CHAPTER 4

Advantages of Thermal Analysis in Polymer Matrix Composites

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To Cite This Chapter:
Kayrici, M., Taser, H.H. & Ozturk, E. (2023). Advantages of Thermal Analysis in Polymer Matrix Composites. In H. Arikan, Y. Uzun & I. Cetin (Eds.), *Current Studies in Basic Sciences, Engineering and Technology 2023* (pp. 34–43). ISRES Publishing.

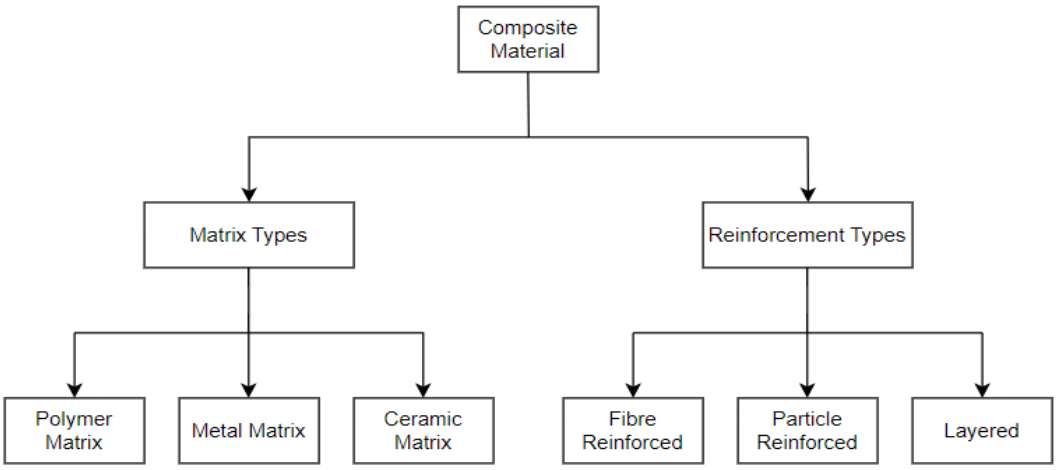
Introduction

A composite material is a new material that is formed by the macro-scale combination of at least two or more materials with sufficiently different physical or chemical properties and different from the initial properties (Kaya, 2016, p. 38).

Today, the aerospace, aviation, and mobility industries are demanding more and more properties from structural materials. Materials for these industries must have excellent lightness and high strength. These properties can only be achieved with composite materials. Nano-additives are also increasingly being developed to provide exceptional mechanical and electrical properties (Lijima, 1991, p. 57).

Composite materials have more than one advantage over other materials thanks to their properties. They are demanded and preferred due to their many advantages such as long service life, lightness, thermal and mechanical durability, and corrosion resistance (Gülmez, 2018, p. 74). Composites are classified according to matrix materials and reinforcing elements. This classification is shown in Figure 1.

Figure 1.
Composite Material Types



Polymer matrix composites have started to be preferred in the field of engineering due to their advantages, both due to the developments in high-yield fibres (carbon, glass, and aramid) and the developments in the use of polymers as matrix materials. Plastics are analysed in two groups thermoplastic and thermoset according to their properties in chemical bond structures (Asi, 2018, p.153).

- Thermoplastics are plastics that can be shaped and can be reshaped by heating.
- Thermosets are heat-resistant and long-lasting plastics that cannot be shaped and are subjected to a curing process.

Thermoplastics

- Polyethylene
- Acrylic Polymers
- Polypropylene
- Poly (Vinyl Chloride)
- Acetates
- Polystyrene
- Polyesters, PET
- Polyamides, PA (Nylon)

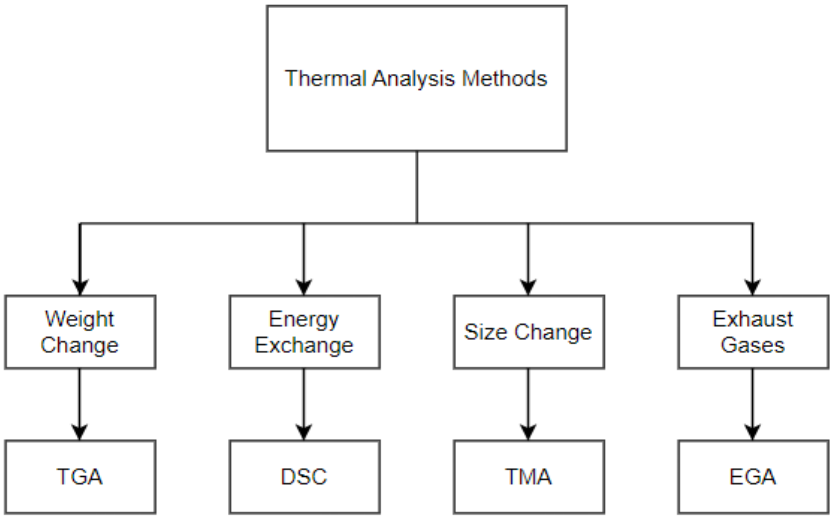
Thermosets

- Polyurethanes
- Phenol-Formaldehyde Resins
- Unsaturated Polyesters
- Reinforced Plastics
- Epoxies
- Styrene-Butadiene
- Amino resins
- Alkyd Resins

Thermal Analysis Methods

Thermal analysis is a group of methods in which the physical (melting and other phase transitions, glass transition) or chemical (degradation, oxidation) properties of a material are measured as a function of temperature, and a controlled temperature is applied to the material (Çelikbilek, 2009, p. 107). These methods are shown in Figure 2.

Figure 2.
Thermal Analysis Methods



Properties to be determined by thermal analysis methods (Coats & Redfern, 2018);

- Heat capacity
- Thermal diffusion
- Purity
- Creating phase diagrams
- Quantitative analysis
- Qualitative analysis
- Estimation of solvent composition
- Structural transformations
- Glass transition temperature
- Thermal resistance

Heat capacity is the amount of heat required for a 1 °C change in the temperature of the sample. In other words, it is the temperature derivative of the heat of a substance. It is obtained by multiplying the mass of the sample by its heat (Kou vd., 2019). Thermal diffusivity is the curve obtained as the sample cools over a certain time interval. During this cooling, heat is released by the phase transformation that will occur in the sample. This heat indicates that there will be a break in the cooling curve and its slope changes (Corcione & Frigione, 2012).

Purity allows us to recognize the sample and confirm its properties. If the sample is only a few milligrams, it allows us to recognize the sample (Groenewound, 2005). The temperature factor in the sample and the diagrams indicating the change in the phases of the compositions are called phase diagrams. Phase diagrams are used to determine the internal structure of the samples and the stable regions that do not change (Lin & Huang, 2010).

Analyses to determine the components used in the sample (qualitative) and the amount of each component (quantitative) (Saikia, 2020, p. 161). The glass transition temperature (Tg) is a phenomenon of amorphous polymers. At this temperature, polymers transition from the glassy to the rubbery state. Tg is an important characteristic of polymer behavior. It marks a region of significant changes in physical and mechanical properties (Fryer vd., 2000).

Thermogravimetric Analysis (TG or TGA)

Thermogravimetric analysis involves heating the initial temperature of the sample from room conditions to a temperature of approximately 1200 °C, while periodically monitoring the changes in its mass (Prime & Bair, 2009).

X (Solid) Y (Solid) + Z (Gas) (Mass decreasing)

Z (Gas) + Y (Solid) X (Solid) (Increasing mass)

The monitored data are expressed as temperature and mass percentage data in a graph called a thermogram or thermal decomposition curve. The parameters that vary periodically are related to the time to stabilize the sample at a certain temperature and the heating rate (D. C. Doyle, 1961).

The thermogravimetric analyzer consists of an oven, an oven temperature control unit, a precision analytical balance, and a data logger. The recorder plots the mass change of the sample under temperature. The precision balance is usually suitable for samples of 5-10 mg (Loganathan, Valapa, Mishra, Pugazethenthi & Thomas, 2017, s. 69).

Figure 3.
Schematic Representation Of The Thermogravimetric Analysis System

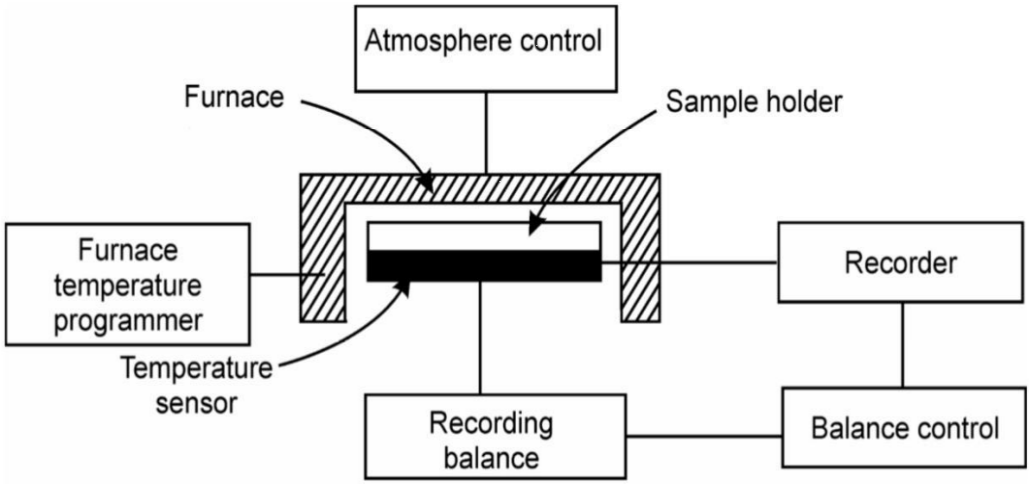
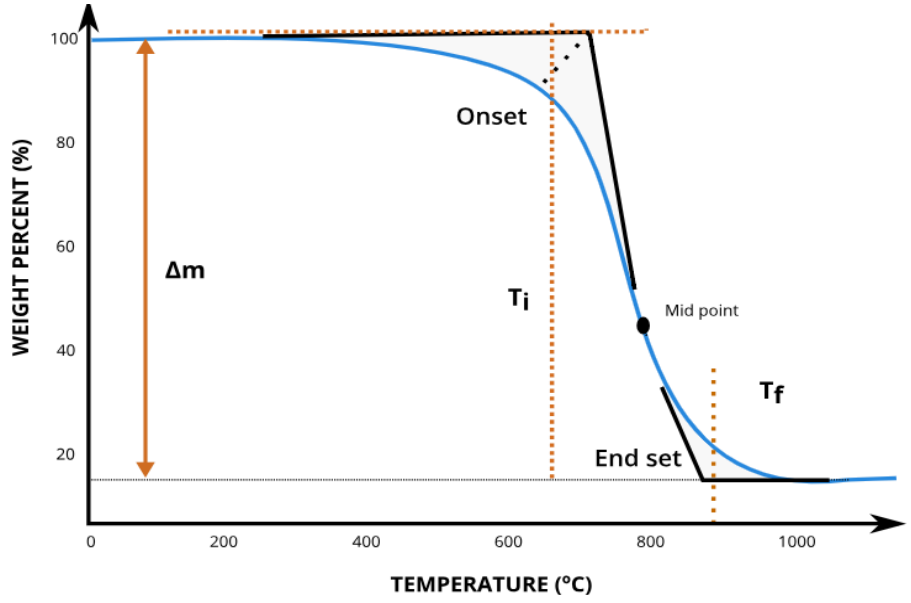


Figure 4.
A Typical Thermogravimetric Analysis Graph



- TGA detects the change in mass with the temperature change applied to the sample. With the change in mass, it is seen that the sample starts to decompose or evaporate. There are also ranges where the temperature change does not change the mass percentage. This indicates that the sample is stable.

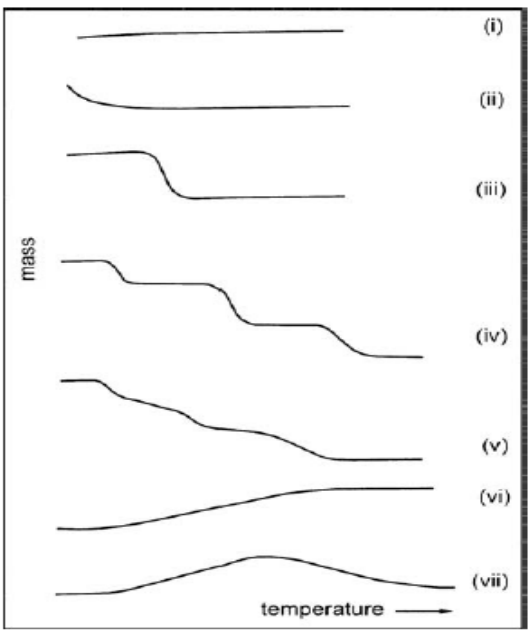
- TGA analysis of the sample heated in a certain temperature range provides mass loss information, composition determination, and ease of seeing the reaction status information in case of decomposition or evaporation. It also gives information about the percentage of composition in the mixture.
- Increasing the ratio of the components added to the mixture or the amount of sample may cause the heat given to be distributed unevenly and the gases released as a result of the reaction cannot be removed sufficiently. As a result of this situation, precise result data may not be obtained.
- The heating rate range applied to the sample is between 1-100°C/min. If the specified heating rate increases, the data to be obtained from the sample will not provide a more general and accurate measurement. If slow heating rates are applied, more accurate results are obtained in the results obtained.

The thermogram curve can be influenced by many factors during its formation. Factors affecting thermogram curves (Saadatkhah vd., 2020):

- Heating rate
- Reference particle size
- Atmosphere environment
- Thermal conductivity
- Sample size
- Gas flow rate

In the TGA analysis applied to the samples, many situations may occur and these situations should be interpreted separately. The situations that occur in TGA analysis are as follows:

Figure 5.
Various Thermogram Types



- i. Indicates that the sample is not affected by temperature change or degradation.
ii. Indicates that weight loss is rapid at the beginning of heating or drying (desorption).
iii. The most common TG curve shows the temperature range in which the material is stable.
iv. Indicates multiple degradation, in a stepwise manner, with stable intermediate degradation products.
v. Indicates multiple degradations and unstable intermediate degradation products.
vi. This curve, which shows an increase in weight, shows the result as an example of the formation of oxidation that usually occurs in metals.
vii. It is a very rare type of curve. It shows first an increase and then a decrease in weight.

Differential Scanning Calorimetry (DSC)

DSC analysis is a thermal analysis method that examines the heat flow difference between the sample and the reference material as a function of temperature by applying for a controlled temperature program. Two techniques are commonly used, Heat Flow DSC analysis and Power Compensated DSC analysis. Heat Flow DSC analysis can directly measure temperature differences and convert them into heat flow differences. Heat Flow DSC analysis can also be expressed as "Quantitative DSC" (Devi vd., 2021).

The sample and the reference used during DSC analysis are placed in the oven. There are two crucibles in the oven. The prepared sample is placed in one of these crucibles and the sample material is placed in the other. The crucibles in the oven are heated with different heaters. Thus, the materials in the crucibles are not given the same heat. The different temperatures applied are measured by thermocouples under the crucibles. The heat difference caused by different temperatures is prepared as a function of temperature. When the thermocouples under the crucibles detect the temperature difference, they give heat to the cold material to equalize the temperature of the two samples (Corcione & Frigione, 2012).

This thermal method, which determines the temperature difference of materials, is widely used in the determination of polymeric materials. The changes that occur with the temperatures applied to the polymers are seen and monitored with differential thermograms (Drzeżdżon vd., 2019). These changes are shown in Figure 7.

Figure 6.

Schematic View of DSC Heat Flow System (Bibi vd., 2015)

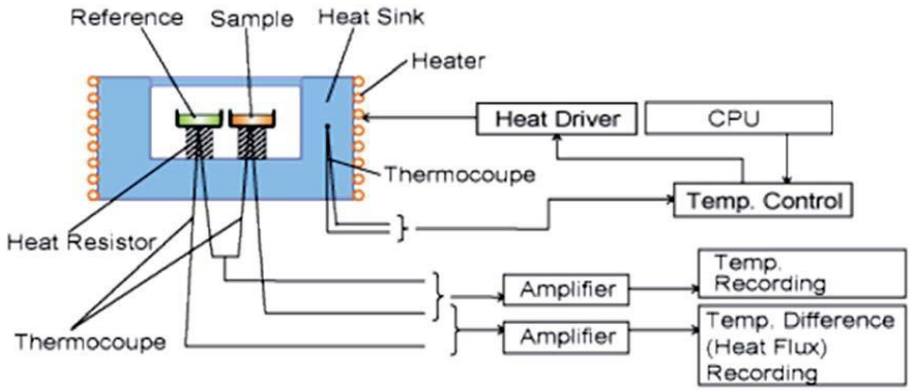
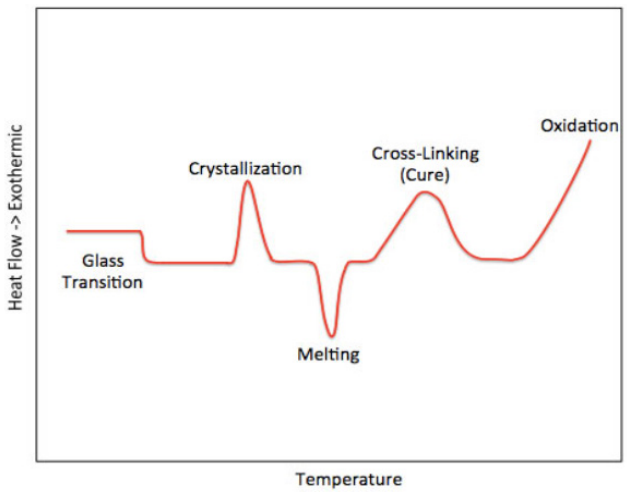


Figure 7.

Differential Thermogram Showing The Changes Encountered İn Polymeric Materials



Factors affecting the glass transition temperature (Tsagaropoulos & Eisenberg, 1995) :

- Heating rate
- Heating and cooling
- Obsolescence
- Molecular weight
- Plasticiser
- Crystallinity
- Copolymers
- Filling material
- Polymer main chain
- Hydrogen bonding

Thermomechanical Analysis (TMA)

TMA is a technique that determines the changes in the dimensions of physically solid or liquid samples as a function of the force and temperature applied to the samples and the elapsed time. This technique is used to determine the glass transition temperature (Tg), the thermal expansion of the sample (CTE), and the resulting compression modulus coefficients as the temperature changes and the force remains constant (Groenewound, 2005).

The expansion or contraction of the sample by the factors acting on the sample, the rubbery structure of the sample (Tg), or the deformation that occurs, determine the differences in the sample size. The data of this analysis method allow us to predict the response of the specimen under different temperatures.

TMA applies a controlled load to the sample in a temperature and atmosphere-controlled environment. This applied force is very small. This occurs without restriction on the expansion or contraction of the sample. A temperature-controlled LVDT (linear variable differential transducer) is used to measure changes in size.

TMA can be used in a wide range of materials, from polymers, composite materials, plastics, elastomers, paints, adhesives, hard solids, rubbers, thin films, liquids, gels, etc. As all materials have a Coefficient of Thermal Expansion (CTE), the technique applies to a wide range of industries (Startsev vd., 2020).

Evolved Gas Analysis (EGA)

It is the method used to determine and monitor the gas molecules released in the samples. This analysis detects the small amount of gas molecules that occur when the temperature reaches above room temperature. Evolved gas analysis can be used to determine the following three factors (Shiono vd., 2015).

- Composition of evolved gases,
- Concentration of evolved gases,
- Development profile according to heating temperature.

Gas molecules begin to form on the surface of materials heated above room temperature. The sample is vacuumed to remove the gases that will be affected by external factors in evolved gas analysis and to obtain more accurate results. If the gas reaction to be formed is dangerous and toxic, it is carried out in the fume chamber. With this analysis, it can be determined whether the gases formed evolve or not. EGA is a useful method for determining the composition of the sample and detecting thermal zones. To determine their composition by mass spectrometry, the chromatography-mass spectrometry (GC/MS) method is then used to determine the thermal event (Friedman, 1970). EGA can be analyzed as quantitative and qualitative methods (Risoluti vd., 2022).

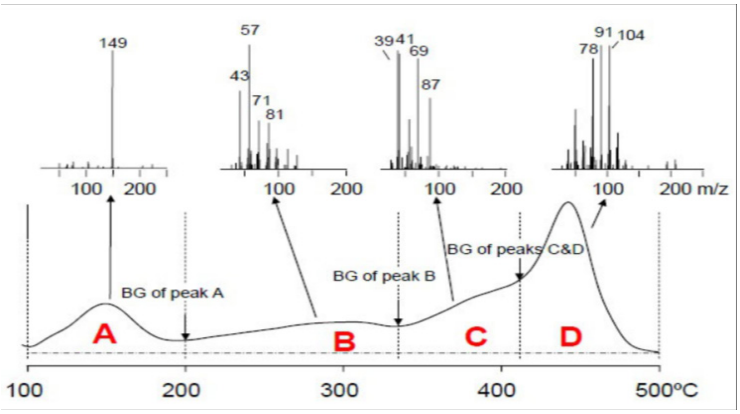
Semi-quantitative

- Comparative study: Good and bad examples

- Plate level failure analysis for hermetic electronic components
- Approval of cleaning quality in UHV quality for SS parts
- Comparative study for gas release at a given temperature
- Direct Gas analysis
- Gas outlet from gas-tight gaskets in hermetic devices
- Efficiency of the receiver in a vacuum cavity
- Gas exit rates
- Gas released in the cavity after the gas outlet (drilling in vacuum)

Figure 8.

Typical EGA thermogram graph



Qualitative screening

- Mass screening as the temperature rises
- The 3D plot of the temperature-mass signal
- Comparative screening: Good and bad examples

Ideal Application Areas of EGA

- Investigation of gas species in solid and gas samples
- Profiling of gas emission according to temperature
- Failure analysis for hermetic packages
- Degassing rates for metals and cleaning research

References

Kaya, A. İ. (2016). Kompozit malzemeler ve özellikleri. *Putech & Composite Poliüretan ve Kompozit Sanayi Dergisi*, *29*, 38-45.

Lijima, S. (1991). Helical microtubules of graphitic carbon. *Nature 354*, 56-58. https://doi.org/10.1038/354056a0

Gülmez, S. (2012). Otomotiv endüstrisinde kullanılan polimer matrisli kompozit malzemeler. *[Yüksek lisans tezi]*. Pamukkale Üniversitesi.

Asi, D. (2018). Polimer matrisli kompozit malzemelerde ilave olarak kullanılan parçacıkların geometrisinin kompozit malzemelerin fiziksel ve mekaniksel

özelliklerine etkisinin araştırılması. *[Doktora tezi]*. Uşak Üniversitesi.

Çelikbilek, M. (2009). TeO2-WO3 sisteminin termal ve mikroyapısal incelenmesi. *[Doktora tezi]*. İstanbul Teknik Üniversitesi.

Coats, A. W. & Redfern, J. P. (1963). Thermogravimetric analysis. *A review Analyst, 88*(1053), 906-924. https://doi.org/10.1039/AN9638800906

Kou, Y., Wang, S., Luo, J., Sun, K., Zhang, J., Tan, Z., & Shi, Q. (2019). Thermal analysis and heat capacity study of polyethylene glycol (PEG) phase change materials for thermal energy storage applications. *The Journal of Chemical Thermodynamics. 128*, 259-279. https://doi.org/10.1016/j.jct.2018.08.031

Corcione, C. E., & Frigione, M. (2012). Characterization of nanocomposites by thermal analysis. Materials. 5(12), 2960-2980. https://doi.org/10.3390/ma5122960

Groenewound, W. M., (Ed.) (2005). Characterisation of polymers by thermal analysis. Elsevier.

Lin, D., & Huang, Y. (2010). A thermal analysis method to predict the complete phase diagram of drug-polymer solid dispersions. *International journal of pharmaceutics. 399*(1-2), 109-115. https://doi.org/10.1016/j.ijpharm.2010.08.013

Saikia, P (2020). Physical and thermal analysis of polymer. *In polymer science and innovative applications* (pp. 153-205). Elsevier. https://doi.org/10.1016/B978-0-12-816808-0.00005-6

Fryer, D. S., Nealey, P. F., & de Pablo, J. J. (2000). Thermal probe measurements of the glass transition temperature for ultrathin polymer films as a function of thickness. *Macromolecules. 33*(17), 6439-6447. https://doi.org/10.1021/ma0003349

Prime, R. B., Bair, H. E., Vyazovkin, S., Gallagher, P. K., & Riga, A. (2009). Thermogravimetric analysis (TGA). Thermal analysis of polymers. *Fundamentals and applications.* 241-317.

Doyle, C. D. (1961). Estimating thermal stability of experimental polymers by empirical thermogravimetric analysis. *Analytical Chemistry. 33*(1), 77-79. http://doi.org/10.1021/ac60169a022

Loganathan, S., Valapa, R. B., Mishra, R. K., Pugazhenthi, G., & Thomas, S. (2017). Thermogravimetric analysis for characterization of nanomaterials. *In Thermal and Rheological Measurement Techniques for Nanomaterials Characterization* (pp. 67-108). Elsevier. https://doi.org/10.1016/B978-0-323-46139-9.00004-9

Saadatkhah, N., Carillo Garcia, A., Ackermann, S., Leclerc, P., Latifi, M., Samih, S., ... & Chaouki, J. (2020). Experimental methods in chemical engineering: Thermogravimetric analysis-TGA. *The Canadian Journal of Chemical Engineering, 98*(1), 34-43. https://doi.org/10.1002/cjce.23673

Devi, N., Srivastava, S., Yogi, B., & Gupta, S. K. (2021). A Review on Differential Thermal Analysis. *Chem. Res. J., 6*, 71-80.

Bibi, S., Bremner, D. H., Macdougall-Heasman, M., Reid, R., Simpson, K., Tough, A., ... & Matthews, K. H. (2015). A preliminary investigation to group disparate batches of licit and illicit diazepam tablets using differential scanning calorimetry. *Analytical methods, 7*(20), 8597-8604. https://doi.org/10.1039/

C5AY01711D

Drzeżdżon, J., Jacewicz, D., Sielicka, A., & Chmurzyński, L. (2019). Characterization of polymers based on differential scanning calorimetry based techniques. *TrAC Trends in Analytical Chemistry, 110*, 51-56. https:/doi.org/10.1016/j.trac.2018.10.037

Tsagaropoulos, G., & Eisenberg, A. (1995). Dynamic mechanical study of the factors affecting the two glass transition behavior of filled polymers. Similarities and differences with random ionomers. *Macromolecules, 28*(18), 6067-6077. https://doi.org/10.1021/ma00122a011

Startsev, O. V., Vapirov, Y. M., Lebedev, M. P., & Kychkin, A. K. (2020). Comparison of glass-transition temperatures for epoxy polymers obtained by methods of thermal analysis. *Mechanics of Composite Materials, 56*(2), 227-240. https://doi.org/10.1007/s10973-008-9128-6

Shiono, A., Hosaka, A., Watanabe, C., Teramae, N., Nemoto, N., & Ohtani, H. (2015). Thermoanalytical characterization of polymers: a comparative study between thermogravimetry and evolved gas analysis using a temperature-programmable pyrolyzer. *Polymer Testing, 42*, 54-61. https://doi.org/10.1016/j.polymertesting.2014.12.011

Friedman, H. L. (1970). Mass spectrometric thermal analysis: a review. T*hermochimica Acta, 1*(2), 199-227. https://doi.org/10.1016/0040-6031(70)85010-9

Risoluti, R., Gullifa, G., Barone, L., Papa, E., & Materazzi, S. (2022). On-Line Thermally Induced Evolved Gas Analysis: An Update—Part 1: EGA-MS. *Molecules, 27*(11), 3518. https://doi.org/10.3390/molecules27113518

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