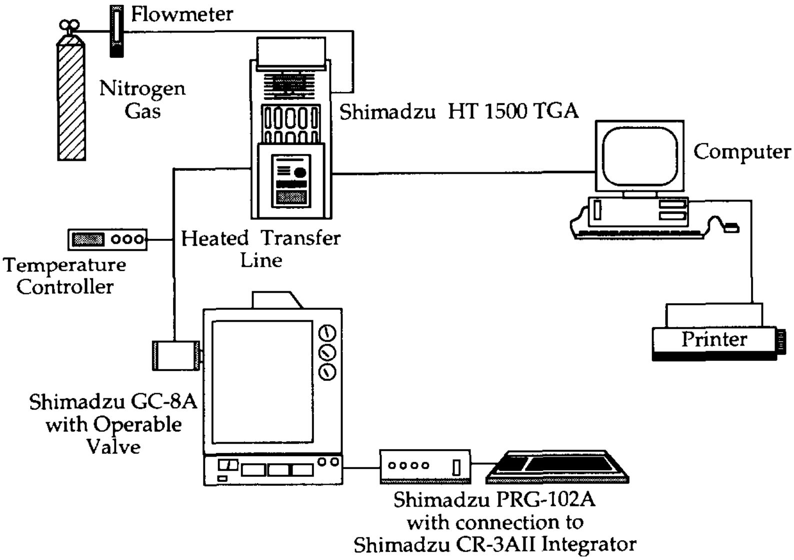

Fig. 1. Shimadzu TG/GC system.

steps such that when the TGA temperature program coincides with a known period of time, an allotted amount of evolved gas sample can be injected into the GC. For this experiment, evolved gas sampling was done from 300 to 500°C, and the time required for one complete run was 5.5 h (including cool-down time).

RESULTS AND DISCUSSION

TG curves

Because the samples in this study contain two-component mixtures at various concentrations, a preliminary TG/DTG evaluation for each component had to be made. For a 100% poly(butadiene) sample, the average decomposition temperature is 430°C, and for 100% poly(styrene), the average decomposition temperature is 380°C. However, when the two components are mixed, the TG/DTG curves show only one broad decomposition peak. Specifically, the decomposition peak temperature on the DTG curve varies with the ratio of poly(styrene) to poly(butadiene). For reference purposes, the TG curves for 100% poly(butadiene), 100% poly(styrene), and a 50/50 mixture of poly(styrene): poly(butadiene) can be seen in Figs. 2–4, respectively.

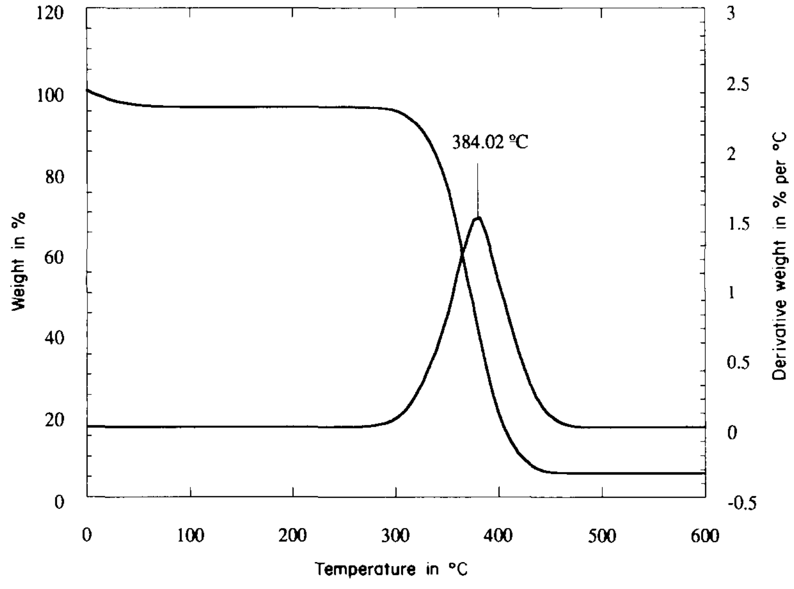

Fig. 2. TG/DTG plot of 100% poly(styrene).

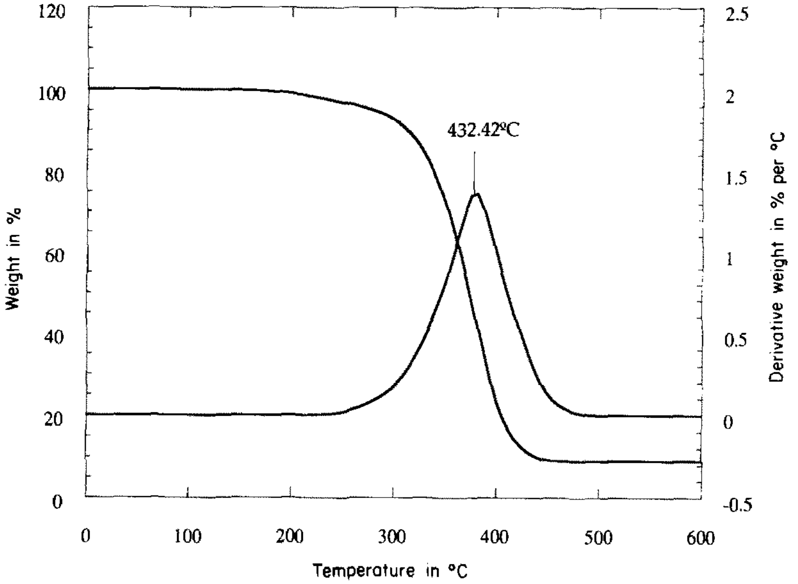

Fig. 3. TG/DTG plot of 100% poly(butadiene).

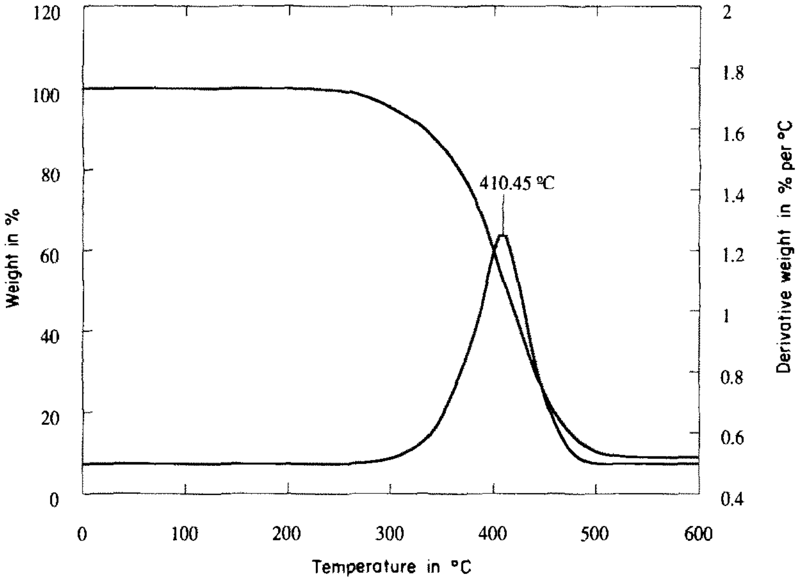

Fig. 4. TG/DTG plot of 50/50 mixture of poly(styrene): poly(butadiene).

Calibration matrix

For this study, it was desirable that sampling should be highly accurate and repeatable within one run. Therefore, for this purpose, all samples were run three times to ensure that the system was repeatable and reproducible. However, several parameters had to be addressed on a matrix-type problem-solving level. For the GC, these are the carrier gas flow rate, the current applied to the column, the attenuation, the injector/detector temperature, and the column temperature. For the GC Chromatopac, these are the slope and the stop time. For the TG, these are the first heating rate, the second heating rate, the sample weight, the nitrogen flow rate for the cell, and the nitrogen flow rate for the purge (the scale).

From the above list, it can be seen that the problems to be addressed are quite extensive and dynamic. But the major problems of the system can be classified into two major areas, and eventually, these will take care of many of the problems listed above. These major problems are the system pressure, sample size, and heating rate. The heating rate is the simplest area to be addressed because it controls the amount of sampling. For instance, in this study, the heating rate for each run was divided into two heating rates in order to save time but not lose any accuracy. Figures 2, 3, and 4, demonstrate this concept: from room temperature to 300°C, a heating rate of 10°C min^{-1} was applied (heating rate 1); and from 300 to 500°C, 1°C min^{-1} was used (heating rate 2).

Solution of the other problems, the system pressure and the sample size, leads to the desired enhancement of the peak height recorded on the chromatogram. If this can be increased, then its reproducibility and repeatability should also increase. Thus, all the GC parameters were changed to enhance the sample peak height. The column, injector, and detector temperatures were raised; the attenuation was lowered; and the primary and carrier gas flow rates were increased. Similarly, the nitrogen flow rates were increased to match the GC carrier flow rate. Of the two problems with the GC Chromatopac, the stop time was increased to allow the new time program to fit within the specified sampling times, and the slope setting was narrowed down to a justifiable range that produced repeatable peaks for any given sample.

The repeatability and reproducibility can be assessed from 100% poly(butadiene) and 100% poly(styrene) curves which are shown in Figs. 5 and 6, respectively. The reproducibility is quite evident. With the new parameters, the repeatability is almost 100%. Even though the graphs are not completely bell-shaped, the false peaks have been eradicated. Moreover, the peak maximums seen on the graphs correspond with the rapid decomposition temperatures that were observed in the respective TG/DTA plots for each sample.

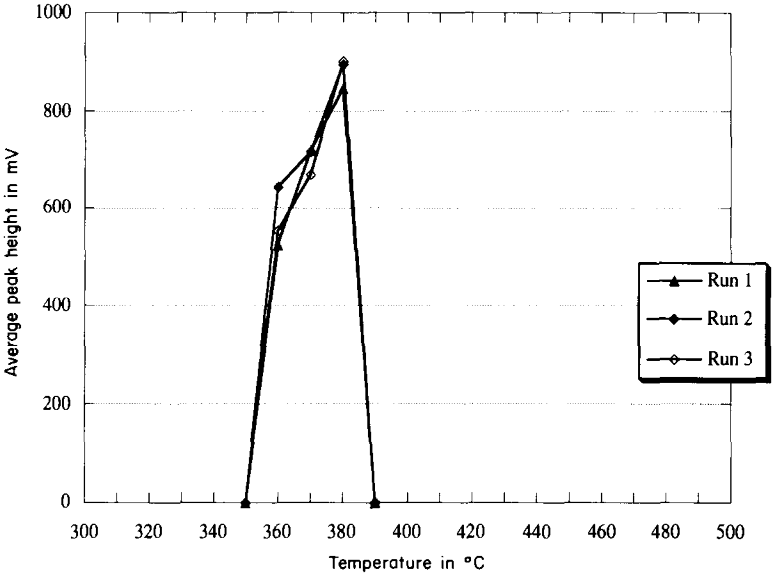

Fig. 5. Repeatability and reproducibility of 100% poly(butadiene) runs.

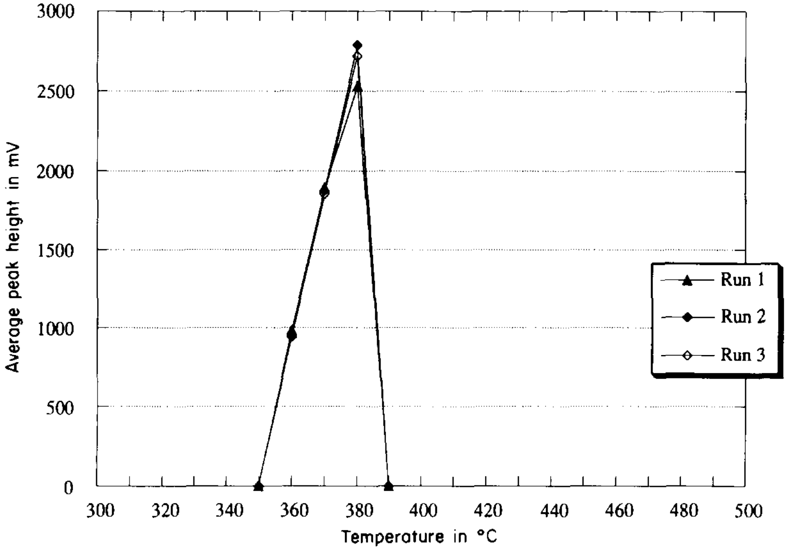

Fig. 6. Repeatability and reproducibility of 100% poly(styrene) runs.

Software development

With the length of time to consider, a software program had to be written, consisting of the steps: 0.01 min, Relay 4, ON; 0.05 min, Relay 4, OFF; 0.21 min, Relay 4, ON; 5.0 min, Relay 4, OFF. This program is a repetitive series of relay commands that turn the sampling valve in the GC through the Shimadzu PRG-102A relay programmer for each individual sampling. The "4" designation is specifically for the valve. In addition, the entire time sequences (in minutes) can be divided into two sub-categories: times 0.01 and 0.05, and times 2.1 and 5.0. The first time sequence is to purge the GC column and open up the sampling tube for the evolved gases to enter (2 μl in volume). The second half of the time sequence is when the peaks are observed, poly(butadiene) at 2.89 min and poly(styrene) at 3.33 min. Therefore, for this optimized project, the program has been expanded to coincide with the two TG heating rates, and by doing so, the system becomes fully automated.

Calibration of the TG/GC system

By calibrating the system, the system data could be fitted to linear graphs and later transferred into the form: $y = \text{slope} \times x + y$-intercept. As mentioned in the theory of the system, each sample should produce a bell-shaped curve from different readings at different temperatures. If this is applied to different samples having different percentage compositions, a linear graph for each component should be produced. In theory, this is a great idea, but for evolved gas techniques, this can be a problem.

In general, the theory stated that the calibration can be made from the area under the curves of each sample. However, for this study, it produced too much error, which could only be reduced if an average was taken for the three largest peaks in a series. Sampling was not possible at one temperature because all the known samples did not produce peaks at one common temperature. Still, by taking the average of the three largest peaks in sequence, the error that is involved is related to the inherent error in the system. This is explained below.

For the calibration, the following samples were run: 100% poly(butadiene) latex film; 100% poly(styrene) latex film; 70/30 mixture of poly(styrene):poly(butadiene); 60/40 mixture of poly(styrene):poly(butadiene); 50/50 mixture of poly(styrene):poly(butadiene).

Poly(butadiene) and poly(styrene) did produce linear graphs; however, the graphs are not linear for the entire composition range. One assumption was made for each run, and this proved to be either helpful or not, depending on which component (butadiene or styrene) was being tested. This assumption was that at zero peak height, there was not any percentage composition. For poly(butadiene) early graphs (not shown) depicted

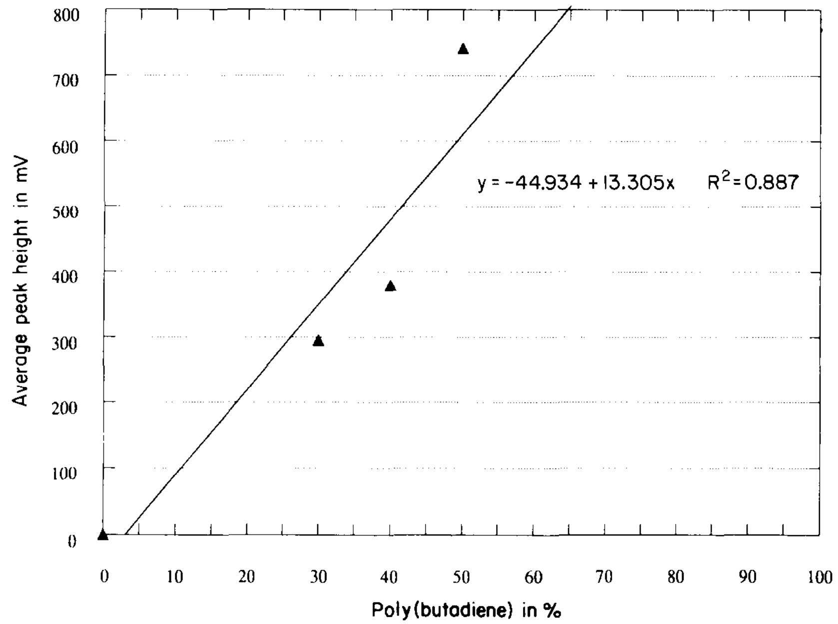

Fig. 7. Poly(butadiene) calibration curve: 40 mg samples.

complete peak height (or column) saturation at 50%. It is true that saturation may be due to the large sample size, but when the sample size was reduced, the repeatability was lower and highly erratic. However, as seen in Fig. 7, if the 100% butadiene point is not included, the R^2 value increases to a modest 0.887, well above the value of 0.62 for the complete rane of poly(butadiene) concentration. This value is reasonably high for the repeatability, but again, it is not very accurate.

When poly(styrene) is calibrated, two curves are produced: one curve for the mid-range values ($50\% < x < 70\%$) of poly(styrene); and another for the low values (<30%) and the extreme value (100%). By not including the 0% and 100% points, the mid-range values have an R^2 value of 0.998 (Fig. 8). However, for the low values and one extreme value, the zero-point assumption and the 100% value have been included; therefore, its R^2 value is 1.000 (Fig. 9).

Even though the R^2 value is improved over several past attempts, the changes are unsuccessful. To be exact, the change in the poly(butadiene) calibration graph reveals that samples containing more than 50% poly(butadiene) cannot be accurately measured; and the two poly(styrene) graphs show that a premise has been set up. Specifically, if the samples are thought to contain less than 40% of poly(styrene), the graph for low concentrations must be used. However, if the samples contain between 40% and 70% of poly(styrene), the samples could be measured accurately with a mid-range plot. These conditions for measuring the percentage of

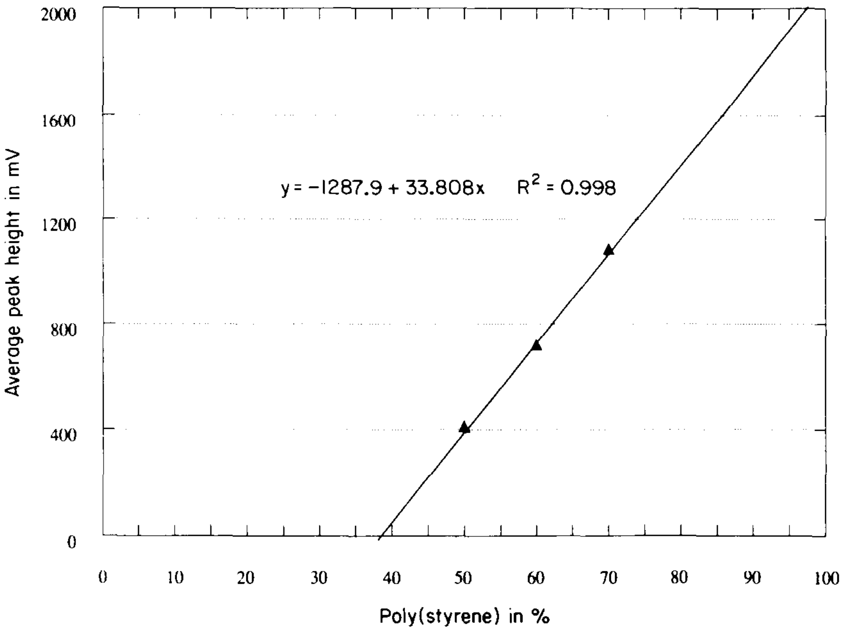

Fig. 8. Poly(styrene) calibration curve for mid-range concentrations: 40 mg samples.

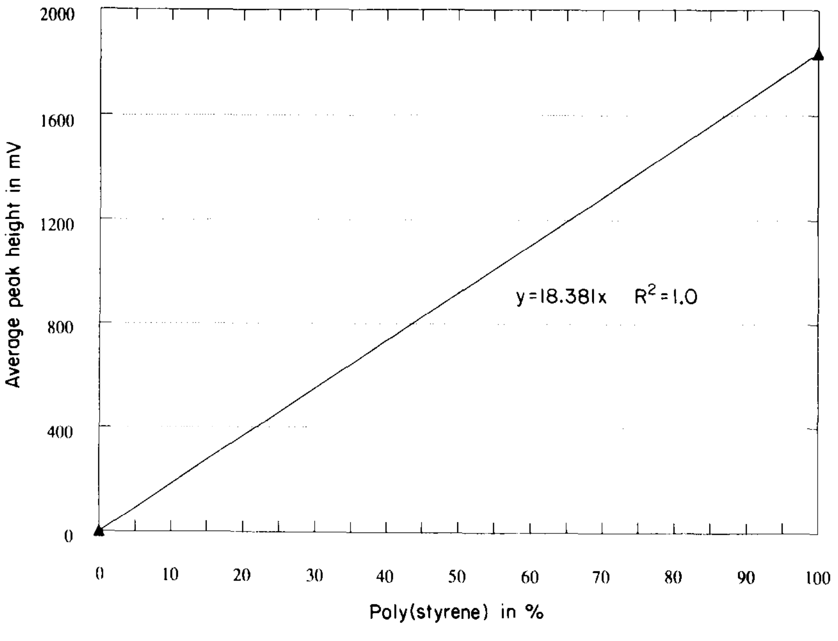

Fig. 9. Poly(styrene) calibration curve for low and high concentrations: 40 mg samples.

both poly(butadiene) and poly(styrene) restrict the system more than can be accounted for, and one inherent problem still exists.

The inherent TG/GC problem

This inherent problem is linked to the theories of decomposing polymers and sample separation in a GC column. In reality, as the temperature is raised in the TG, the polymers decompose into various reactive radical forms and different molecular weight fragments. The newly formed radicals might subsequently react to produce other high molecular weight compounds, which cannot be separated in the GC column because this column is designed to separate individual compounds with relatively low molecular weights. Thus the decomposing polymer creates uncontrollable problems.

The secondary products mentioned may not be a problem in FTIR because a specific wavenumber is being measured; however, in GC, this is the major problem that is inherent to the TG/GC system, and it cannot be corrected and/or specifically controlled.

For this study, Fig. 10 has been created to demonstrate what a typical GC chromatogram would look like for a given sampling under the prescribed four-step software program. The two largest peaks (with square tops) are temperature gradient curves that are more than likely caused from the gas flowing into the cooler column from the heated gas line. The gray area represents the region of secondary products. Considering that the lowest possible reading is approximately 30% component saturation, this gray area demonstrates the inherent error. The gray area may be a reflection of how the OV-17 column handled the newly formed secondary products, but after reviewing the literature, the OV-17 column was found to be the best choice. Thus, any product formed or decomposed in the region will be measured,

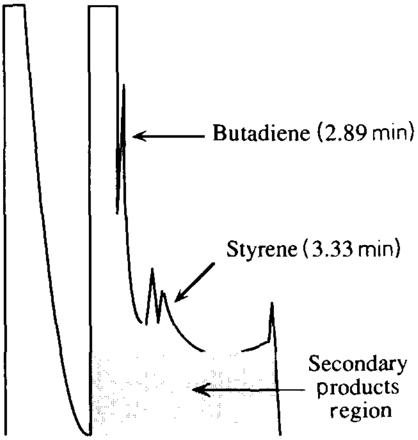

Fig. 10. Typical GC chromatogram.

and because the system is looking for the statistically large poly(butadiene) and poly(styrene) segments for measurement, their respected radical form is dominating enough to be measured. But as said before, it is highly likely that the radicals will form new products, and these increased reactivities take away from the percentage radical form that the GC is looking to measure. Thus, this causes problems that the researcher has no control over.

CONCLUSIONS

The determination of percentage chemical composition of polymeric films using a coupled TG/GC system proved to be very repeatable but not very accurate. With further study, this technique could be improved if the inherent problems with the system were overcome.

TG/GC is a very good technique for the qualitative analysis of an unknown sample, but not for a quantitative assessment. Overall, TG/FTIR is the better choice for this type of study.

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