

DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**INVESTIGATION OF PHOTOTHERMAL
RADIOMETRY METHOD FOR THERMAL
CHARACTERIZATION OF POLYMER
COMPOSITES**

by
Halil Doğacan KOCA

September, 2023

İZMİR

INVESTIGATION OF PHOTOTHERMAL RADIOMETRY METHOD FOR THERMAL CHARACTERIZATION OF POLYMER COMPOSITES

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**by
Halil Doğacan KOCA**

September, 2023

İZMİR

Ph.D. THESIS EXAMINATION RESULT FORM

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Halil Doğacan KOCA

INVESTIGATION OF PHOTOTHERMAL RADIOMETRY METHOD FOR THERMAL CHARACTERIZATION OF POLYMER COMPOSITES

ABSTRACT

Considering the advances in material technology, determining the thermophysical properties of polymer composites has great importance for engineering design. Among characterization techniques, the photothermal radiometry (PTR) method is a noncontact and nondestructive method utilized to obtain the thermophysical characterization of various materials. The basis of PTR method relies on detecting variations in infrared radiation (IR) emitted by the modulated laser absorption beam from the material surface. Polymer composites are favorable samples for PTR measurements since they have strong IR emissivity that allows obtaining thermal diffusivity at low excitation power and low frequency range.

In the scope of the thesis, a specially modified modulated PTR method with a low-frequency operating range and back detection configuration is designed and developed to measure the thermal diffusivity of the polymer composites. The accuracy and validation of the experimental setup are determined. For this purpose, the experimental measurements are compared with the results from the classical PTR method.

Finally, the thermal diffusivity of EPDM composites reinforced with carbon black and graphene nanoplatelets fillers and their hybrid combinations are investigated using the developed low frequency PTR method. Based on the results, the synergistic effect of carbon fillers on the thermophysical properties of hybrid polymer composites was investigated.

Keywords: Photothermal radiometry, thermal characterization, thermal diffusivity, polymer composites, thermal conductivity

POLİMER KOMPOZİTLERİN ISIL KARAKTERİZASYONU İÇİN FOTOTERMAL RADYOMETRİ YÖNTEMİNİN İNCELENMESİ

ÖZ

Malzeme teknolojisindeki gelişmeler dikkate alındığında, polimer kompozitlerin termofiziksel özelliklerinin belirlenmesi mühendislik tasarımı açısından büyük önem taşımaktadır. Karakterizasyon teknikleri arasında fototermal radyometri (FTR) yöntemi, çeşitli malzemelerin termofiziksel karakterizasyonunu belirlemek için kullanılan temassız ve tahribatsız bir ölçüm yöntemidir. FTR yönteminin temeli genel olarak modüle edilmiş bir lazer ışınının malzeme yüzeyinde soğurulması ile yayılan kızılötesi (KÖ) radyasyondaki değişikliklerin tespit edilmesi prensibine dayanmaktadır. Polimer kompozitler, düşük uyarım gücünde ve düşük frekans aralığında ısı yayılım katsayısının elde edilmesini sağlayan güçlü KÖ radyasyon emisyonuna sahip olmaları sayesinde FTR ölçümleri için uygun örneklerdir.

Bu tez kapsamında, polimer kompozitlerin ısı yayılım katsayılarını ölçmek için, düşük frekanslı çalışma aralığına ve arka tespit konfigürasyonuna sahip, özel olarak modifiye edilmiş modüle edilmiş bir PTR yöntemi tasarlanmış ve geliştirilmiştir. Deney düzeneğinin doğruluğu ve geçerliliği belirlenmiştir. Bu amaçla deneysel sonuçlar klasik FTR yönteminde elde edilen sonuçlarla karşılaştırılmıştır.

Son olarak, grafen nanoplakalar, karbon siyahı dolgu maddeleri ve bu dolgu maddelerinin hibrit kombinasyonları ile güçlendirilmiş EPDM nanokompozitlerinin ısı yayılım katsayıları, geliştirilen düşük frekanslı FTR yöntemi ile incelenmiştir. Sonuçlara dayanarak, karbon bazlı nanomalzemelerin hibrit polimer nanokompozitlerin termal özellikleri üzerindeki sinerjik etkisi araştırılmıştır.

Anahtar kelimeler: Fototermal radyometri, ısı karakterizasyon, ısı yayılım, polimer kompozitler, ısı iletkenlik

CONTENTS

	Page
Ph.D. THESIS EXAMINATION RESULT FORM	ii
ACKNOWLEDGMENT	iii
ABSTRACT	v
ÖZ.....	vi
CONTENTS	vii
LIST OF FIGURES.....	x
LIST OF TABLES	xiii
CHAPTER ONE INTRODUCTION.....	1
1.1 Motivation and Overview of Thesis	1
1.2 Objectives of Thesis	2
CHAPTER TWO LITERATURE REVIEW.....	3
2.1 Introduction.....	3
2.2 Photothermal Techniques	4
2.2.1. Photopyroelectric Technique	6
2.2.2. Photoacoustic Spectroscopy.....	8
2.2.3. Photothermal Beam Deflection.....	9
2.2.4. Laser Flash Technique	10
2.2.5. Photothermal Reflectance	11
2.2.6. Photothermal Radiometry	12
2.3 Related PTR Studies of Composite Materials	16
2.4 Application Area of PTR	20
CHAPTER THREE THEORY	24
3.1 Introduction.....	24
3.2 Thermal Diffusion Length	24
3.3 Theoretical Background of PTR.....	25
3.4 Slope Method.....	31

3.5 PTR Signal.....	36
3.6 Thermal Conductivity	38
CHAPTER FOUR MATERIALS AND MORPHOLOGY ANALYSIS.....	40
4.1 Introduction.....	40
4.2 Materials	40
4.2.1 EPDM Polymers	40
4.2.2 Graphene Nanoplatelets	41
4.2.3 Carbon Black	42
4.2.4 Hybrids.....	43
4.3 Preparation of EPDM Composites.....	44
4.4 Methods	46
4.5 Morpholgy Analysis	47
4.6 Conclusions	49
CHAPTER FIVE DEVELOPMENT OF LOW FREQUENCY PTR.....	51
5.1 Introduction.....	51
5.2 Experimental Configuration	51
5.2.1 Laser.....	53
5.2.2 Modulation.....	54
5.2.3 IR Lens.....	55
5.2.4 Thermopile Sensor	56
5.2.5 Lock-in Amplifier	57
5.3 Normalization of PTR	58
5.4 Validation of PTR.....	60
5.4.1 HDPE/MWCNT Nanocomposites	60
5.4.2 HDPE/Al Nanocomposites	61
5.5 Calibration of PTR Signal	62
5.6 Conclusions	64
CHAPTER SIX THERMAL CHARACTERIZATION OF EPDM COMPOSITES.....	65

6.1 Introduction.....	65
6.2 EPDM/GNPs Composites.....	65
6.3 EPDM/GNPs-CB Hybrid Composites.....	67
6.4 Conclusions	70
CHAPTER SEVEN CONCLUSIONS & FUTURE WORKS.....	71
7.1 Conclusions	71
7.2 Future Works	72
REFERENCES	73
APPENDICES	92

LIST OF FIGURES

	Page
Figure 2.1 Physical processes in photothermal spectroscopy	4
Figure 2.2 Photothermal phenomena of optical heating of the sample.....	5
Figure 2.3 Conventional experimental setup for the PPE technique	7
Figure 2.4 a) FD-PPE experimental setup, and b) design of a BD-PPE cell	8
Figure 2.5 Experimental setup for the PA method and PA cell	9
Figure 2.6 Principle of photothermal beam deflection spectroscopy	10
Figure 2.7 Experimental setup of laser flash method.....	10
Figure 2.8 Conventional experimental setup for the PR technique	12
Figure 2.9 Experimental setup of front-detection photothermal radiometry	14
Figure 2.10 Experimental setup of back-detection photothermal radiometry.....	15
Figure 2.11 Thermal diffusivity measurement results according to expanded graphite volume fraction. Measurement errors are also provided	18
Figure 2.12 The comparison between thermal conductivity determined from the absolute value of PTR amplitude and from $k=\alpha C$	20
Figure 2.13 The comparison between thermal conductivity determined from the PTR amplitude value and from $k=\alpha C$	22
Figure 2.13 A schematic view of the frequency/spatial scan PTR experimental setup	23
Figure 3.1 A semi-infinite and homogeneous solid sample excited by a modulated radiation. The surface is the plane $x = 0$	26

Figure 3.2 Special scenarios arising from the interactions between three characteristic lengths: μ , d and β^{-1} in (a) optically thick materials (Case 1) and (b) in optically thin materials (Case 2).....	27
Figure 3.3 Experimental phase and amplitude values with linear fits of BD-PTR frequency spectra for a typical opaque polymer composite	33
Figure 3.4 The flow chart of the thermal diffusivity measurement procedure	35
Figure 3.5 Temperature of sample, where T_{ac} , T_0 , and T_{dc} are the alternative, ambient and continued temperatures, respectively.....	37
Figure 4.1 Schematic representation of GnPs-CB network in EPDM matrix.....	43
Figure 4.2 Schematic view of preparation process of EPDM based composites.....	46
Figure 4.3 SEM pictures of a) EPDM/CB20, b)EPDM/CB50, c) EPDM/CB20/G1-3phr, d) EPDM/CB20/G1-7phr, e) EPDM/CB50/G1-3phr, and f) EPDM/CB50/G1-7phr nanocomposites.. ..	48
Figure 4.4 TEM images of (a) EPDM/CB50, and (b) EPDM/CB50/G1-7phr composites	49
Figure 5.1 The schematic view of photothermal radiometry experimental setup.....	52
Figure 5.2 Illustration of modified low frequency PTR.....	52
Figure 5.3 Laser output power measurement.....	53
Figure 5.4 Determination of focal point.....	56
Figure 5.5 Transmission of ZTP135-SR thermopile sensor	57
Figure 5.6 A scheme of the principle of lock-in amplifier.....	58
Figure 5.7 Amplitude and phase of the electronic transfer function.....	59
Figure 5.8 Demonstration of BPW21R sensor and electric circuit diagram of transimpedance amplifier	60

Figure 5.9 Experimental measurement of thermal diffusivity of HDPE reinforced with
a) M12-MWCNT and b) M58-MWCNT composites according to MWCNT
volume fraction..... 61

Figure 5.10 Experimental measurement of thermal diffusivity of HDPE reinforced
with Al nanoparticles as according to Al volume fraction 62

Figure 6.1 Relative thermal conductivity of the EPDM composites according to phr of
GnPs loadings..... 67

Figure 6.2 Relative thermal conductivity of EPDM/hybrid composites according to
GnP loadings 68



LIST OF TABLES

	Page
Table 2.1 General detection methods in photothermal spectroscopy.	5
Table 2.2 Summary of studies utilized PTR method for investigation of polymer composites:	17
Table 4.1 Properties of graphene nanoplates	45
Table 4.2 Formulation of the EPDM-based nanocomposites	46
Table 5.1 Uncertainty Sources	63

CHAPTER ONE

INTRODUCTION

1.1 Motivation and Overview of Thesis

The Photothermal radiometry (PTR) method has proven to be an effective and versatile method for the nondestructive assessment and thermophysical characterization in a wide range of material types such as semiconductors, metals, opaque materials, multi-layer composites, coatings and thin films. The PTR provides information on the thermophysical and absorption properties of materials or components by varying the modulation frequency between 0.1 Hz and 1 MHz. The method can also be utilized as a tool for surface characterization and detecting defects of subsurface and contact resistances (Liu & Mandelis, 2009). However, the high installation cost of the experimental setup and the large number of system parameters are considered to be disadvantageous. These disadvantages prevent PTR from being as practical as similar testing instrumentation used for industrial materials.

To eliminate the disadvantages of the photothermal radiometry method due to the simultaneous measurement of different properties in a wide sample range, a modified low frequency PTR as a promising user-friendly and easy-to-install instrumentation technique was developed for polymer composites. Polymer composites easily ensure the requirement of being opaque to excitation irradiation and, within the infrared radiation (IR) range, they are suitable samples for PTR measurements. The generated PTR signal is reasonably high since it has a strong IR emissivity (Chirtoc et al., 2016). That allows low excitation powers and obtaining thermal diffusivity at low frequency range and enables improvements to be made on experimental equipment used for excitation, modulation and detection in the experimental setup.

This study is divided into four main sections. The 2nd Chapter presents a literature survey including thermal characterization methods in detail. After that, studies in which photothermal radiometry was developed and used to measure the thermal diffusivity of polymer composite were stated. The theoretical background of

modulated photothermal radiometry is detailed in the 3rd Chapter. In Chapter 4, detailed information on measured samples is indicated. In Chapter 5, the new experimental setup, explaining the sub-equipment used for excitation, modulation, and detection is presented. The calibration and validation of the experimental setup are also evaluated in this section. In Chapter 6, the EPDM composites reinforced with carbon nanofillers are introduced as measurement samples and the results and discussions are given. Finally, the conclusions and future works are specified in the 7th Chapter.

1.2 Objectives of Thesis

The focus of this thesis is to develop a modulated low frequency photothermal radiometry method for thermal characterization of polymer composites. The followings are the objectives:

- Design and development of modulated low frequency photothermal radiometry for the thermal characterization of polymer composites
- Assessment of accuracy and validation of modulated low frequency photothermal radiometry
- Investigation of thermal conductivity of EPDM composites reinforced with carbon black and graphene nanoplatelets fillers and their hybrid combinations. Research on the synergistic effect of carbon-based fillers on thermal properties of hybrid polymer composites.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

In the literature, various methods have been utilized to measure the thermal conductivity of polymer composites. Thermal conductivity measurement methods are mainly divided into steady state and transient state techniques.

Steady state measurement techniques use Fourier's law for thermal conductivity calculations, and measurement is conducted once the system reaches a thermally steady state. In these approaches, thermal conductivity is evaluated based on the heat power applied using an absolute value or referencing another material. Heat flux meter and guarded hot plate techniques are examples of steady-state methods (Rides et al., 2009). In steady state measurement methods, obtaining accurate results is difficult due to the uncertainties and heat losses due to the temperature sensor (Kramer & Chen, 2014).

Compared to steady state methods, unstable state or transient methods are more advantageous due to their short test time, high sensitivity and the ability to measure small samples (Mehra et al., 2018). Some transient measurement methods provide the thermal characterization of materials by using photothermal effects on the sample.

The literature review is divided into three sections. In the first one, an overview of photothermal methods is presented. The second section explains the numerous studies that utilized photothermal radiometry for the thermal characterization of polymer composites. In the third one, we present the application areas of the photothermal radiometry method.

2.2 Photothermal Techniques

Photothermal (PT) techniques have been widely used to determine the thermal and non-thermal (optical, electronic, elastic, etc.) characterization of various materials, thanks to their outstanding sensitivity and ability to conduct nondestructive evaluations of materials in a short time (Vargas & Miranda, 2003). PT spectroscopy has been utilized to obtain the sample temperature, acoustic velocity, thermal conductivity, thermal diffusivity, thermal effusivity, specific heats, bulk sample flow rate and thermal expansion coefficient in solids. (Bialkowski, 2019). PT effects can be determined through multiple approaches that form the foundation of different PT methods (Almond & Patel, 1996; Hess & Boccara, 1989). The basic physical processes in the signal generation of PT spectroscopy are demonstrated in Figure 2.1.

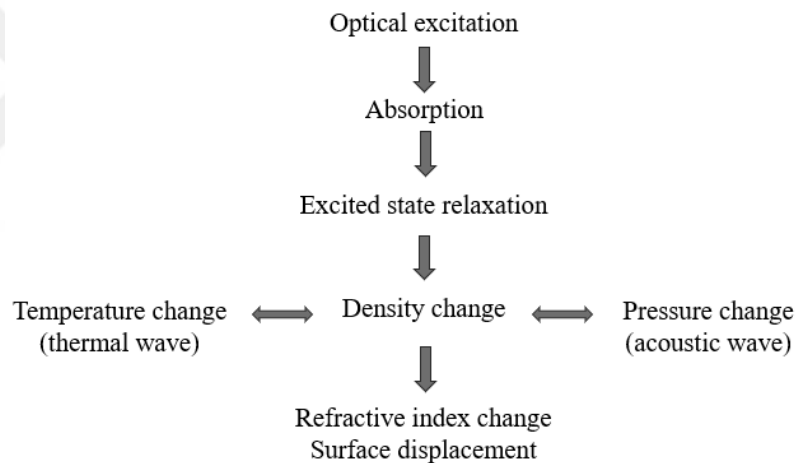


Figure 2.1 Physical processes in photothermal spectroscopy (Bialkowski, 2019).

In PT spectroscopy, a sample absorbs laser light energy, leading to an increase in its internal energy, and will relax with different de-excitation processes such as photochemical reactions and/or radiative de-excitation. Generally, the excitation of the sample is performed by using a pump laser within the visible wavelength spectrum. Photothermal effects emerge when the excess stored energy is transformed into heat until it reaches a state of thermal equilibrium (Chirtoc et al., 2016; Tritt, 2005). PT phenomena of optical heating of the sample are illustrated in Figure 2.2. The optical energy absorption will lead to a temperature variation, which influences the sample's

density in combination with other properties. Pressure is one of the parameters dependent on temperature generally utilized in PT spectroscopy. When the temperature increase within the absorbing sample's volume transpires more rapidly than this volume can expand, it results in an increase of local pressure (acoustic wave) (Galovic et al., 2010).

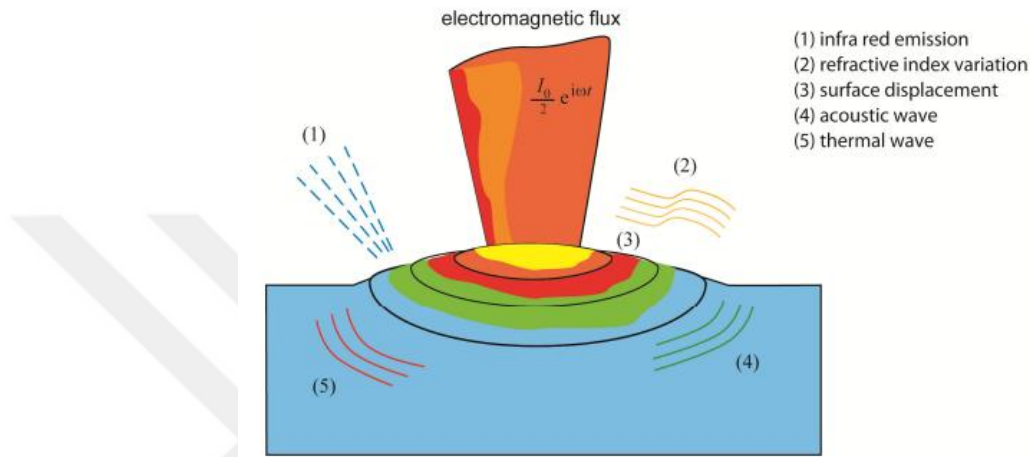


Figure 2.2 Photothermal phenomena of optical heating of the sample (Galovic et al., 2010).

The fundamental of PT techniques relies on measuring variations in pressure, density or temperature resulting from optical absorption. In addition, sensitive PT techniques rely on detecting the refractive index variation that arises with changes in the density and temperature of the material (Bialkowski, 2019). These techniques are determined in Table 1.1 according to measured properties.

Table 2.1 General detection methods in photothermal spectroscopy (Bialkowski et al., 2019):

Parameter	Detected Property	Detection method
Temperature	Temperature	Calorimetry
	Infrared emission	Infrared emission
		PTR
Pressure	Acoustic wave	PA spectroscopy
Density	Refractive index	PT lens
		PT interferometry
		PT deflection
		PT diffraction
	Surface deformation	PT deflection
		PT mirror

In recent years, contact and noncontact photothermal methods have been widely utilized for the thermal and optical characterization of different composite materials. In contact PT techniques, a heat or temperature flow measurement sensor is positioned in contact with a sample and dynamic temperature changes in the sample can be measured directly. Besides, in noncontact PT methods, the detection is carried out remotely and therefore, temperature changes due to various physical phenomena such as pressure variation, infrared emission, etc., that occur in a sample during thermal excitation (Kuriakose, 2013).

In general, contact PT methods directly measure the dynamic temperature changes in a material due to periodic heating. Because effective direct contact is necessary, materials must have the property of adhering well to prevent any voids or air gaps. For this reason, the range of applications is restricted but can be expanded through the help of suitable coupling fluids (Kusiak et al., 2013). On the other hand, each non-contact PT Technique stands out for its unique measurement ability and application potential. In comparison with the contact techniques, the virtue of non-contact probing is to provide more applicability (Kusiak et al., 2013). In recent years, many experimental PT methods have been developed and applied. Several common PT techniques are introduced in the following sections.

2.2.1. Photopyroelectric Technique

The photopyroelectric (PPE) technique, first developed in 1984 (Mandelis, 1984; Dadarlat et al., 1984), is a contact PT method that utilizes the pyroelectric properties of materials to measure temperature variations in samples exposed to modulated radiation. The pyroelectric effect relies on the ability of piezoelectric crystals to produce a temporal voltage due to heat flux changes leading to spontaneous polarization. In the typical PPE technique, a modulated laser light source ensures necessary temperature variation within the sensor by interacting with the material that is in contact with it. The pyroelectric sensor produces electrical signals that encapsulate both the optical and thermal properties by integrating the temperature

oscillations, and these signals are transmitted to a lock-in amplifier through a preamplifier (Chirtoc et al., 2016). Commonly used pyroelectric sensors are polymers such as polyvinylidene difluoride, ceramics such as Pb-Zr-Ti oxides and crystals such as LiTaO₃. A conventional experimental view of the PPE technique is demonstrated in Figure 2.3; the laser light beam is modulated by using an acoustic-optical modulator (AOM) and the photopyroelectric signal is analyzed by a lock-in amplifier (Dadarlat & Neamtu, 2009). The thermal properties of the samples are obtained by analyzing these PPE signals and using a convenient theoretical model (Chirtoc & Mihilescu, 1989).

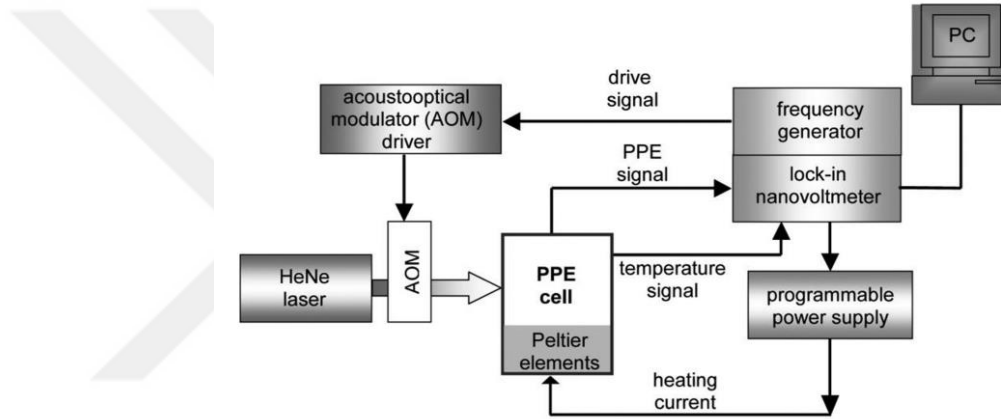


Figure 2.3 Conventional experimental setup for the PPE technique (Dadarlat & Neamtu, 2009).

The PPE technique has been widely used thanks to its advantages such as simplicity, non-destructive character and high sensitivity. Two different PPE detection configurations, namely back detection (BD) and front detection (FD), are generally employed for spectroscopic and calorimetric studies, respectively (Dadarlat et al., 2022). Figure 2.4.a. demonstrates the experimental setup of FD-PPE including the pyroelectric sensor being directly exposed to irradiation and the material being contact with the rear surface of the sensor. Conversely, Figure 2.4.b. shows the BD-PPE cell involves a modulated laser beam that strikes the sample's front surface with a pyroelectric sensor positioned at the sample's rear surface.

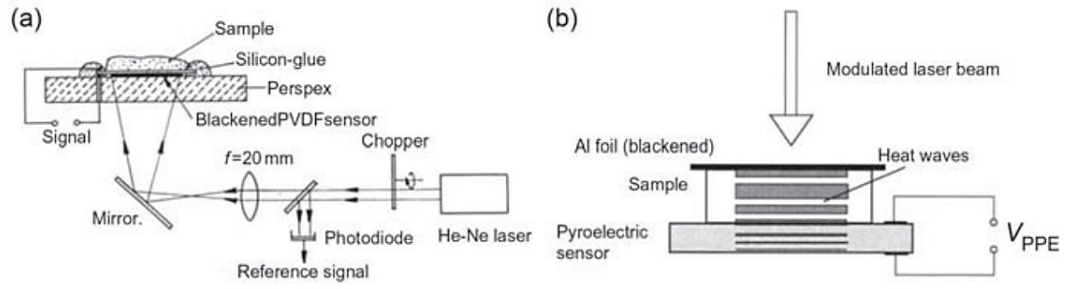


Figure 2.4 a) FD-PPE experimental setup, and b) design of a BD-PPE cell (Bicanic et al., 1994).

2.2.2. Photoacoustic Spectroscopy

The basic principle behind the photoacoustic (PA) method relies on detecting generated acoustic waves from the sample under exposure of periodical excitations, typically from a laser. The PA technique was first introduced by Rosencwaig & Gersho (1976) to measure thermal diffusivity by adding optical thermal energy conversion in the equation of heat diffusion. This technique has advantages under various measurement conditions (e.g., under a magnetic field) (Kuriakose, 2013).

The photoacoustic effect is based on generating acoustic waves within a material due to photon absorption. When the sample absorbs the excitation source, contraction and thermal expansion of the material's surface bring about the neighboring air to compress and expand periodically, producing an acoustic signal (Bialkowski et al., 2019; Hua, 2013). The sample is positioned in a PA cell with a dedicated microphone. The acoustic signal is measured by a microphone and sent to a lock-in amplifier which enhances the detection sensitivity (Rincon et al., 2018). These detected PA signals are stored as amplitude and phase values and analyzed to obtain the sample's thermal properties. The conventional experimental setup for the PA method is demonstrated in Figure 2.5.

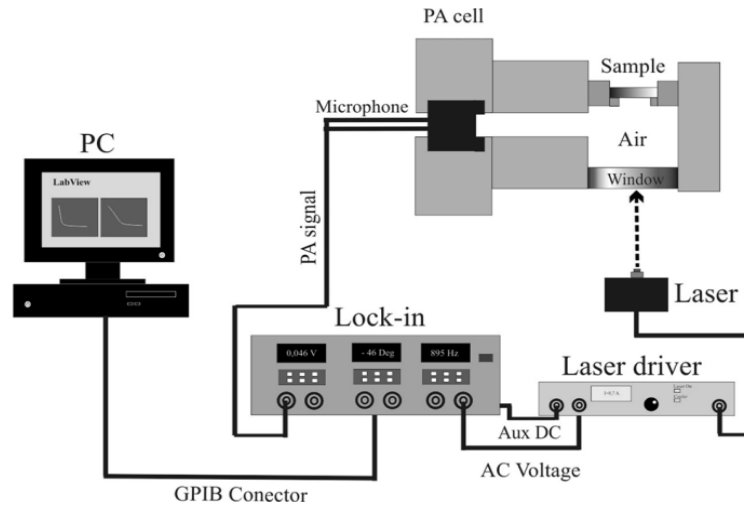


Figure 2.5 Experimental setup for the PA method and PA cell (Ramirez-Rincon et al., 2018).

2.2.3. Photothermal Beam Deflection

The spectroscopy of photothermal beam deflection (PBD), also known as the mirage effect, measures the gradient in refractive index corresponding to the temperature variation of the surrounding gas adjacent to the heated surface. As demonstrated in Figure 2.6, a thermally excited sample generates thermal perturbations in the adjacent gas medium, resulting in changes to its refractive index (Warrier et al., 2016). This technique was first described by Boccara et al. (1980). A conventional setup consists of a probe laser and pump laser to detect the refractive index variation and generate thermal waves on a sample surface, respectively, and a position-sensitive detector is also employed to monitor the probe beam deflection. The energy through the heated sample by the pump laser beam requires a finite amount of time to diffuse, and a phase variation arises between the deflected probe beam and the modulated pump beam. The PBD technique obtains phase difference that shows the values in compliance with the sample's thermophysical properties by using suitable theoretical models and analyzing the detector output (Kim et al., 2009).

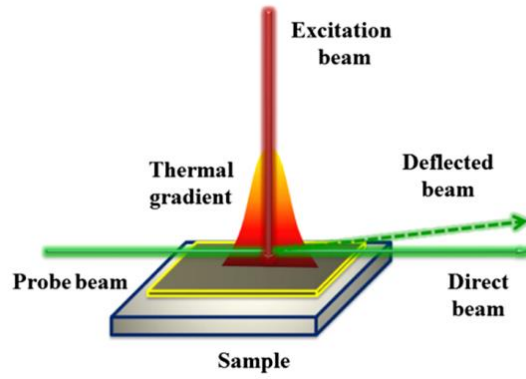


Figure 2.6 Principle of photothermal beam deflection spectroscopy (Warrier et al., 2016).

2.2.4. Laser Flash Technique

The laser flash technique (LFT), first developed by Parker et al. (1961), is commonly utilized to measure thermal diffusivity experimentally. In this time domain technique, the sample's front surface is heated by the energy of a short laser pulse, and the temperature increase of the rear side is detected as a function of time (Chirtoc et al., 2016). The schematic illustration of the experimental setup of the laser flash method is demonstrated in Figure 2.7.

The LFT allows for quick and reliable measurement of thermal conductivity across a broad temperature range between 148-3073 K (Abad et al., 2017). However, LFT requires surface coating, limiting the sample's use for other tests. Also, it cannot be used for the measurement of sub-micrometer thick films due to laser pulse width and detector response limitations (Wang et al., 2019). The LFT measures the thermal flux diffusion speed based on the propagation of the temperature wave in the sample. In contrast, other PT techniques can individually assess phase and amplitude changes, offering more precise local thermal measurements (Hua et al., 2015).

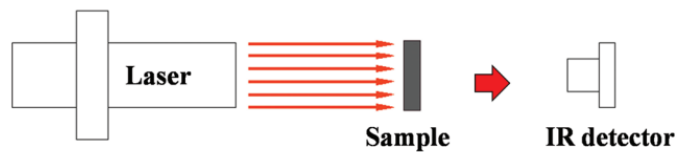


Figure. 2.7 Experimental setup of laser flash method (Wang et al., 2019).

2.2.5. Photothermal Reflectance

The photothermal reflectance (PR) method relies on the optical reflectivity change of a sample in response to the temperature variation and was first introduced by Rosencwaig (1985). A conventional experimental setup of PR is demonstrated in Figure 2.8. One modulated laser is utilized to heat the sample, while a separate probe laser is utilized to detect the variation in optical reflectance, which indicates changes in temperature. The reflected beam power depends on the material's reflectivity, and a detector detects reflectivity variations in the signal through an optic bandpass filter. The phase lag to the reference signal is analyzed with a lock-in amplifier. The system phase shift is obtained by detecting the phase value of the reflected heating laser while the probe laser is deactivated. Thermal diffusivity is obtained from the change of the signal phase to the phase shift of the system. (Bu et al., 2008; Hua et al., 2015).

This technique has some requirements: i) a specimen exhibits a significant temperature coefficient of optical reflectivity, ii) high reflectivity at the wavelength of probe laser and iii) high absorptivity at a modulated wavelength of heating laser. All these necessitates can be met by applying a specific metal film coating to the sample that absorbs photons of specific wavelengths and polishing the sample to increase overall reflectance (Hua Z., 2013).

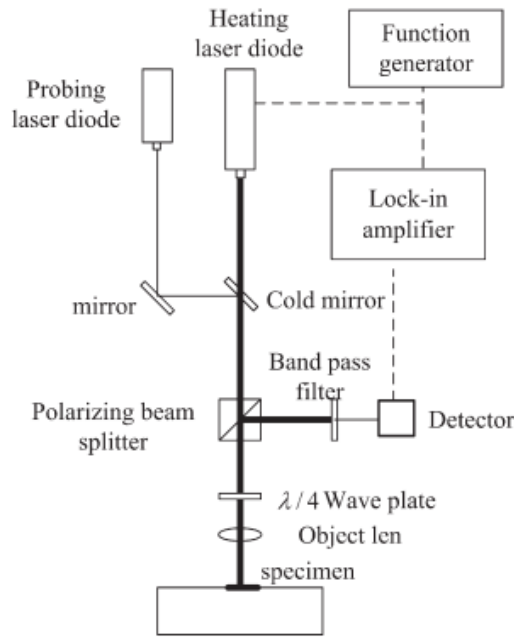


Figure 2.8 Conventional experimental setup for the PR technique (Bu et al., 2008).

2.2.6. Photothermal Radiometry

Among noncontact PT techniques, PTR was first introduced by Nordal & Kanstad (1971). The PTR method is a noncontact and nondestructive measurement method utilized to detect the thermophysical properties of various materials (Guo et al., 2017). The most important capability of PTR is the nondestructive characterization ranging from depths of micrometers to millimeters in inhomogeneous materials or composites via probing the thermal diffusion length by modulation frequency scanning of the incident laser power (Qu et al., 2008).

The basis of method is generally relying on the heating of the material by laser power and the investigation of the IR emitted by the material (Planck's Law) (Nordal & Kanstad, 1971). The IR detector is not sensitive to the laser beam (visible beam). Comprehensive theories of periodically modulated PTR for solids have been formulated in the past by Santos & Miranda (1981) and Tam et al. (1982), and recently Fuente et al. (2011) and Salazar et al. (2011).

A laser beam with the appropriate wavelength is used as the heat source to create a small perturbation of the sample temperature. The sample is heated periodically using a modulated laser beam at a frequency scan. In the classical PTR method, this beam is directed by an AOM (acousto-optical modulator), and the modulated beam is sent through the lens onto the sample. The IR emitted from the sample is collected utilizing parabolic mirrors and then focused on a HgCdTe infrared detector cooled with liquid nitrogen. For a small temperature increase, the measured signal is directly related to the sample's temperature change which is influenced by its thermophysical properties (Almond & Patel, 1996). The signal amplified by the preamplifier in the detector is transmitted to the locking amplifier. The thermal characterization of the sample is specified according to the phase and amplitude values of the signal. It is desired to exclude the effects of the laser beam from the signal received by the lock-in amplifier and to include only sample-induced variations. For this reason, the laser beam directed on the sample is measured by using a photosensor. The measurement results obtained from the sample are examined by correlating them with the photosensor measurement called transfer function. The thermal characterization of samples is carried out with analysis of the phase and amplitude values of the signal.

In this method, one modulated or pulsed laser is utilized to generate a temperature fluctuation. If the heat source is modulated periodically, the heat diffuses away from the absorption location, creating an increase to a non-stationary temperature field that acts similar to a diffusive wave which is critically damped in mathematical terms (Chirtoc et al., 2016). The pulsed PTR effect is where temperature and radiation from the sample surface change harmonically. Both are equivalent in principle. One could say that pulsed detections are quicker than frequency scan. However, periodical modulation provides the needed integration time for the lock-in amplifier to improve the frequency spectrum's signal-to-noise ratio (Chirtoc et al., 2016). Kusiak et al. (2013) presented two different PTR setups –modulated and pulsed, to investigate the thermal properties of thin films. They reported that both techniques show a good agreement on measurement results. The modulated PTR offers greater accuracy and ease of use, while the pulsed PTR provides simultaneous detection of volumetric specific heat and thermal conductivity. The advantage of using modulated PTR over

the pulsed technique is that there is no necessity to know the absorbed heat flux and the absolute temperature.

There are two configurations called BD-PTR (excitation at the opposite side relative to detection) and FD-PTR (excitation at the same side relative to detection). FD-PTR configuration is also referred to as the reflection technique relies on the detected IR emitted from the sample's surface (Figure 2.9). This configuration can be utilized for thick samples and usually provides a high signal-to-noise ratio, since the temperature variations are most significant at the heating point. The amplitude values of thermal waves are the highest at the sample's surface, and if the measured sample is thermally thick making it undetectable at the rear surface (Fleming, 2014). The FD-PTR configuration enables to detect the relative changes of the thermal diffusivity (α) from simultaneous fits on phase and amplitude curves and of the thermal effusivity (e) from the amplitude level of PTR signal.

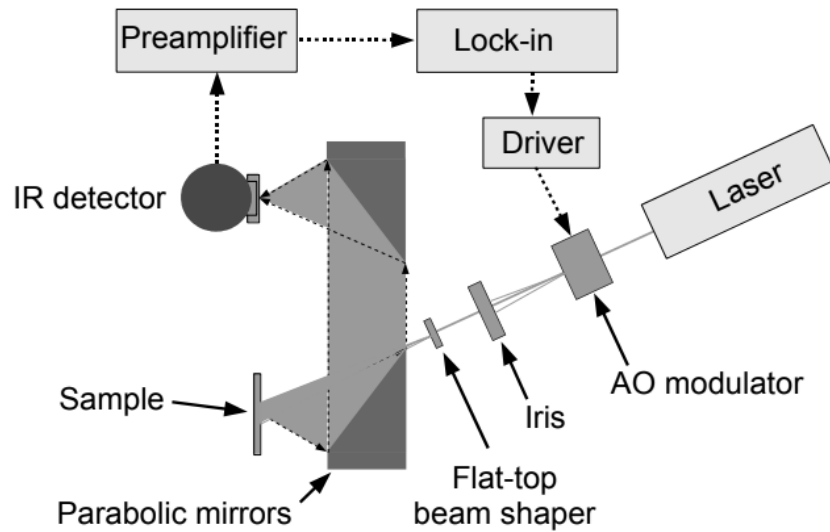


Figure 2.9 Experimental setup of front-detection photothermal radiometry (Horny et al., 2016).

In the BD-PTR configuration, also known as the transmission technique, the thermally induced change on the sample's surface goes through the measured sample and is observed at the back surface (Figure 2.10) (Fleming, 2014). This configuration has a lower signal-to-noise ratio, and it is not proper to use for thermally thick samples. Nevertheless, the BD-PTR method is less influenced by surface features compared to

FD-PTR (MacCormack et al., 1997). The BD-PTR method is more dependable for thermal diffusivity measurement as a consequence of a straightforward self-check process involving matching slopes in both phase and amplitude plots (Chirtoc et al., 2012a).

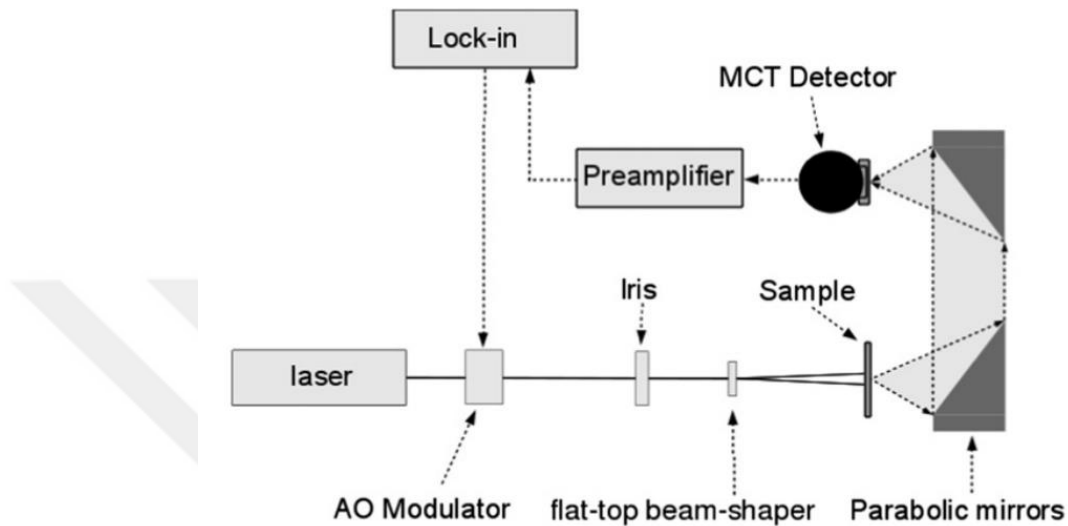


Figure 2.10 Experimental setup of back-detection photothermal radiometry (Chirtoc et al., 2012-b).

Photothermal radiometry (PTR) is advantageous over other techniques thanks to the detection of optical and thermal properties of the material simultaneously, no need to know the emissivity and surface temperature of the material, the non-contact and low error rate measurements. However, the high cost of installation and the excess of parameters to be considered in the installation of the test apparatus are seen as disadvantages. To obtain a reliable measurement, many parameters, such as the detection system (detector, optical geometry, filters and mirror) and laser operation modulation in the installation, must be precisely set up. Many trials should be carried out, especially for a system to be installed for the first time. Wang et al. (2019) compared the merits and disadvantages of characteristics of frequency domain methods such as the 3ω method, calorimetric method, temperature wave analysis method, Ångström's method, photo-thermoelectric method, thermo-reflectance method, modulated PTR, and PA method. The limitation of the PTR method has been reported as the obligatory use of normalization procedures to eliminate the instrumental impact.

Fuente et al. (2012) compare the ability of PPE and PTR methods to determine the most appropriate technique to detect the thermal diffusivity and the optical absorption coefficient of materials. They carried out many measurements on a diverse range of homogeneous samples, opaque and transparent, good and poor thermal conductors. The main advantage of PTR is that it is a noncontact technique ensuring in situ measurements of materials in industrial applications while PPE is a contact technique. The primary virtue of the PPE method is that it has a high signal-to-noise ratio. Thus, with just a few milliwatts of power excitation, the PPE technique ensures quasi noise free signals, while watt-level excitations are needed for the PTR technique. In conclusion, they specified that both methods are complementary and utilized alternatively according to the characteristics of the material.

2.3 Related PTR Studies of Composite Materials

Polymers are extensively utilized in both industrial applications and daily life owing to their ease of processing, lightweight, excellent chemical stability and low cost. However, the low thermal conductivity of polymers remains a significant obstacle to their use in applications such as electronic-packaging and heat exchangers (Chen et al., 2016). Outstanding efforts have been made in exploring the potential of heat-conducting polymer materials. In addition to improving the morphology and structure of polymers, studies have been carried out to provide better heat conduction by adding thermally conductive fillers (Mehra et al., 2018). Thanks to their low cost, high thermal conductivity, hardness and high strength, the demand for ceramic, carbon or metal fillings has increased.

Table 2.2 Summary of studies utilized PTR method for investigation of polymer composites:

Authors	PTR Configuration	Filler	Matrix	Measured Properties
Fuente et al. (2011)	FD	CNT	PLLA	α
Chirtoc et al. (2012a)	BD and FD	EG	HDPE	α, e, β, C
Chirtoc et al. (2012b)	BD	EG, UG	HDPE	α
Medina-Esquivel et al. (2012)	BD	Fe	polyester resin	α
Nesteros (2013)	FD	SWCNT	polymer based	α, k, β
Kuriakose (2013)	FD	MWCNT, SWCNT	PANI	α, e, k
Diaz-Bleis et al. (2014)	BD	carbonyl iron	agar	α
Roussel et al. (2015)	FD	Ag	PANI	α, e, k
Islam (2016)	FD	GO	PANI	α, e, k, C
Horny et al. (2016)	FD	EG	PLA and PBS	α
Evgin et al., (2016)	FD	MWCNT	HDPE	α
Koca et al., (2017)	FD	Al	HDPE	α, e, k
Harris (2018)	BD	CNT, Graphite	polyurethane	α
Evgin et al. (2020)	FD	GnPs	HDPE	α
Radouane et al. (2021)	FD	graphite	epoxy	α, e, k
Evgin et al. (2021)	FD	hybrid (GnPs&MWCNT)	HDPE	α

With the advances in material technology, determination of the thermophysical properties of materials has a great importance for engineering design. In the literature, some studies (Fuente et al., 2011; Medina-Esquivel et al., 2012; Chirtoc et al., 2012a; Chirtoc et al., 2012b; Kuriakose, 2013; Nesteros et al., 2013; Diaz-Bleis et al., 2014; Roussel et al., 2015; Horny et al., 2016; Islam, 2016; Evgin et al., 2016; Koca et al., 2017; Harris, 2018; Evgin et al., 2020; Evgin et al., 2021; Radouane et al., 2021) used the PTR to determine the thermophysical properties of polymer based composites. Table 1.2 summarizes these studies that utilized PTR method for the investigation of polymer composites. The table involves information on the configuration, filler type,

matrix type and measured properties by PTR method. It should be noted that all these studies have modulated excitation. It can be seen that the PTR method can be used for polymer composites with different filling materials and different matrix materials.

Chirtoc et al. (2012a) determined the thermal and optical properties of high-density polyethylene (HDPE) polymer reinforced with expanded graphite (EG5 and EG50) of 5 μm and 50 μm filler sizes. The methods utilized were FD and BD modulated PTR and flash IR thermography with BD configuration. The α was measured using FD-PTR and BD-PTR methods, while the e , C (volumetric heat capacity) and β (optical absorption coefficient) were measured using FD-PTR method. The directly determined α values are compared with those figured out from the C and e , and also by using flash IR thermography results. There is a strong consistency between α values determined by these three different techniques and those calculated from the mix of the C and e . The maximum scatter between different measurement techniques is less than 15%. Overall, the PTR technique can handle the characterization of semi-transparent materials better in comparison with BD-flash. Also, they concluded that FD-PTR configuration enables to determine the relative variations of the C and e from amplitude levels of signal, and of the α and β from simultaneous fits on phase and amplitude curves (Chirtoc et al., 2012a).

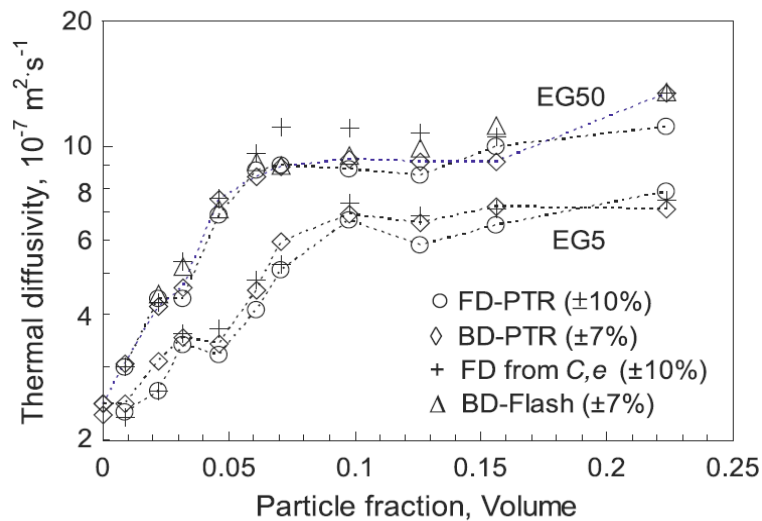


Figure 2.11 Thermal diffusivity measurement results according to expanded graphite volume fraction. Measurement errors are also provided (Chirtoc 2012a).

Nesteros (2013) indicated that PTR can characterize the optical and thermal properties polymer-based composites. They reported that the PT signal (phase and amplitude) is highly sensitive to changes in SWCNT's (single wall carbon nanotube) concentration and the film thickness of the polymer. They also found that the addition of CNTs led to an enhancement in thermal conductivity and should be a corresponding decrement in signal amplitude. Horny et al. (2016) measured the thermal diffusivity of PBS and PLA polymer composites using modulated FD-PTR. They noticed that the uncertainty of the method is 5%. For the thermal characterization of PANI/MWCNT (multi-wall carbon nanotube) composites, Kuriakose (2013) used the PTR measurements as a validation of results from another PT method.

Chirtoc et al. (2012b) validated the BD-PTR measurement results with laser flash measurements on the HDPE composites filled with EG and unexpanded graphite (UG). They reported that the primary source of error (7%) resulted from the change of thickness over the surface of the sample. Medina-Esquivel et al. (2012) also utilized the modulated PTR with BD configuration for the thermal characterization of polyester resin composites reinforced with carbonyl iron particles. In addition, Harris (2018) selected the BD-PTR for the thermal characterization of polyurethane matrix reinforced with CNT and graphite flakes due to the simplicity of the experimental setup and its ability to obtain through-thickness properties easily.

Koca et al. (2017) examined the thermal properties of HDPE polymers reinforced with nano-sized Al fillers by using modulated PTR. The relative thermal conductivity of polymer composites was computed from PTR measurements and the measurements of density, specific heat capacity and thermal diffusivity (measured from FD-PTR). As seen in Figure 2.12, the thermal conductivity values determined with PTR measurements closely align with the one computed by three independent values. The uncertainty of measurements is indicated as 5%.

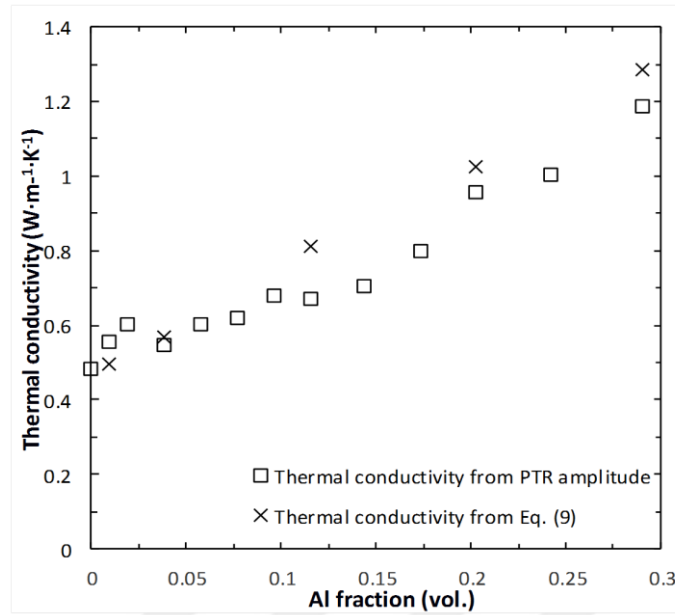


Figure 2.12 The comparison between thermal conductivity determined from the PTR amplitude value and from $k = \alpha C$ (Koca et al., 2017).

Islam (2016) determined the thermal diffusivity, thermal conductivity, volumetric heat capacity and thermal effusivity of PANI composites reinforced with reduced graphene oxide (GO) by modulated FD-PTR. They computed the C using α and e values. Roussel et al. (2015) investigate the thermal diffusivity and thermal conductivity of polyanilines (PANI) composites reinforced with Ag filler. By utilizing modulated PTR, both thermal property of the materials is simultaneously obtained ensuring the computation of the thermal conductivity.

2.4 Application Area of PTR

The PTR provides valuable insights into the thermophysical and absorption properties of materials that are crucial for both scientific research and engineering applications as well as for environmental monitoring. This method can also be utilized as a tool for surface characterization and detecting defects of subsurface and contact resistances (Liu & Mandelis, 2009). The PTR method has been evaluated in the literature for different vital application areas. Beyond its applications in applied physics, PTR has also been utilized in biomedical studies, including research on skin,

teeth, bone and hair (Fomina & Proskurnin, 2022; Guo et al., 2018; Xing et al., 2019; Biris et al., 2009; Torres et al., 2009).

Guo et al. (2018) demonstrated that wavelength modulated PTR (WM-PTR) can be utilized to carry out precise and accurate non-invasive blood alcohol measurement via the alcohol levels which are dependent on the interstitial fluid (ISF) by determining the alcohol (ethanol) absorption band in the IR range. Xing et al. (2019) determined that detecting non-cavitated proximal caries poses a challenge, and PTR is a suitable technique capable of scanning from occlusal, lingual and buccal directions of a proximal surface. Guo et al. (2019) indicated a non-invasive and non-contacting biosensor utilizing WM-PTR to assess blood glucose concentration (BGC) levels by probing ISF in the fingers of humans. They indicated a strong correlation between the BGC measurement results and the WM-PTR signals showing that WM-PTR offers a reliable noninvasive glucose measurement in the ISF.

Biris et al. (2009) presented the nanophotothermolysis including long laser pulses for the treatment of scattered cancer cells with a focus on real-time monitoring of laser heating of individual cancer cells labeled with CNT. Torres et al. (2009) showed that the PTR method can be used as a depth profilometric method for examining dental resin photopolymerization. They found a correlation between the α and the average curing level that enabled an analysis of the photopolymerization depth dependence utilizing depth profiles of the thermal wave.

The fact that the system parameters of the PTR method can differ according to the material under characterization increases the interest in the method and encourages researchers to do new studies for the assessment of the capabilities of the system. The flexibility that occurs by PTR enables its use in a wide range of fields and applications (Corona & Kandadai, 2023).

Mandelis (2001) presents the PTR as a promising nondestructive testing instrumentation technique for industrial materials by investigating case studies including semiconductor Si wafers, engineering steels and thermal-barrier coatings.

Salazar & Mendioroz (2022) utilized the modulated PTR in order to characterize the quality of laminated materials. They reported that the depth and size of delamination of layers, which occur due to defects in laminated materials, could be measured by modulated PTR.

Zeng et al. (2020) developed a general specialized PTR for high-temperature characterization considering both temperature uniformity and heat loss. They reported that the method provides an easy-to-use tool for determination of the thermal conductivity at high-temperatures. This method can be used for materials with broad applications, such as concentrated solar power, turbines, coatings of thermal barrier, nuclear reactors etc. Figure 2.13 demonstrates the PTR configuration for high temperature measurement.

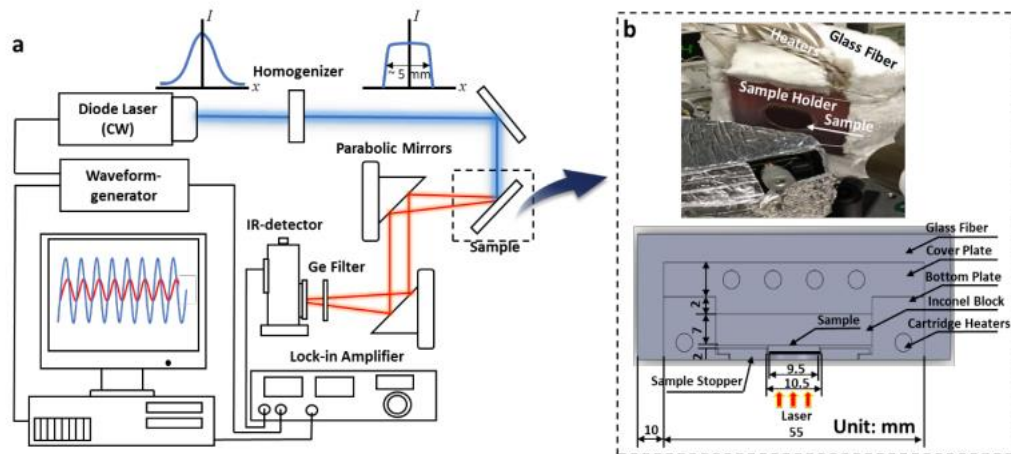


Figure 2.13 (a) Configuration PTR for high temperature measurement and (b) illustration of the high-temperature sample holder (Zeng et al, 2020).

Pawlak et al. (2014) evaluated the correlation between the carrier concentration and the PTR signal in semiconductors. They identified a linear correlation between the Hall carrier concentration and the IR absorption coefficient. They also noticed that the relationship of these properties makes PTR convenient for use in an industrial environment for a contactless and fast carrier concentration measurement and can be utilized for the measurement of other semiconductors. Dadarlat et al. (2011) designed a combined experimental setup that simultaneously used both PPE calorimetry and

PTR together with the thermal wave resonator cavity method. The goal of this novel method is to obtain the thermal effusivity of solids inserted as backing layers in a detection cell. They reported that the PTR can provide information on the first and third layers of a sandwiched cell.

Hamaoui et al. (2020) introduced a new photothermal radiometry setup that combines the spatial domain and frequency scans, supported by a 3D heat diffusion model. The new measurement system enables experimentally obtaining both isotropic and anisotropic thermal properties in various types of materials, including membranes. In this setup, a laser diode is governed by using a frequency generator. A lens converges the beam and focuses it onto the mirror, then transmits it into the sample. The IR signal emitted from the surface of sample is collected by a reflective microscope objective and focused on a detector. The schematic view of the new PTR system is demonstrated in Figure 2.14. The mirror is positioned on the convex spherical mirror's blind side (Hamaoui et al., 2020).

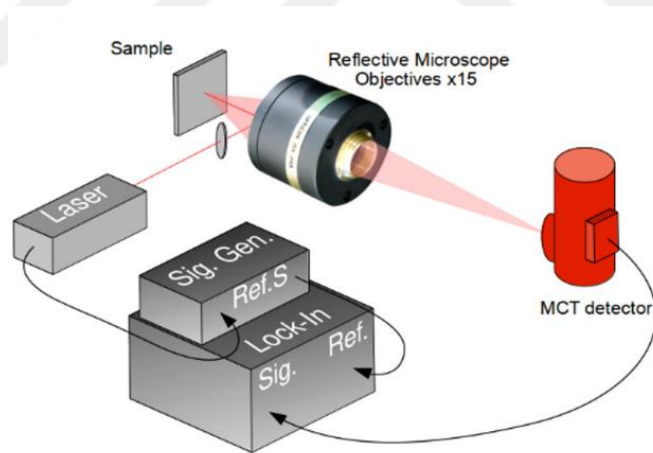


Figure 2.14 A schematic view of the frequency/spatial scan PTR experimental setup (Hamaoui et al, 2020).

CHAPTER THREE

THEORY

3.1 Introduction

This chapter primarily includes the theoretical descriptions of photothermal radiometry with back detection configuration developed in this research. The discussion began with an explanation of thermal diffusion length and the equation of heat diffusion, followed by an analysis of 1D heat transfer for the periodical temperature oscillations in a heated body generated by a periodic heat source. Later, the slope method is introduced to determine the thermal diffusivity by recording both the amplitude and phase profile slopes.

3.2 Thermal Diffusion Length

The thermal conduction in solid samples is reached through the synergy of the electron and quasi-particles, known as phonon transport. Here, a phonon represents a quantized unit of lattice vibrational energy that contributes to heat diffusion through the oscillation of the material's lattice structure. In the case of metallic materials, electrons primarily dominate the process of thermal conduction. However, the thermal conduction process in polymers can be attributed to the process of phonon transfer. During the process of phonon transfer, different forms of phonon scattering arise. This contains scattering between individual phonons as well as scattering between phonons and interfaces, which is influenced by the presence of defects in the material. (Zhang et al., 2019). To understand the phonon conduction in materials, which is affected by various factors, the thermal diffusion length is an essential parameter for determining the heating regime (Hamaoui, 2018).

The thermal diffusion length, μ , gives the distance (m) where an appreciable energy transfer occurs from the surface of a periodically heated body. A phase lag, represented by the term $(x/\mu + \pi/4)$ in the complex exponent, exists between the thermal response of the sample and the laser light excitation (Marin, 2009). The phase at the heating

spot's center is specified by both the heating laser diameter and the thermal diffusion length. If the laser beam is focused and thermal diffusion length is considerably greater than the diameter of the heating laser, then the phase value will initiate at 0° at the center of the spot and decay from there. As the spot size expands, the phase lag at the laser spot's center will also increase until it reaches -45° , where the thermal diffusion length becomes much smaller than the diameter of the laser spot, providing 1D heating (Fleming, 2014).

$$\mu = \sqrt{\frac{2\alpha}{w}} = \sqrt{\frac{\alpha}{\pi f}} \quad (3.1)$$

At high-frequencies, thermal waves propagate faster but nearer, and this causes the thermal diffusion length will be very short. At low-frequencies, thermal waves propagate more slowly but further; hence this causes an increase in thermal diffusion length and allows us to have more useful information about the sample.

3.3 Theoretical Background of PTR

When a sample absorbs electromagnetic radiation, it will relax through various de-excitation processes. Photothermal effects occur when the stored excess energy in electronically excited states is transformed into heat energy till the achievement of thermal equilibrium. The temperature change is detected according to temperature dependent thermophysical properties of the material and those of the neighboring medium (Chirtoc et al., 2016).

The determination of the periodical temperature oscillations in a heated body with a periodical heat source is pointed out in Figure 3.1. These thermal oscillations can be defined as thermal waves. An isotropic and homogenous semi-infinite or opaque solid that neglects what happens at the back surface is considered a sample.

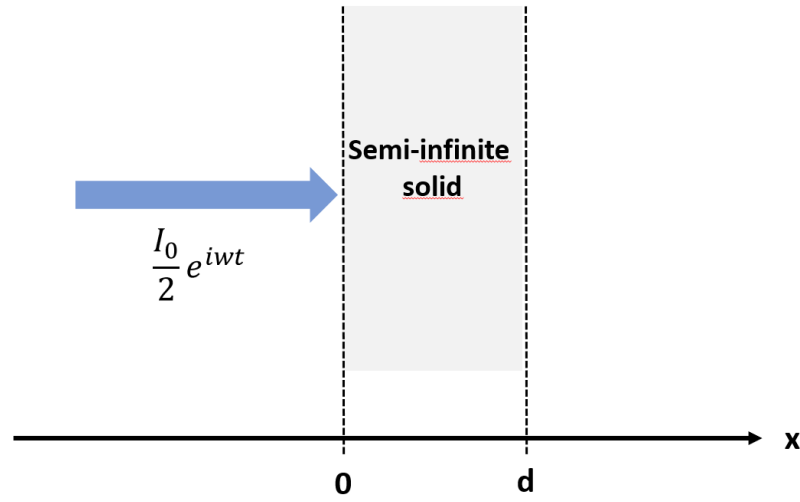


Figure 3.1 A semi-infinite and homogeneous solid sample excited by a modulated radiation. The surface is the plane $x = 0$.

The incident radiation energy is completely absorbed by the surface of the sample and entirely converted into heat. Using the configuration mentioned in the experimental setup section, the heating spot shape is circular, and the surface of the sample is illuminated uniformly. For this reason, it is considered as 1D heating. This consideration is due to the fact that the spot size of the laser in meters is smaller than the detector's opening, leading to a 1D heating (Hamaoui et al., 2018). In addition, Almond & Patel (1996) determined that when the size of the heating spot is greater than 20 times the thermal diffusion length, the heating regime adheres to a 1D solution, at which the sample's surface is heated uniformly.

A medium is said to be optically thick or opaque if on average a photon generally cannot pass through the medium without being absorbed. On the other hand, a transparent medium is said to be optically thin. In the case of 1D heat diffusion through a semi-transparent slab, there are three key characteristic lengths: the thermal diffusion length (μ), thickness (d) and the optical absorption coefficient (β^{-1}) of the sample. Figure 3.2 gives the special scenarios arising from the interactions between these three important characteristic lengths: μ , d and β^{-1} . The favorable case in the back detection PTR is Case 1b., $\beta^{-1} < \mu < d$ (nearly thermally thick) for photothermal spectroscopy.

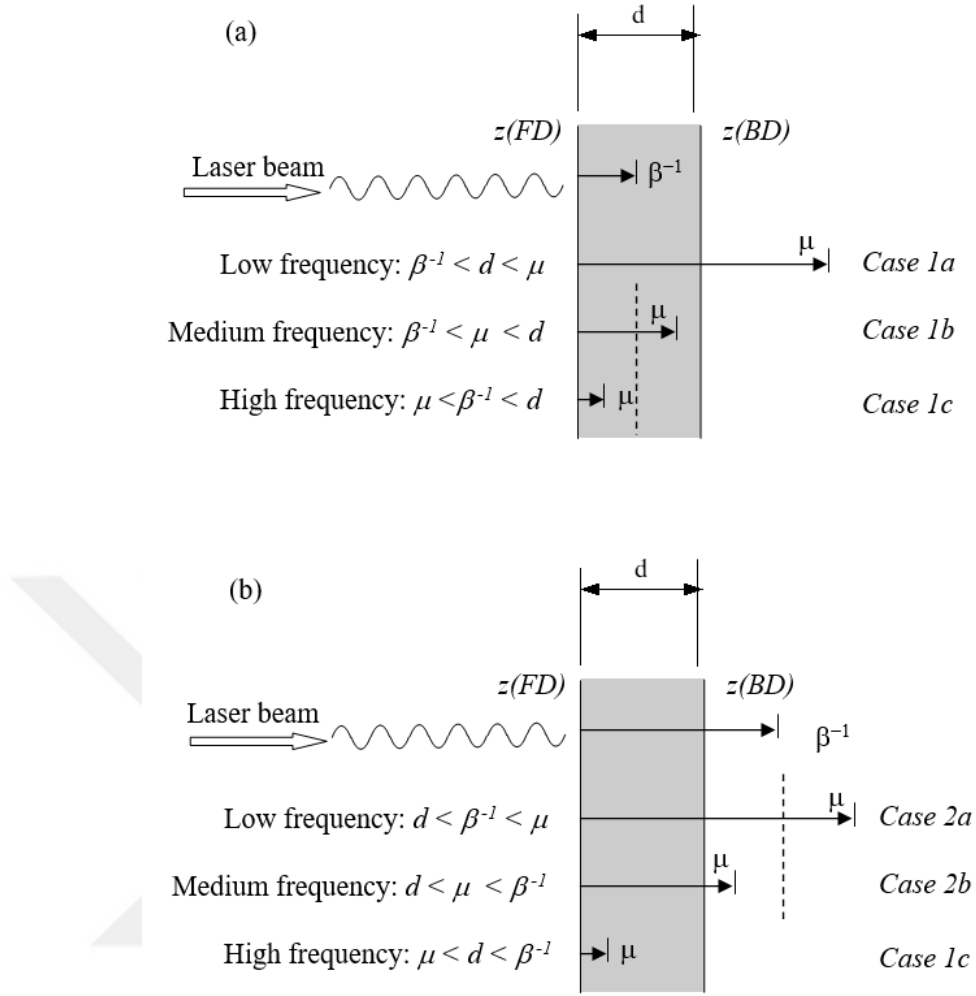


Figure 3.2 Special scenarios arising from the interactions between three characteristic lengths: μ , d and β^{-1} in (a) optically thick materials (Case 1) and (b) in optically thin materials (Case 2) (Chirtoc et al., 2016).

The temperature variation within the solid sample, denoted as $T(x, t)$, can be found by solving the equation of heat diffusion (Marin et al., 2009).

$$\frac{\partial^2 T(x, t)}{\partial x^2} - \frac{1}{\alpha} \frac{\partial T(x, t)}{\partial t} = 0 \quad \text{for } x \geq 0 \text{ and } t > 0 \quad (3.2)$$

To simulate a standard IR radiometry setup, we take into account an optically-opaque sample neighbored by air, which absorbs a sinusoidal modulated laser light source at its surface located at $x=0$, enabling a 1D description (Martinez et al., 2015). To ease of understanding, we assume all the incoming laser light energy is transformed

into heat. The modulated component of the laser intensity is represented by the real part (Re denotes the real part) of $(I_0/2)e^{i\omega t}$, where t is the time, I_0 (W/m²) is the laser source intensity, and $\omega = 2\pi f$ represents the angular modulation frequency. The temperature field's sinusoidal part in the sample can be determined by the equation of heat diffusion. The boundary condition (Salazar et al., 2010):

$$-k \frac{\partial T(x,t)}{\partial x} \Big|_{x=0} = \text{Re} \left[\frac{I_0}{2} e^{i\omega t} \right] + H(T_{x=0} - T_\infty) \quad (3.3)$$

$$-k \frac{\partial T(x,t)}{\partial x} \Big|_{x=d} = H(T_{x=d} - T_\infty) \quad (3.4)$$

H [W/m²K] is the overall heat transfer coefficient that states for both radiative and convective heat losses from the sample's surfaces $H = h_{rad} + h_{conv}$, where h_{conv} is the part for natural convection and h_{rad} related to radiation (Martinez et al., 2015). In the context of stationary heat conduction, Biot's number, Bi , is calculated as $Bi = R_T H$, where $R_T = d/k$ is the thermal resistance for conduction in a homogenous solid sample (Cowan, 1961). Bi number gives the ratio of the thermal resistance of the solid sample that opposes radiation and convection heat losses. When c , conduction heat transfer, in dependence on the laser light intensity I_0 , is more efficient than heat losses by radiation and convection; thus, these losses can be neglected (Martinez et al., 2015).

For non-stationary periodical heating, a frequency-dependent equivalent of the Biot number, M , is used instead of Bi number (Chirtoc, 2009):

$$M = \frac{H\mu}{k} \quad (3.5)$$

M gives the fraction of the solid sample's thermal impedance that counteracts losses due to the radiation and convection heat transfer. The frequency-dependent equivalent of the Biot number is a dimensionless quantity that also be expressed in terms of $e = k/\sqrt{\alpha}$ and the argument, z , which can be considered as the thermal impedance, in analogy, as the temperature gradient between two surfaces of a thermal conductor

divided by the heat flux passing through the conductor. In this context, z represents the ratio between the variation in the thermal wave flux and thermal wave amplitude (Marin et al., 2009):

$$M = \frac{H}{\left[e(\pi f)^{\frac{1}{2}} \right]} = Hz \quad (3.6)$$

When M is much less than 1 ($M \ll 1$), at high frequency limits, the effectiveness of heat transfer by conduction within the sample is significantly more effective than the heat loss due to radiation and convection heat transfer, so that the effects of convection and radiation can be neglected. Martinez et al. (2015) determined that for poor thermal conductors, the combined effect of convection and radiation becomes important at modulation frequencies under 1 Hz. In the modulation frequency range where detection is achieved, the maximum temperature difference remains below 1°C. Since it is calculated that $M < 0.01$ at the minimum frequency operating in this study (0.1 Hz), radiation and convection induced heat losses are not taken into consideration. Thus, to solve Eq. (3.2), the periodic component is assumed as below:

$$T(x, t) = \theta(x)e^{i\omega t} \quad (3.7)$$

Omitting the Re symbol, substituting equation (3.7) in equation (3.2), we obtain;

$$e^{i\omega t} \left(\frac{d^2\theta(x)}{dx^2} - \frac{i\omega}{\alpha} \theta(x) \right) = 0 \quad (3.8)$$

Thus, a partial differential equation given by Eq. (3.2) can be simplified into an ordinary differential equation including constant coefficients, determined by Eq. (3.9),

$$\frac{d^2\theta(x)}{dx^2} - \sigma^2\theta(x) = 0 \quad (3.9)$$

The thermal wave exhibits an oscillatory spatial dependence of the form e^{iwt} , with a complex thermal wave vector (Almond & Patel, 1996):

$$\sigma = \sqrt{\frac{iw}{\alpha}} = (i + 1) \sqrt{\frac{w}{2\alpha}} = \frac{(1+i)}{\mu} \quad (3.10)$$

From the Eq. (3.9), the general solution for the temperature's spatial dependence can be expressed in the following form:

$$\theta(x) = A \exp(-\sigma x) + B \exp(\sigma x) \quad (3.11)$$

In the equation, A and B are arbitrary constants. To find these constants, we consider that as x approaches infinity $T(x)$ must be finite and then the constant B is zero. In this context, Boundary condition (3.3) becomes

$$-k \left. \frac{d\theta(x)}{dx} \right|_{x=0} = \frac{I_0}{2} \quad (3.12)$$

The constant A is determined by enforcing the flux continuity boundary condition at the sample's surface (Almond & Patel, 1996). For $x=0$, inserting the proposal Eq. (3.11) into Eq. (3.12):

$$\frac{I_0}{2} = -k \left. \frac{d\theta(x)}{dx} \right|_{x=0} = (-k)(-\sigma)A \exp(-\sigma x) \quad (3.13)$$

Thus, we obtain the arbitrary constant as $A = I_0/(2k\sigma)$. And the full solution of Eq. (3.3) (Marin et Al., 2009):

$$\begin{aligned} T(x, t) &= \theta(x) e^{iwt} = \frac{I_0}{2k\sigma} \exp(-\sigma x + iwt) \\ &= \frac{I_0}{2e\sqrt{w}} \exp\left(-x \sqrt{\frac{w}{2\alpha}}\right) \exp i \left(wt - x \sqrt{\frac{w}{2\alpha}} - \frac{\pi}{4} \right) \end{aligned} \quad (3.14)$$

3.4 Slope Method

In the case of 1D heat propagation, where the illumination encompasses the entire width of a thin sample, it has been shown that heat losses affect both the slope of amplitude and phase of the oscillating temperature in such a way that the product of these slopes cancels the impact of losses: $m_{phase} \times m_{amplitude} = -\pi f / \alpha$ (Wolf et al., 2004). This method is highly effective for good thermal conductors, alloys, metals, SiC, etc., but this approach fails when applied to filaments and thin films that have low thermal conductivity (Mendioroz et al., 2009).

Mendioroz et al. (2009) investigated the effect of the measurement conditions on the measurement of thermal diffusivity utilizing the slope method to broaden its applicability to various samples. They particularly focused on filaments and thin plates due to the great interest in the thermal property characterization of thin films, and due to the heat loss impacts tend to significantly influence the thermal field of the surface. They also investigated the temperature oscillating of an opaque and anisotropic sample excited by a periodical laser beam.

The slope method needs the employment of low frequencies to minimize the impact of diffraction effects, particularly in the case of materials with poor thermal conductivity. In these conditions, the thermal wave propagates a considerable distance away from the excitation area before vanishing (Mendioroz et al., 2009). All slopes approach to each other with the increasing modulation frequency, indicating that both the heat losses and the dimensions of the material become less influential on the results.

On the other hand, Salazar et al. (2009) determined that using low frequencies also leads to overestimated measurement of the α of poor conductors due to losses. This impact is particularly significant for filaments and thin plates where the overestimations of more than one order of magnitude.

Mendioroz et al. (2009) also recommended using experimental data far away from the laser spot, where phase and amplitude exhibit linear behavior, to get accurate values of the α of anisotropic and isotropic filaments and thin slabs. In this study, since the slope method is considered for the low frequency-dependent equivalent of Biot number, ($M \ll 1$), convective and radiative heat losses are neglected.

In periodic modulation, the photothermal signal from the material's surface (at $x = 0$) is inversely proportional to e . It decreases as a function of $f^{1/2}$, and has a phase lag of -45° (Chirtoc et al., 2016). From Eq. (3.13), amplitude and phase are stated in Eq. (3.15) and (3.16).

$$A = \frac{I_0}{2e\sqrt{w}} \exp\left(-x\sqrt{\frac{w}{2\alpha}}\right) \quad (3.15)$$

$$\varphi = -\frac{x}{\mu} - \frac{\pi}{4} \quad (3.16)$$

As mentioned in the previous section, the BD-PTR signal is effective in the region at which the sample is both nearly-thermally thick ($\mu \leq d$) and opaque. The experimentally obtained phase value (φ') can be specified in Eq. (3.17) using Eq. (3.16) and (3.2) for back detection ($x=d$):

$$\varphi' = \varphi + \frac{\pi}{4} = -d\sqrt{\frac{\pi f}{\alpha}} - \frac{\pi}{4} + \frac{\pi}{4} = -d\sqrt{\frac{\pi f}{\alpha}} \quad (3.17)$$

Eq. (3.14) can be formed in Eq. (3.18) and Eq. (3.19) in logarithm:

$$A\sqrt{f} = \frac{I_0}{2e\sqrt{2\pi}} \exp\left(-d\sqrt{\frac{\pi f}{\alpha}}\right) \quad (3.18)$$

$$\ln[A\sqrt{f}] = \ln\left[\frac{I_0}{2e\sqrt{2\pi}} \exp\left(-d\sqrt{\frac{\pi f}{\alpha}}\right)\right] = \ln\left[\frac{I_0}{2e\sqrt{2\pi}}\right] - d\sqrt{\frac{\pi f}{\alpha}} \quad (3.19)$$

From Eq. (3.19), the experimental amplitude obtained from sample detection and electro-optical setup is stated in Eq. (3.20) and (3.21), respectively.

$$\ln[A\sqrt{f}] \quad (3.20)$$

$$\ln\left[\frac{I_0}{2e\sqrt{2\pi}}\right] \quad (3.21)$$

The thermal characterization of samples is carried out by processing the phase and amplitude of the PTR signal. The amplitude and phase values of sample measurement selected as an example for the two material groups mentioned in the Material Section are given in Table A3.1 and A3.2 in the Appendix. The PTR signals are normalized by using the electro-optical transfer function of the experimental setup, which is detected with a photodiode, to make allowances for the phase shift and attenuation. The normalization procedure is explained in more detail in Section 5.3.

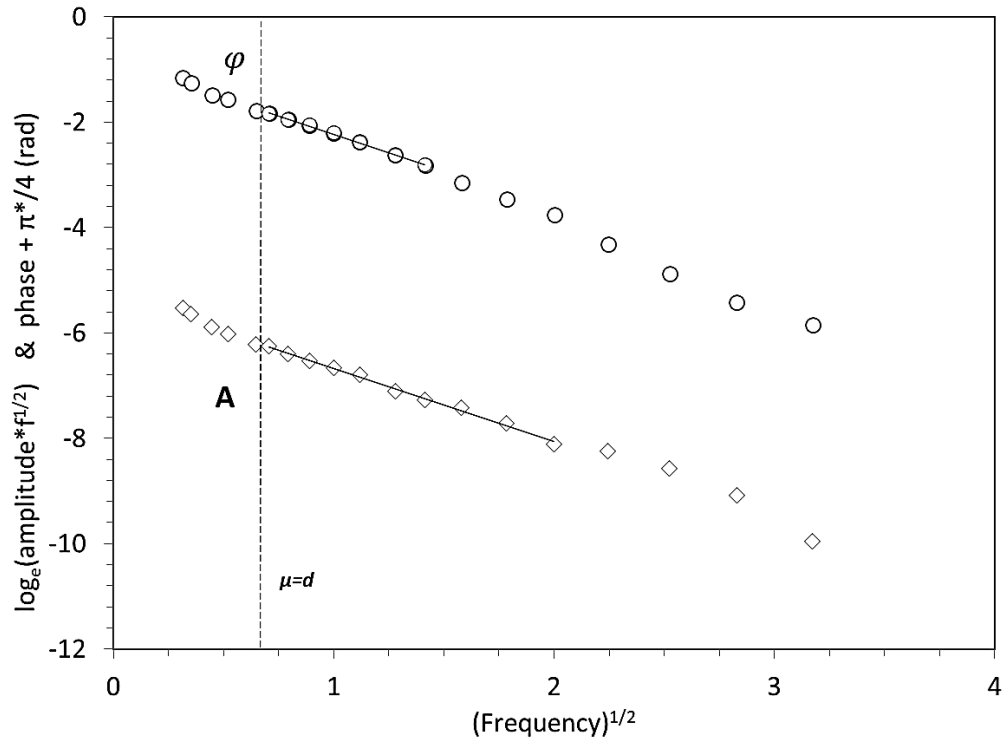


Figure 3.3 Experimental phase and amplitude values with linear fits of BD-PTR frequency spectra for a typical opaque polymer composite

The thermal diffusivity value is determined straightforwardly in the frequency range where the logarithm of the amplitude and the phase data plotted versus $f^{1/2}$ have the same slope (m). Note that the $\ln(f^{1/2}A)$ versus $f^{1/2}$ curve becomes a straight-line with a negative slope. Chirtoc et al. (2012) determined that the BD-PTR signal is useful in the region where the sample is opaque and nearly-thermally thick ($\mu \leq d$) (Figure 3.3). The thermal diffusivity can be obtained with the knowledge of the thickness of the sample as $\alpha = \pi d^2 / (\text{slope})^2$. No amplitude calibration is required for this calculation method. In this sense, the PTR is a self-checking method for errors caused by semi-transparency. This procedure has been used by many researchers using PT techniques and is closely related to the method developed by Angstrom (1862) and recently proposed variants of them (Fuente et al., 2011; Marin et al., 2013; Martinez et al., 2015). The flow chart of the thermal diffusivity measurement procedure is demonstrated in Figure 3.4.

By taking advantage of the fact that both the amplitude and phase curves have straight-line curves, an additional check can be made that there is a systematic agreement between the results of the two curves at a certain level of confidence. The confidence level (c) can be interpreted by determining the Pearson's correlation coefficient (r_{xy}) of the curves in the frequency range where the slope method is applied. Pearson's correlation coefficient measures the linear relationship between two variables, calculated as the ratio of their covariance to the product of their standard deviations:

$$r_{xy} = \frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^n (x_i - \bar{x})^2 \sum_{i=1}^n (y_i - \bar{y})^2}} \quad (3.22)$$

$\bar{x}$ and $\bar{y}$ gives the means of the variables. n is the total number of observations. The correlation coefficient is utilized to assess the degree of linear association between two variables. Besides, it can be indicated that a r_{xy} very close to one might also be achieved for a clear curve relationship (Van Loco et al., 2002). If r_{xy} is higher than the critical value of the correlation coefficient (r_c), it is observed that the examined correlation is statistically significant at the selected significance level.

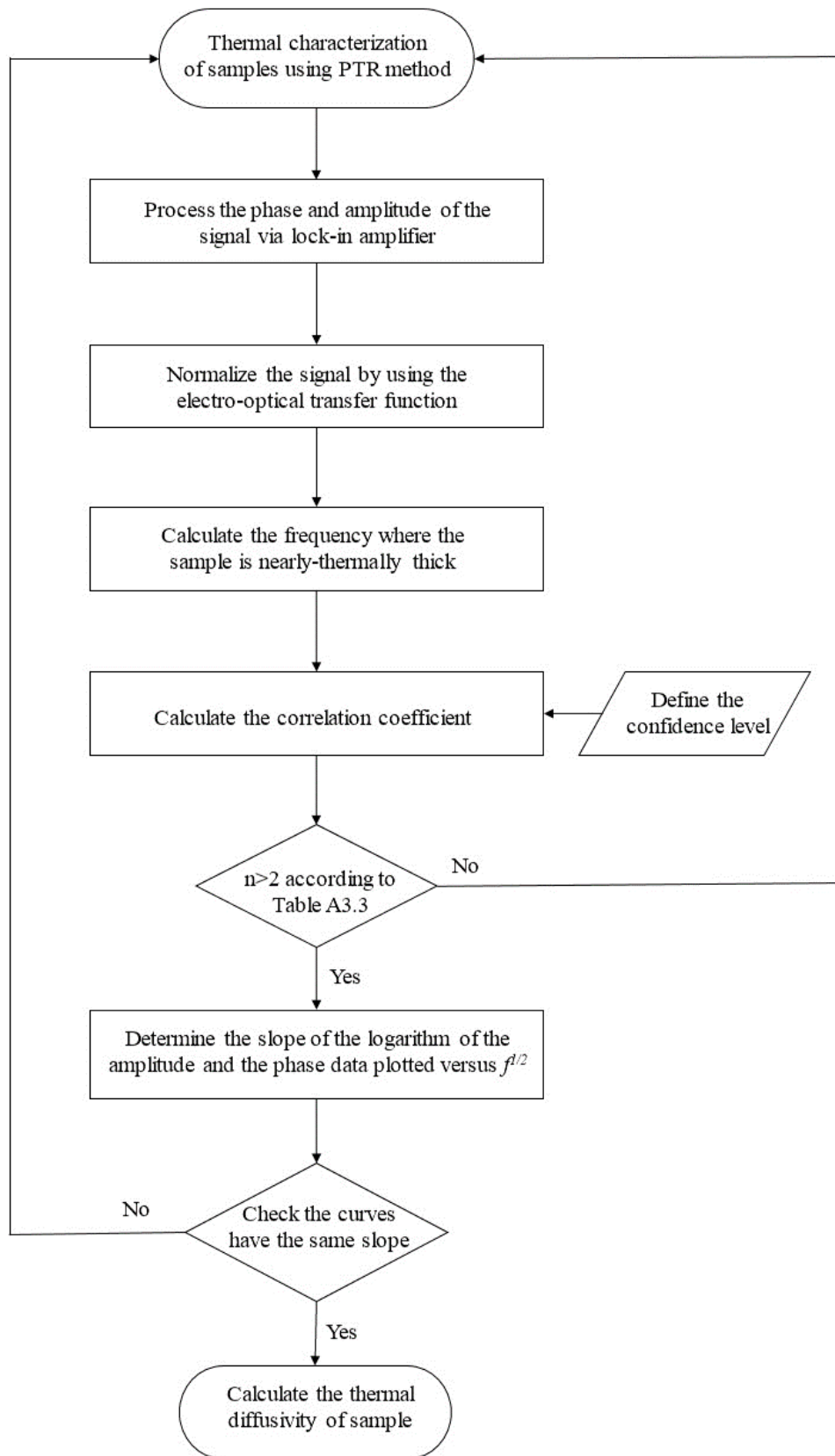


Figure 3.4 The flow chart of the thermal diffusivity measurement procedure

The confidence level shows the probability that the actual value of Pearson's correlation coefficient is within a confidence interval. The level and interval of confidence are utilized to measure the uncertainty statistically and assess how reliable the results are. Selecting a higher confidence level makes the results more reliable. A confidence level of 99% is considered in PTR measurements. The critical value of the correlation coefficient is given in Table A3.3 in the Appendix as a function of degree of freedom (n-2) and confidence level or significance level (α_p).

3.5 PTR Signal

The PTR signal is detected by a lock-in amplifier and includes all incoming radiation contacting the detector regardless of the origin of the radiation. For this reason, the signal is a mix of radiation emitted from the measurement sample and the neighboring medium. For the sample's part, the PTR signal corresponds to both the quantity of radiation emitted by the sample and the percentage of this emitted radiation that reaches the detector (Fleming, 2017). However, it is possible to make several appropriate simplifications for easier analysis. For instance, a typical laboratory room can generally be evaluated as a blackbody emitter in a constant temperature environment (Fleming, 2017).

Any material that is above absolute zero in temperature emits thermal radiation. The spectral variation of the emitted radiation is given by the Planck radiation formula that depends on the material surface temperature:

$$W(\lambda, T) = \frac{C_1}{\lambda^5} \frac{1}{e^{\left(\frac{C_2}{\lambda T}\right)} - 1} \quad (3.23)$$

where T is absolute temperature, $C_1 = 3.74 \times 10^4 \text{ W} \cdot \mu\text{m}^4 \cdot \text{cm}^{-2}$ and $C_2 = 1.44 \times 10^4 \mu\text{m} \cdot \text{K}$ are the radiation constants and λ is the wavelength (μm). A change in this latter will result in a variation in the energy radiated related to the material's thermophysical properties. The total radiant emittance from a point on a surface at a given particular temperature T , derived from the Stefan-Boltzmann law:

$$W = \varepsilon \sigma_{SB} T^4 \quad (3.23)$$

In the equation, σ_{SB} is the Stefan-Boltzmann constant that has a value of $5.67 \times 10^{-12} \text{ W} \cdot \text{cm}^{-2} \cdot \text{K}^{-4}$, ε represents the emissivity at a point. The ε is equal to 1 for an ideal blackbody. The variation in the thermal emission can be calculated using Eq. 3.24 (Almond & Patel, 1996)

$$\delta W \approx 4\varepsilon \sigma_{SB} (T_0 + T_{dc})^3 T_{ac} \quad (3.25)$$

Figure 3.5 shows T_{ac} , T_0 and T_{dc} are the alternative, ambient and continued temperatures, respectively. T_{ac} is the modulated part of the surface temperature of the sample.

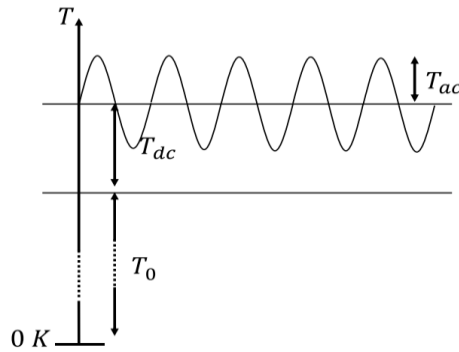


Figure 3.5 Temperature of a sample, where T_{ac} , T_0 , and T_{dc} are the alternative, ambient and continued temperatures, respectively.

It is beneficial to state the photothermal signals in terms of z ($\text{m}^2 \cdot \text{K} \cdot \text{W}^{-1}$) instead of temperature since the former is independent of the specific photothermal method utilized and of the excitation power (Chirtoc, 2009; Chirtoc et al., 2016). The z is defined as the ratio of temperature increase to the heat flux resulting from the absorbed excitation radiation power. If the heat transfer losses to the surrounding air are ignored, the z at the back side is given the 1D approximation by Eq. 3.26 (Chirtoc, 2009):

$$z(BD) = \frac{\text{ac temperature rise}}{\text{average heating power density}} = z_0 \frac{2M^{-1}}{(1-\tau^2)} \quad (3.26)$$

where $M = \exp[(1+i)d/\mu]$ and $\mu = \sqrt{\alpha/(\pi f)}$ in the solid sample. The symbol $\tau = (1-i)\beta\sqrt{\alpha/2\omega}$ is the nondimensional thermo-optical parameter, including the angular velocity $\omega = 2\pi f$. The factor $z_0 = (1-i)(\sqrt{2\omega e})$ gives the surface impedance of a semi-infinite and opaque sample. In the BD configuration, the beneficial case for photothermal spectroscopy is that the measured sample is nearly thermally thick region. For this region, Eq. (3.25) reduces to (Chirtoc et al., 2012):

$$z(BD) = 2z_0 e^{-(1+i)\frac{d}{\mu}} \quad (3.27)$$

In the experimental setup, the complex PTR signal S is a convolution of the z determined by Eq. 3.26, and the PTR signal is normalized with the transfer function of the experimental setup, which is detected with a photodiode. The normalization is important to disable the effect of frequency dependence on electronic instruments. Under the assumption of 1D heat flow, the statement of the PTR signal for an opaque slab is presented by Eq. 3.28 (Chirtoc et al., 2016):

$$S_{PTR} \propto \varepsilon(T_0 + T_{dc})^3 z(f) \quad (3.28)$$

3.6 Thermal Conductivity

The thermal conductivity characterizes the thermal transfer by heat conduction when there is a temperature change. This property is a vital thermophysical property for understanding steady state heat transfer. The thermal conductivity of the measurement samples was calculated from the following relationship:

$$k = \alpha \rho c_p \quad (3.29)$$

The α of materials is obtained by low frequency PTR and the theoretical density (ρ) and specific heat capacity (c_p) values were determined by the theory of mixing law. For the ρ of the composites reinforced with filler, the mixture law:

$$\rho = \varphi_{vol}\rho_f + (1 - \varphi_{vol})\rho_m = \rho_m + (\rho_f - \rho_m)\varphi_{vol} \quad (3.30)$$

where, ρ_f and ρ_m are the density of filler and matrix materials, respectively. The density values yield $\rho_m=860 \text{ kg/m}^3$ for pure EPDM, $\rho_f=1900 \text{ kg/m}^3$ for CB filler and $\rho_f=2047 \text{ kg/m}^3$ for GnPs. The mixture law for c_p of nanocomposites:

$$c_p = \varphi_{wt}c_{pf} + (1 - \varphi_{wt})c_m = c_m + (c_f - c_m)\varphi_{wt} \quad (3.31)$$

where c_f and c_m represent the specific heat capacity of the filler and matrix, respectively. The specific heat capacity values yield $\rho_m=2150 \text{ J/kgK}$ for pure EPDM, $\rho_f=780.5 \text{ J/kgK}$ for CB filler and $\rho_f=756.1 \text{ J/kgK}$ for GnPs.

CHAPTER FOUR

MATERIALS AND MORPHOLOGY ANALYSIS

4.1 Introduction

In this chapter, detailed information on measured samples, EPDM polymers and their composites reinforced with CB and GnPs fillers and their hybrid combinations, are presented. The preparation process of EPDM composites, including carbon-based fillers, is given. To contribute to the evaluation of the experimental results, morphological analysis is also included in this section. The particle size effect of GnPs and the synergistic effect on the conductivity mechanism of these carbon fillers were investigated by electron microscopy. The morphology of the samples was examined by using TEM and SEM analysis.

4.2 Materials

4.2.1 EPDM Polymers

Ethylene propylene diene monomer (EPDM) is one of the fast-growing elastomers due to its high elasticity, easy processing, low cost, fatigue, weather and moisture resistance and thermal stability (Giri & Wan, 2016). It is commonly used in many applications such as hoses, seals, electrical insulators and flexible polymers; it is an appropriate candidate for cable terminal protectors, electrical cables, etc. (Athawale & Joshi, 2016). However, EPDM is known to be weak in thermal conductivity (Araby et al., 2019).

Along with rapidly growing developments in polymer technology, thermal management is critical to the long service life and high work stability of electronic equipment. In general, the low thermal conductivity and local temperature rise are negative factors for the service life and safety of EPDM-based materials (Ma et al., 2019). For this reason, significant efforts have been made to discover the potential of thermally conductive EPDM-based composites to enhance their application areas. A

better thermal conduction mechanism can be achieved by the addition of conductive fillers. Thus, EPDM-based composites reveal their potential for use in extensive applications such as thermal interface adhesives, cable engineering, electromagnetic radiation shielding, and many other fields. Carbon-based fillers are comprehensively utilized in designing target composites with desired properties by considering the environmental conditions and the intended use of the application. The most common fillers are graphene nanoplatelets (GnPs), carbon black (CB), carbon nanotubes (CNTs) and graphite (Safdari et al., 2013; Kwon et al., 2021) due to their high conductivity and exceptionally low-density properties.

4.2.2 Graphene Nanoplatelets

GnPs are short stacks of graphene layers and are available at a moderate price compared to carbon nanotubes. (Krieg et. Al, 2018). This promising nanofiller is utilized in thermally conductive composites because of their relatively low fabrication cost, high aspect ratio, superior physical properties and easy production (Huang et al., 2018; Chinkanjanarot et al., 2018). Several studies have been conducted on the addition of GnPs into composites with various matrices, such as high-density polyethylene (Evgin et al., 2020), epoxy (Chinkajorot et al. 2018) and EPDM (Ma et al., 2019; Lu et al., 2019).

Chinkajorot et al. (2018) reported that the thermal conductivity of cycloaliphatic epoxy composites reinforced with GnPs enhanced with increased filler loading, dispersion, and GnPs aspect ratio. Lu et al. (2019) determined that the thermal conductivity of EPDM nanocomposites increases from 0.23 W/mK to 0.79 W/mK (nearly four times) at 8wt. % of GnPs. The thermal conductivity of GnPs/EPDM composites is still less than that of individual graphene sheets, primarily due to the weak thermal conductivity of EPDM and to the heat conduction in graphene being restricted by flake boundaries rather than the intrinsic properties of graphene. Evgin et al. (2020) examined the particle size effect of GnPs filler on the thermal conductivity of HDPE composites. They reported that the most significant thermal conductivity enhancement (corresponding to $\approx 89\%$) was obtained with GnPs of a larger lateral size,

which has a better distribution in the matrix and ensures conductive pathways. They also specified that the lateral size of GnPs filler has a more significant influence on thermal conductivity compared to their thickness. An optimum thickness determination is needed to obtain the outstanding thermal conductivity (Evgin et al., 2020).

The large interface area of GnPs provides enhancements in thermal and mechanical properties as long as the stacking of graphene sheets (Araby et al., 2015). However, the GnP structure ensures a 2-D path consisting of graphene sheets bonded together by van der Waals forces (Imran et al., 2018). Therefore, GnPs tend to aggregate easily, and it is difficult for them to disperse in the matrix because of the strong van der Waals attraction force between graphene layers and the high surface area of GnPs, which can adversely affect the conductivity mechanism of the composite material. To overcome this obstacle, the synergistic effect that arises from the combination of fillers with various aspect ratios and unique geometric shapes can provide conductivity improvement (Wei et al., 2010; Valentini et al., 2016).

4.2.3 Carbon Black

At the present time, carbon black is a cost effective and widely applied reinforcing filler in rubber manufacture (Fan et al., 2020; Krieg et al., 2018). Thanks to the graphite crystallite structure of carbon black filler, there is a remarkable improvement in the thermal conductivity of rubber, which is crucial for both the service life and safety of rubber (Song et al., 2019). Many kinds of research have been made to improve the thermal properties of based matrix by adding carbon black.

Abdel-Aal et al. (2008) determined that the thermal conductivity of epoxy composite increased from 0.2 W/mK to 0.4 W/mK by adding 10 wt % CB. Song et al. (2019) noticed that the connective structure of CB plays a vital role in enhancing the thermal conductivity of rubber composites. The improvement becomes more noticeable with CB filler loading increases. They also indicated that the CB aggregates with more branched chains facilitate better. Hiremath et al. (2021) reported an

enhancement in thermal conductivity as a function of carbon black loading, which can be increased from 0.17 W/mK to 0.23 W/mK by adding 25 vol. % of CB filler into the pure polydimethylsiloxane. They also reported that the proposed polymer nanocomposite structure has the potential for use in many applications, such as energy harvesting, micro switches, relay switches and soft robotics.

4.2.4 Hybrids

The addition of different kinds of fillers has a positive effect on cost reduction and provides a balanced conductivity mechanism for composites. Hybrid carbon-based fillers, including graphite intercalation compounds, particularly GnPs and CB, can offer cost-effective solutions for improving elastomers exhibiting outstanding properties (Valentini et al., 2016; Mondal & Khatsgir, 2017). The loading of CB enhances the conductivity mechanism by forming bridges between oriented GnPs and provides a synergistic effect (Nilsson et al., 2013). Figure 4.1 demonstrates the schematic representation of GnPs and CB filler network in the matrix. However, the mechanism of thermal conduction in polymer composites becomes more complex with the use of hybrid fillers. Experimental measurements are often less or much less than theoretical values resulting from non-ideal filler distribution and unforeseen interfacial thermal resistance between matrix and combined filler. An optimum loading ratio among various types of fillers is utilized to improve the thermal conductivity (Huang et al., 2018; Evgin et al., 2021).

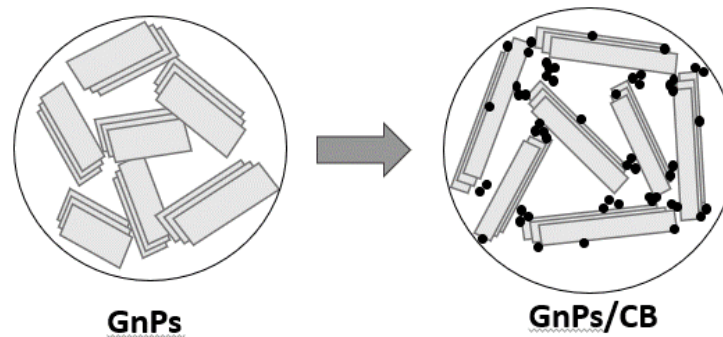


Figure 4.1. Schematic representation of GnPs-CB network in EPDM matrix.

Several studies on the synergistic effect of carbon fillers such as CB and GnPs on the thermal conductivity of polymer composites are available (Raza et al., 2012; Valentini et al., 2016; Shahamatifard et al., 2022). Ali Raza et al. (2012) investigated the thermal conductivity of rubbery epoxy composites reinforced with CB and GnP fillers with two different average widths of 5 μm and 15 μm . The thermal conductivity of hybrid composite reinforced with 4 wt. % CB and 14 wt. % GNP-15 is four times higher than that of the rubbery epoxy matrix. Because the high aspect ratio of GnPs increases the density of the conducting networks, the large GnP fillers have stronger thermal transport behavior.

Valentini et al. (2016) reported that replacing CB particles with GnPs prevents the aggregation of CB and increasing the linked conductive paths enhances the thermal conductivity. The highest synergistic effect in thermal conductivity is obtained for the EPDM composite containing 24 wt. % CB and 2 wt. % GnPs. Shahamatifard et al. (2022) investigated the synergistic effect between GnPs and CB with different aspect ratios in natural rubber (NR) composites. They reported that the addition of GnPs filler has a vital role in creating a conductive network and ensuring a thermal conductivity increasing up to $\approx 50\%$ compared to the reference NR/CB. GnPs with higher lateral size and thickness have higher thermal conductivity.

4.3 Preparation of EPDM Composites

Ethylene-propylene-diene monomer (Keltan 4450S, SpecialChem, US), carbon black (N 550, from MAKROchem S.A., Poland), oil (Unipetrol, Slovakia), 2,2,4-trimethyl-1,2-dihydroquinolin (AOX-TMQ) (Nord Chemie, Italy), stearic acid (OLEOCHEM a.s, Czechia), zinc oxide (ZnO) (Oddział Huta Oława, Poland), tetramethyl thiuram disulfide (TMTD) (RDC S.r.l., Italy), and sulfur (CHEMICAL PLANTS "Siarkopol" TARNOBRZEG Ltd., Poland) was ensured by the industrial partner. Four kinds of GnPs were supplied by Nanografi Co. Ltd. (Turkey), and their physical properties are determined in Table 4.1. EPDM/GnPs mixtures were produced in a wide range of up to 20 phr (parts per hundred rubber) of GnPs loadings.

Table 4.1 Properties of graphene nanoplates

Properties	G1	G2	G3	G4
Purity (%)	99.9	99.9	99.9	99.9
Thickness (nm)	5	5	5	3
Diameter (μm)	30	18	7	1.5
Specific Surface Area (m^2/g)	170	170	170	800
Conductivity (S/m)	1100-1600	1100-1600	1100-1600	1500-1980

The EPDM nanocomposite samples were produced in a Brabender Plasticorder internal mixer (PLE 331, Brabender GmbH, Germany) with a 30 ml mixing chamber at 100 °C. The rotors operated at 50 rpm of mixing speed for 7 minutes. Each ingredient was fed to the mixer at a mixing speed of 30 rpm. Figure 4.2 shows the processing time and compound recipe for samples with all ingredients. During the preparation process, firstly EPDM material was melt-mixed for 1 min. Afterward, GnP nanofillers, 1 phr of AOX-TMQ, 5 phr of ZnO, and 1 phr of stearic acid were added to the mixing chamber and mixed for 3 min. Then 10 phr of oil was added followed by continuous mixing for 2 min. The melt-mixing process is completed by adding 2.5 phr of TMTD and 0.5 phr of sulfur at intervals of 30 seconds, respectively. Carbon black fillers were added to the mixing chamber in 2 equal amounts at the 1st and 4th minutes to prepare hybrid nanocomposites. After mixing, measurements samples were vulcanized using compression molding at 160 °C without pressure for 30 seconds in a hot press (Fontijne 200, Fontijne, The Netherlands). Then, vulcanization was carried out under pressure (5 MPa) for 10 min.

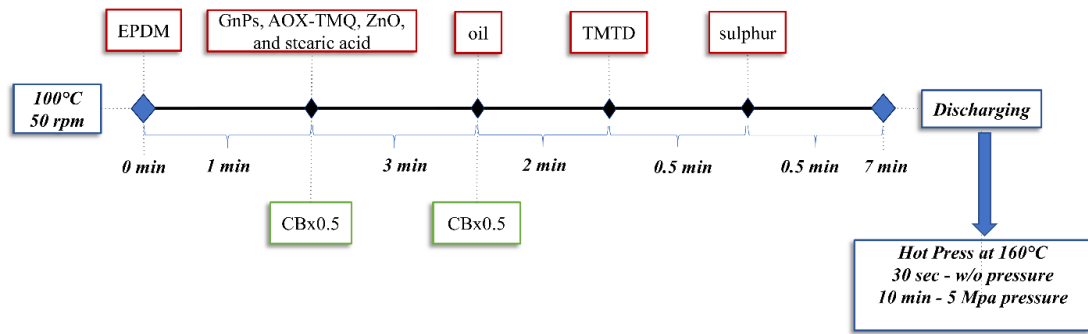


Figure 4.2 Schematic view of preparation process of EPDM based composites.

EPDM/GnPs composites were produced in a wide range of up to 20 phr of GnPs contents. During the preparation of hybrid nanocomposites, GnPs fillers were added at different additive loadings up to 7 phr and 15 phr in EPDM nanocomposites containing 20 phr and 50 phr CB, respectively (Table 4.2). These GnP loadings were selected because it was observed that the internal mixer does not allow the addition of GnP particles higher than 7 phr due to the high viscosity of the 50 phr EPDM/CB dispersion.

Table 4.2 Formulation of the EPDM-based nanocomposites

Samples	GnPs (phr range)	CB (phr)
EPDM/GnPs	0, 1, 5, 7, 10, 15, 20	-
EPDM/CB20/G1	0, 1, 3, 5, 7, 10, 15	20
EPDM/CB50G1	0, 1, 3, 5, 7	50

4.4 Methods

Scanning electron microscopy (SEM, electron microscope XL 30S FEG, Phillips) and transmission electron microscopy (TEM; microscope Tecnai G2 Spirit Twin 12; FEI) were used to examine the dispersion and morphology of GnPs and CB particles in the EPDM matrix. For SEM analysis, samples were fractured in liquid nitrogen and then gold coated to prepare the surface observation of the samples. For TEM analysis, the ultrathin sections of the samples were obtained using ultramicrotome with cryoattachment (Ultracut UCT; Leica), operating at temperatures of -150 °C for the

sample and -45 °C for the cutting. These sections were placed on standard copper grids for TEM and procured by bright field imaging with an accelerating voltage of 120 kV.

4.5 Morpholgy Analysis

The properties of composites are significantly affected by the distribution of fillers in which the particle shape, size and orientation play a crucial role (Cai et al., 2019). Figure 4.3 demonstrates the EPDM composites with 20 and 50 phr of CB and the hybrid composites including 20 and 50 phr CB with 3 and 7 phr GnPs. The presence of both GnPs and CB particles in the matrix is visible by SEM study, with good dispersion of CB filler in the EPDM matrix. CB fillers are visible as agglomerated small particles. The composites containing 20 phr CB start forming a conductive network but they are not permanent. Continuous conductive networks can be seen in the EPDM/CB50 composites (Figure 4.3.e-f). GnPs are dispersed uniformly throughout the matrix, and considerably apart from each other with fewer connections.

TEM micrographs offer a more detailed view of the dispersion of nanofillers in the examined composites. These micrographs are bright-field images that reveal the fillers appear darker than the EPDM matrix, owing to both diffraction contrast and Z-contrast. While SEM images show a homogenous distribution of fillers in the polymer matrix, the TEM images point out that the homogeneity of filler particles is not perfect, and agglomerated fillers can be seen.

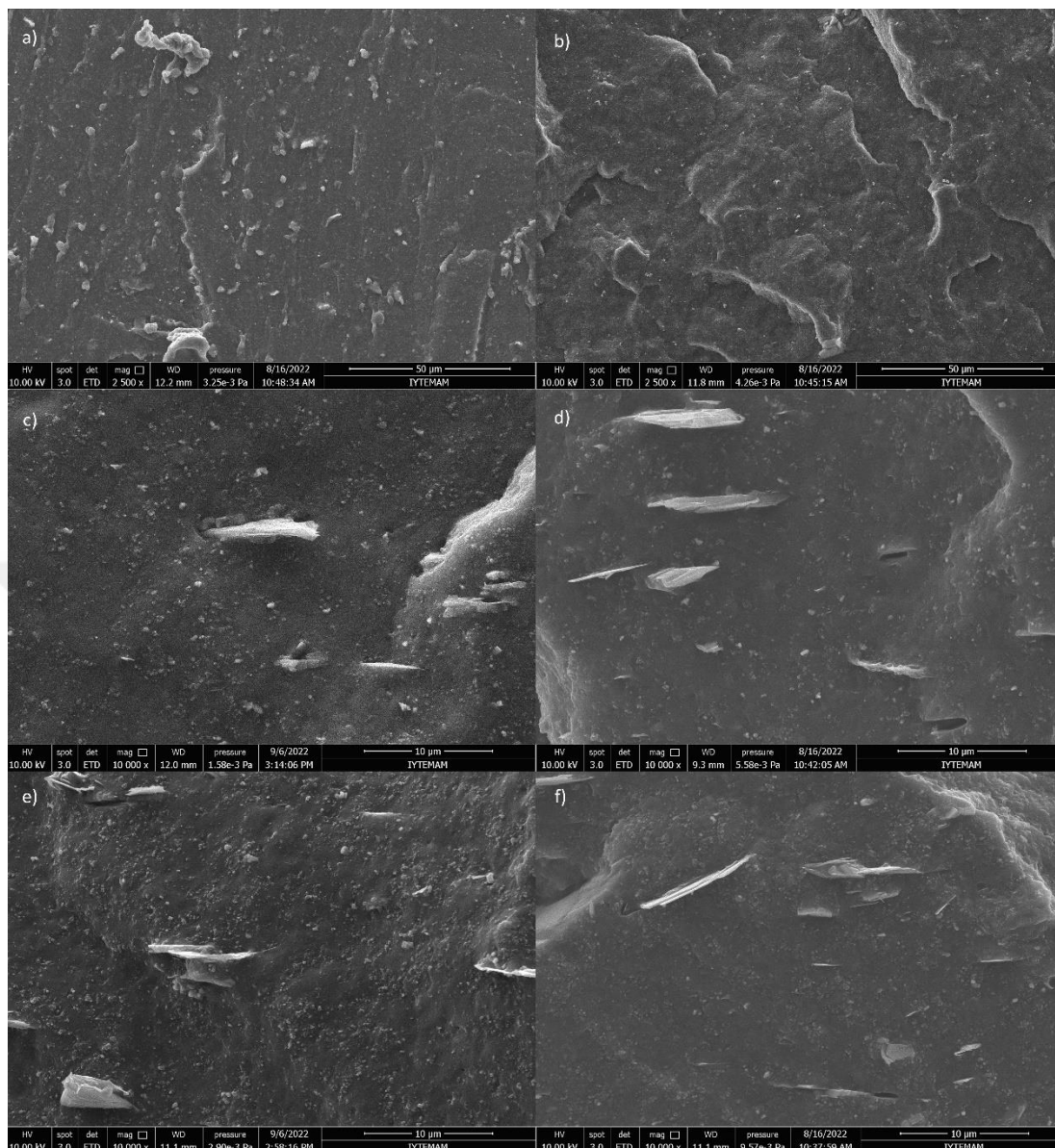


Figure 4.3 SEM pictures of a) EPDM/CB20, b) EPDM/CB50, c) EPDM/CB20/G1-3phr, d) EPDM/CB20/G1-7phr, e) EPDM/CB50/G1-3phr, and f) EPDM/CB50/G1-7phr nanocomposites.

SEM and TEM analysis reveal that GnPs in the EPDM matrix are not physically interconnected. A continuous conductive network in composites cannot be formed by GnPs fillers. The interconnected GnPs within the EPDM matrix are not uniform, and notable aggregates are observed. These aggregates contribute to the lower thermal conductivity than expected.

The most homogenous filler dispersion was obtained in the EPDM composites with 50 phr CB loading. The TEM micrographs of the EPDM/CB50 and EPDM/CB50 composites with 7 phr of G1 loading are demonstrated in Figure 4.4a and Figure 4.4b, respectively. Figure 4.4a illustrates that the CB fillers are uniform and relatively well distributed throughout the EPDM matrix. Figure 10b clearly shows both CB and GnPs fillers in the EPDM matrix, identified as black spots and black lines, respectively. For EPDM composites containing 50 phr of CB loading, a catenated network structure is established by CB particles within the EPDM. As previously mentioned in the SEM analysis, CB aggregates are attached to the surfaces and edges of the graphene nanoplatelets, even though GnPs are slightly worse distributed throughout the polymer matrix.

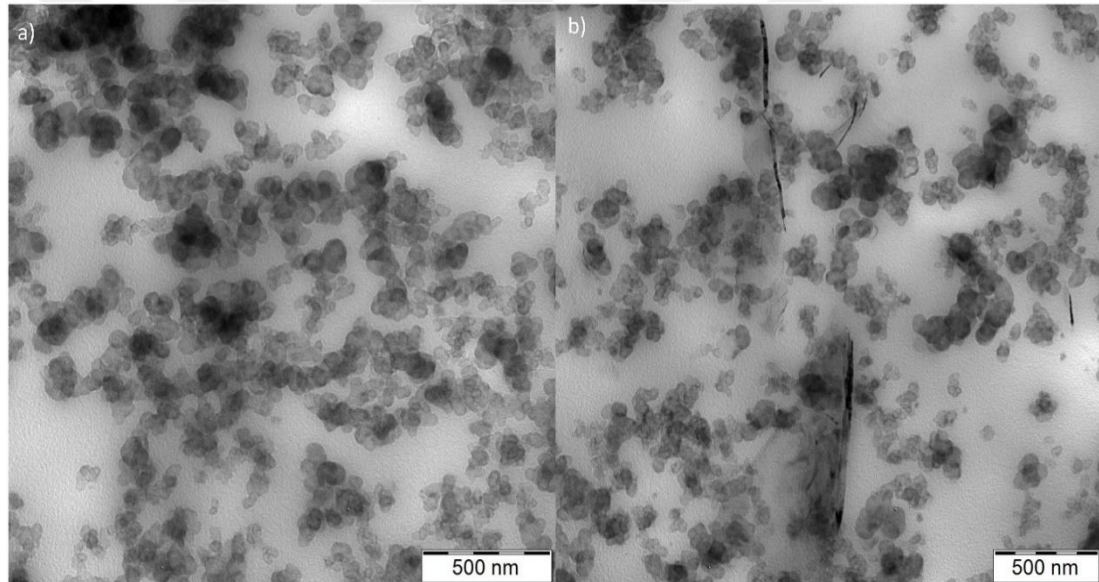


Figure 4.4 TEM images of (a) EPDM/CB50, and (b) EPDM/CB50/G1-7phr composites.

4.6 Conclusions

In this chapter, detailed information on investigated EPDM composites reinforced with GnPs and CB fillers and their hybrid combinations are given. The addition of different kinds of fillers has a positive effect on cost reduction and provides a balanced conductivity mechanism for composites. An optimum loading ratio between various constituent fillers is utilized to enhance the thermal conductivity. The particle size

effect of GnPs and the synergistic effect on the conductivity mechanism of these carbon fillers were evaluated by electron microscopy.

The morphology of the samples was examined to observe the distribution and dispersion of carbon fillers in the polymeric matrix. In the context of morphological analysis, GnPs fillers are not physically interconnected, but they were distributed relatively uniformly in the EPDM matrix, although they were not fully separated and did not form a 3D network structure. The most uniform dispersion was obtained in the EPDM composites with 50 phr CB loading. In hybrid composites, CB aggregates are attached to the edges and surfaces of the GnPs, even if GnPs are slightly worse distributed throughout the polymer matrix.

CHAPTER FIVE

DEVELOPMENT OF LOW FREQUENCY PTR

5.1 Introduction

This chapter presents the design parameters and structure of modified low frequency photothermal radiometry with back detection configuration. The sub-equipment used for excitation, modulation, and detection processes are explained in detail. The normalization procedure, which is needed to calibrate the system by measuring the transfer function, is described. The calibration and validation of the experimental setup are also discussed in this section. To obtain the validation of the system, the experimental results performed with the developed system are compared with the obtained results acquired using the classical PTR method.

5.2 Experimental Configuration

The new experimental setup, modified low frequency PTR, is designed according to back detection configuration because of the reliable diffusivity measurement (Chirtoc et al., 2012a). The laser diode beam, operating with the thermoelectric cooler, carries out excitation on the sample surface. The frequency range (0.1 - 10Hz) of the laser beam is provided by an optical chopper that creates a signal from a continuous beam. The IR signal that occurs on the sample surface is collected by an IR lens and focused on the detection window of the thermopile sensor. The signal, including phase and amplitude, of the sensor was fed to an amplifier and then connected to a lock-in amplifier. The schematic view of the experimental setup is demonstrated in Figure 5.1.

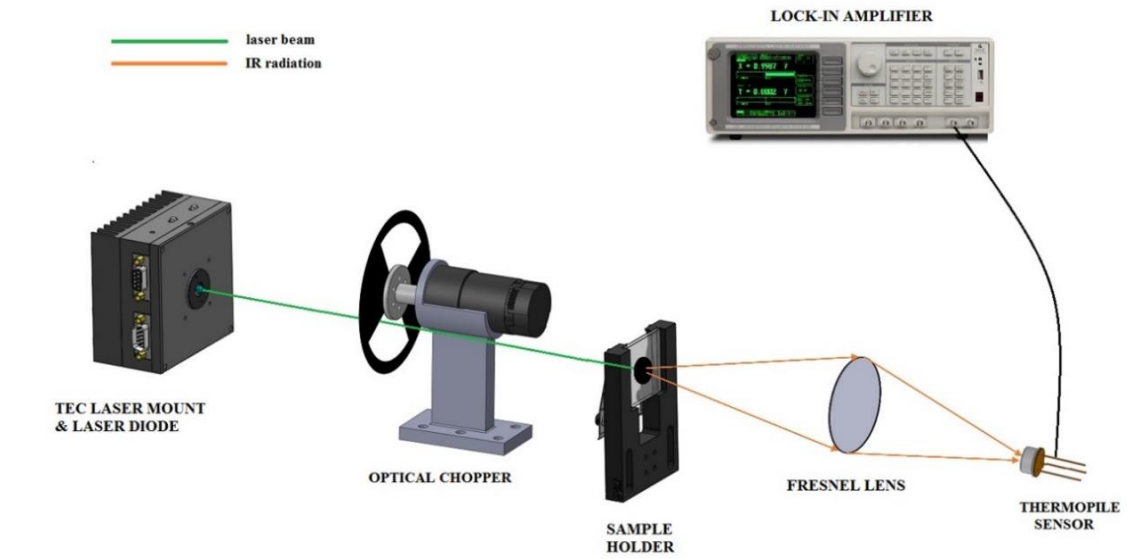


Figure 5.1 The schematic view of photothermal radiometry experimental setup.

The equipment setup and operation are built on a Thorlabs optical breadboard, which has a black anodized coating to minimize unwanted reflections, for assembling prototype optical components. A custom-made housing designed with black foamboard supported by aluminum profiles protects the system from laser light entering. In this section, experimental components and their functioning are explained briefly in the following sections. An illustration of the experimental setup is demonstrated in Figure 5.2.

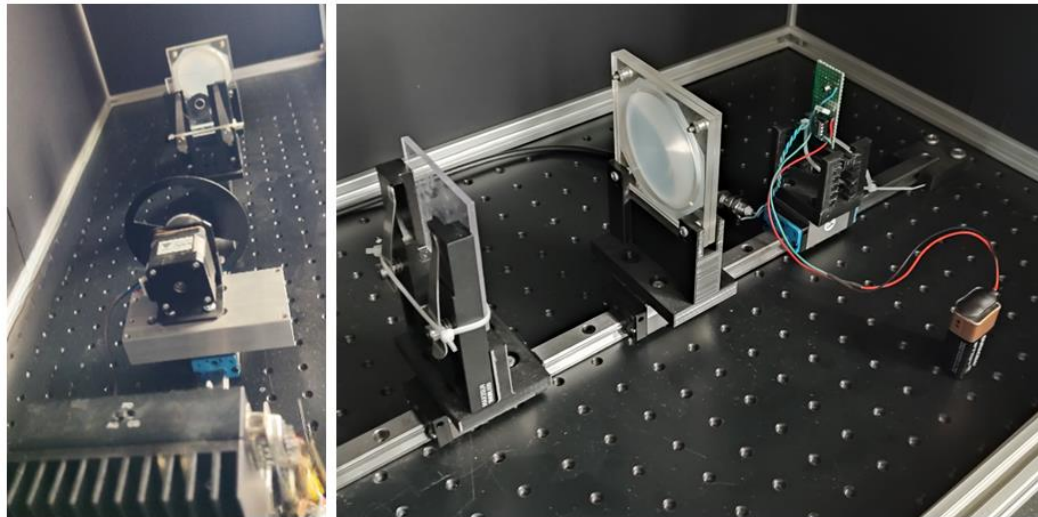


Figure 5.2 Illustration of modified low frequency PTR

5.2.1 Laser

Lasers are utilized in PTR measurements to heat a sample contactless and provide periodic excitation that produces a periodical temperature field in the material. 30-mW laser diode beam of wavelength, corresponding to the green color ($\lambda=532$ nm) in the electromagnetic spectrum, operating with the thermoelectric cooler, is used in the experimental setup of modified PTR. The laser diode is positioned inside a Temperature-Controlled Laser Diode Mount (TCLDM9, Thorlabs). The laser diode driver IP500 (Thorlabs) and the TEC driver MTD415T (Thorlabs) are used for controlling the laser diode. The TEC controller circuit controls the laser mount's temperature; temperature reference is set to 25°C as suitable with the operating temperature of the diode laser. The laser output power was measured with a Newport 1916-R model optical power meter connected to a photodetector (Figure 5.3).



Figure 5.3 Laser output power measurement.

During excitation, the diameter of the laser spot is also a critical characteristic parameter that needs to be considered. Depending on the size of the detection area, it can be beneficial to have either a significantly larger or smaller laser spot size (Hamaoui, 2018). Hamaoui et al. (2020) determined that thermal diffusion length (μ) relative to the other parameters, laser spot size (r_0) and detector radius (f_0), and it generates three special cases (Cahill, 2004; Capinski et al., 1999):

- (1) If the r_0 is significantly larger than f_0 and μ , the heat transfer is approximated as a 1D transfer

- (2) If r_0 and μ are significantly smaller than the f_0 , the heat transfer is approximated as 1D transfer
- (3) If μ is roughly the same order of magnitude as r_0 and f_0 , the heat transfer is approximated as 3D transfer.

The relation among μ , r_0 , and f_0 defines the boundary between a 1D and 3D heat transfer model. Generally, the 1D heat transfer model is primarily applied in straightforward calculations, and the 3D model is applied for more complex cases.

The fundamental of back detection modulated PTR is to modulate the laser's heating intensity periodically and compare it with the corresponding in-phase temperature variation of the sample's back surface. The profile of phase lag encapsulates the data regarding the thermophysical properties of the measured sample. In theory, a 3D model offers greater accuracy compared to a 1D model because it accounts for the effects of 3D heat transfer. Nevertheless, the added complexity of employing a 3D model can substantially lengthen computation time, and the sensitivity of specific parameters may not be provided (Wang, 2019). In general, a 3D model necessitates a more complex inverse fitting process with multiple parameters to isolate the parameters of interest, as it relies on the implicit analytical solution, which requires much time and may not guarantee unique solutions. (Zhao et al., 2004).

5.2.2 Modulation

The laser beam passes through a chopper. The frequency range of the laser beam is regulated by an optical chopper composed of a NEMA-14 stepper motor and a custom designed blade. The speed-controlling of the chopper mechanism is implemented by the Arduino-Uno board, which can run on personal computers and allows controlling frequency. The optical chopper provides a signal from a continuous beam. When the laser light moves through the opening window of the chopper, the material undergoes a short heating period during each passing window.

The optical chopper is driven at a specified frequency that can vary from 0.1Hz to 10Hz. This frequency range is selected especially for the thermal characterization of polymer composites with back detection (BD) PTR. In BD configuration, the useful case of a nearly thermally thick region (as detailed in Section 3) can be obtained for polymer composites within this frequency range. Thanks to the modulation performed in the low frequency range, an optical chopper has been implemented into the system instead of the AOM used in the classical PTR system.

The modulation is controlled by a frequency counter (Goodwill Instek, YFC8131H); the maximum error was found to be 1.1% (demonstrated in Figure 3). To eliminate this error rate in measurement results, the output frequency measured from the frequency counter is adjusted in the fitting process instead of the input frequency. It also has been observed that there is no oscillation at output frequency, and a stable frequency response is obtained.

5.2.3 IR Lens

An IR lens containing two aligned fresnel lenses (LOT-Oriel Brand, 12 cm focal point) is used to collect the thermal emission of the sample and focus on the detection window of the thermopile sensor. The material of the fresnel lens is polycarbonate. The focal point of the fresnel lens was verified by changing the thermopile-lens and detector-lens distances and taking amplitude measurements on the sample (Figure 5.4). It is found that the maximum amplitude value is obtained in the condition that the focal point is 12 cm.

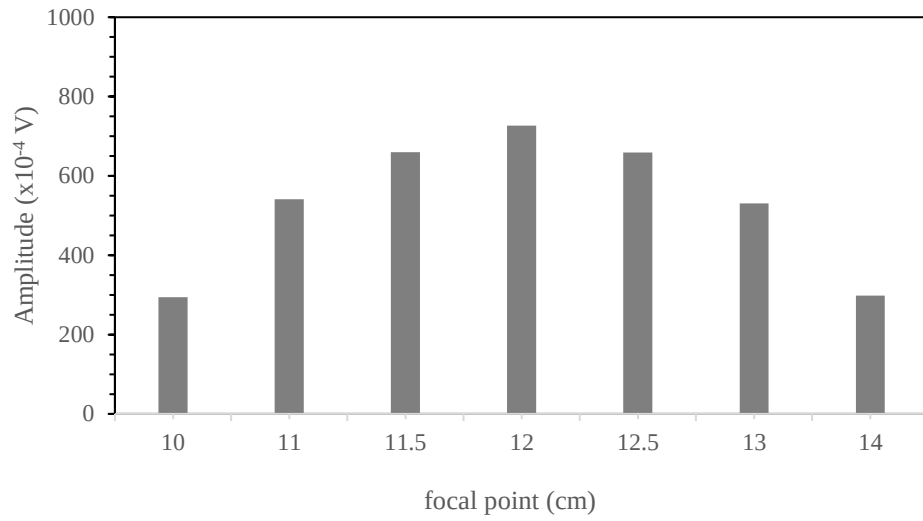


Figure 5.4 Determination of focal point.

5.2.4 Thermopile Sensor

The IR thermopile sensor (ZTP135SR Model) is used for radiometric measurements. This sensor is sensitive to the wavelength of the IR emitted from the sample, and it produces voltage signals and demonstrates a consistent response to DC radiation.

The ZTP-135SR thermopile sensor is composed of thermo-elements and an IR filter, which is compatible with the spectral range from 5 μm to 20 μm wavelengths (Song et al., 2012), as specified in Figure 5.5. The detection window of the sensor has a 0.7x07 mm² active area. The responsivity of the sensor is 62 Volts/Watts. The bandwidth of ZTP135-SR is $\approx 110\text{Hz}$. The signal of the sensor is amplified with an AD820 Opamp with a non-inverting amplifier.

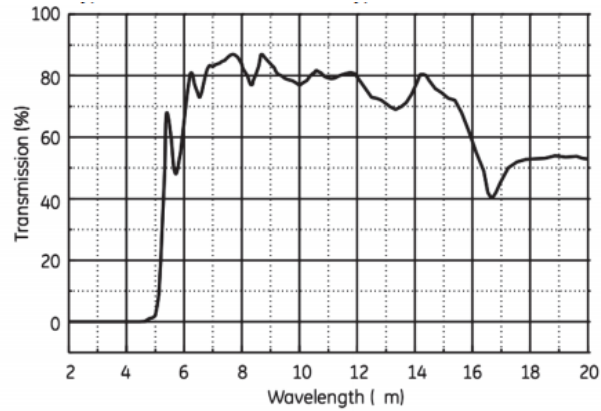


Figure 5.5 Transmission of ZTP135-SR thermopile sensor (Song et al, 2012).

In the classical PTR system, a liquid nitrogen cooled HgCdTe IR detector (KLD-1-J1/DC/11, Kolmar Technologies), with 1 mm² windows area, designed for linear response with a sensitivity for IR radiation wavelength emitted from the sample among 2 and 12 μm wavelength spectral range. The PTR signal, amplified by the preamplifier in the detector, is transmitted to the lock-in. The responsivity of the detector is higher than 40,000 Volts/Watts. The bandwidth of this model is 2 MHz.

Although there is a great difference in responsivities between the detector used in the classical method and the thermopile sensor used in modified low frequency PTR, it is foreseen that this difference is not affect the results if the sample material is limited to polymer composite materials reinforced with carbon or metal-based fillers. Chirtoc et al. (2016) specified that the polymer composites are ideal candidates for PTR detection since they easily meet the necessity of being opaque for both the excitation radiation and in the IR spectrum. They also exhibit strong IR emissivity, resulting in a reasonably high PTR signal.

5.2.5 Lock-in Amplifier

The radiometric measurements are transformed into voltage and pre-amplified, and this amplified signal is then fed into a lock-in amplifier (SR850 Model, Stanford), which is used to measure the periodic signal. The thermal characterization of the material is determined according to the amplitude value of the signal at the reference frequency and the phase change among the reference and detected signal obtained by

the lock-in amplifier. Sensitivity, phase resolution, frequency range, time constant and capability of signal-to-noise are the necessary specifications for the using a lock-in amplifier. In principle, lock-in amplifiers process the input signal by multiplying it using a reference signal and then integrating the resulting product over a set period. The amplitude and phase values of the input signal are determined by combining the outputs, which include the reference and the experimental outputs (Hamaoui, 2018). Figure 5.6 demonstrates the principle of measurements carried out with a lock-in amplifier.

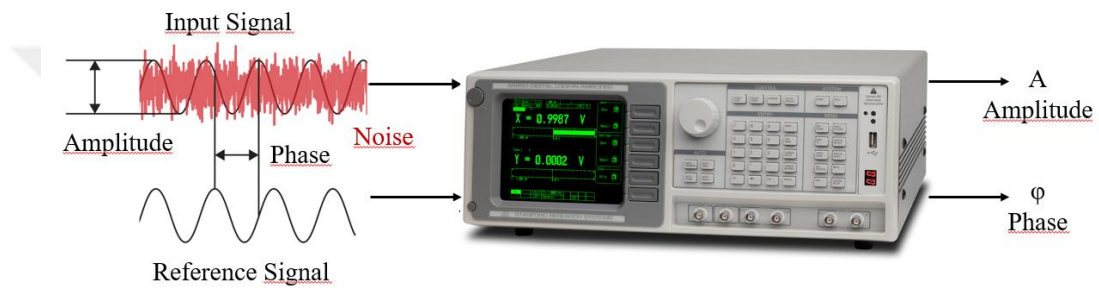


Figure 5.6 A scheme of the principle of lock-in amplifier (Canseco, 2023).

During the detection, the output signal contains some mixed noise caused by external sources and electronic chains. Lock-in amplifiers are remarkably effective at detecting small periodic signals and limiting the bandwidth of noise for small frequency ranges. Even under high noise levels, a lock-in amplifier accomplishes to reduce these noise signals (Fleming, 2017). Further insights about the lock-in amplifiers can be seen in the datasheet of Stanford Research Systems (SRS, Model SR850 DSP Lock-In Amplifier).

5.3 Normalization of PTR

PTR signal is based on the measurement of amplitude and phase data, which is obtained by the detection of change in thermal radiation emitted from the sample's surface due to the absorption of a laser heating source. An accurate measurement is very important since the phase and amplitude of the PTR signal can be altered during the periodic signals received by the experimental equipment. To take into account the

phase shift and attenuation of the response obtained from the experimental measurement, it is necessary to calibrate the system by measuring the transfer function.

Hamaoui (2018) determined that the transfer function is a signal combination of a photodiode reference sample at high and low frequencies. While the response of the lock-in amplifier is non-linear at low frequency ranges, AOM and detector attenuate the PTR signal and are out of phase at high frequencies. At high frequencies, in order to consider the attenuation and the phase shift of the AOM and detector, a frequency scan of an opaque and thick sample is used for the normalization. At low frequencies, the transfer function, obtained by a photodiode, PTR signal is used to normalize the PTR signal to consider attenuation and the phase shift of the lock-in amplifier. The phase change of the detector is not included in this step (Hamaoui, 2018).

In this study, since the detection is performed at low frequencies, the normalization of the measurement system is ensured only with the electronic transfer function. To remove the response of the equipment, the phase and detected amplitude of the transfer function are subtracted from the detected phase and divided by the amplitude, respectively (Figure 5.7).

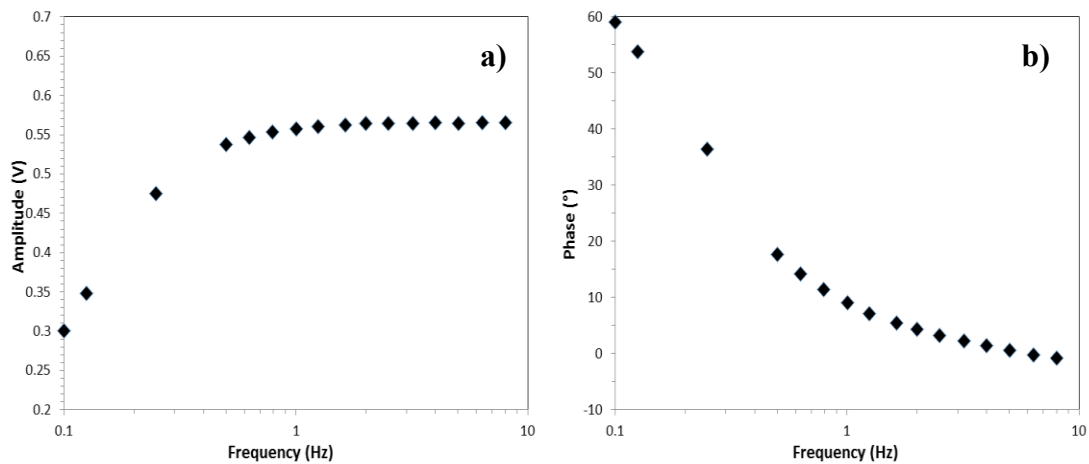


Figure 5.7 Amplitude and phase of the electronic transfer function.

The electronic transfer function is determined by a BPW21R photodiode (purchased from a local brand). As seen in Figure 5.8, there is a transimpedance

amplifier circuit, which converts the current in the diode to voltage, embedded at the output of the BPW21R Photodiode.

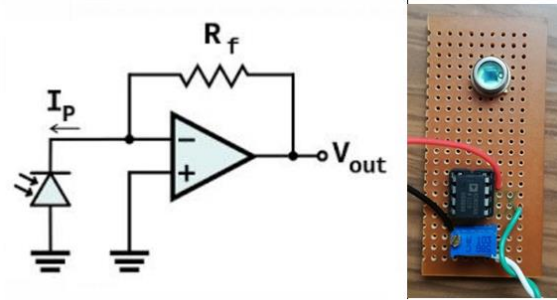


Figure 5.8 Demonstration of BPW21R sensor and electric circuit diagram of transimpedance amplifier.

5.4 Validation of PTR

In this section, the validation of the experimental setup is determined. For this purpose, the experimental results performed with the developed system are compared with the obtained results acquired using the classical PTR method. The experimental measurements were performed on HDPE composites reinforced with MWCNT and Al filler materials. HDPE composite materials mentioned in this section have been previously measured with the classical PTR method, and the results have been published in journals (Evgin et al., 2016; Koca et al., 2017).

5.4.1 HDPE/MWCNT Nanocomposites

HDPE composites reinforced with MWCNT filler material have a vol. fraction of up to 10%. The two different aspect ratios (length/diameter) of CNT fillers are in the range of 200-400 (M58) and 300-5000 (M12). The thermal diffusivity of these CNT/HDPE samples was measured before in the study of Evgin et al. (2016). The measurements were performed with the classical front detection PTR method. Detailed information about the sample is determined in related reference (Evgin et al., 2016).

The thermal diffusivity values of HDPE composites reinforced with M12-MWCNT/ and M58-MWCNT samples obtained from modified low frequency PTR with BD configuration are compared with the classical FD-PTR results (Evgin et al.,

2016), as seen in Figure 5.9. The difference between the results of classical PTR and modified low frequency PTR is less than 3%. Experimental thermal diffusivity results of HDPE/MWCNT are provided in Table A5.1 in the Appendix.

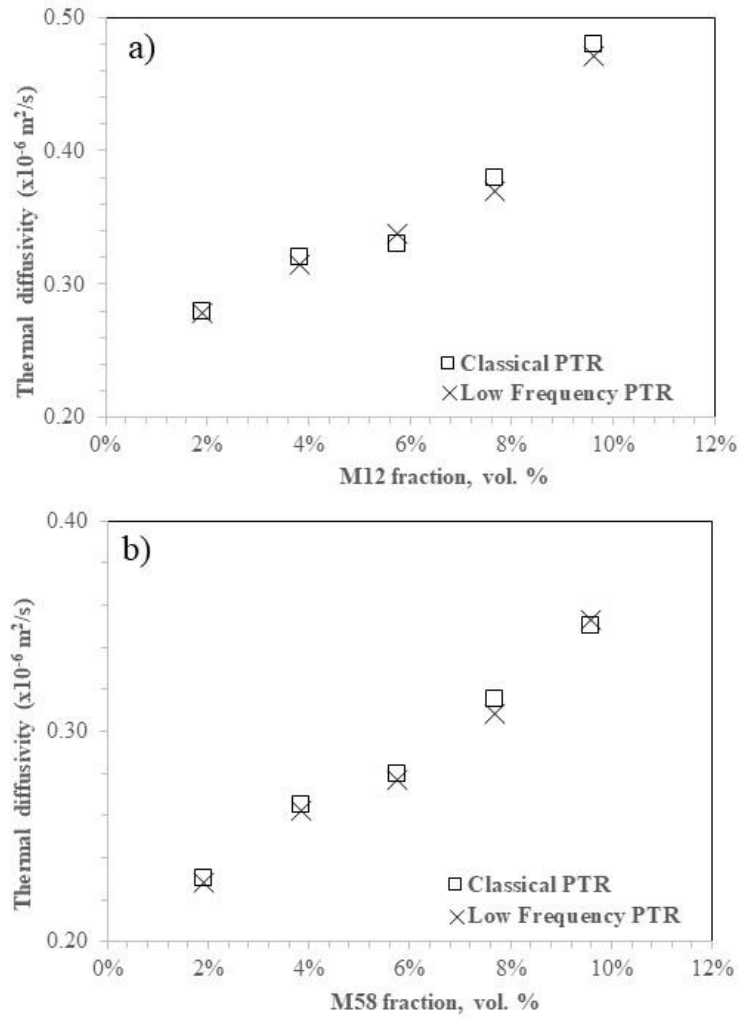


Figure 5.9 Experimental measurement of thermal diffusivity of HDPE reinforced with a) M12-MWCNT and b) M58-MWCNT composites according to MWCNT volume fraction.

5.4.2 HDPE/Al Nanocomposites

Thermal diffusivity of HDPE samples reinforced with Al nanoparticles was measured before in the study of Koca et al. (2017). The measurements were performed with the classical PTR method with front detection configuration. HDPE composites reinforced with nanosized Al particle samples were prepared to filler volume fraction

up to 29%. Detailed information about the sample is determined in related reference (Koca et al., 2017).

Figure 5.10 demonstrates the experimental measurement of HDPE/Al composites obtained from both modified low frequency BD-PTR and the classical FD-PTR (Koca et al., 2017). The difference between the results of classical PTR and modified low frequency PTR is less than 3%. The experimental thermal diffusivity results of HDPE/MWCNT are given in Table A5.2 in the Appendix.

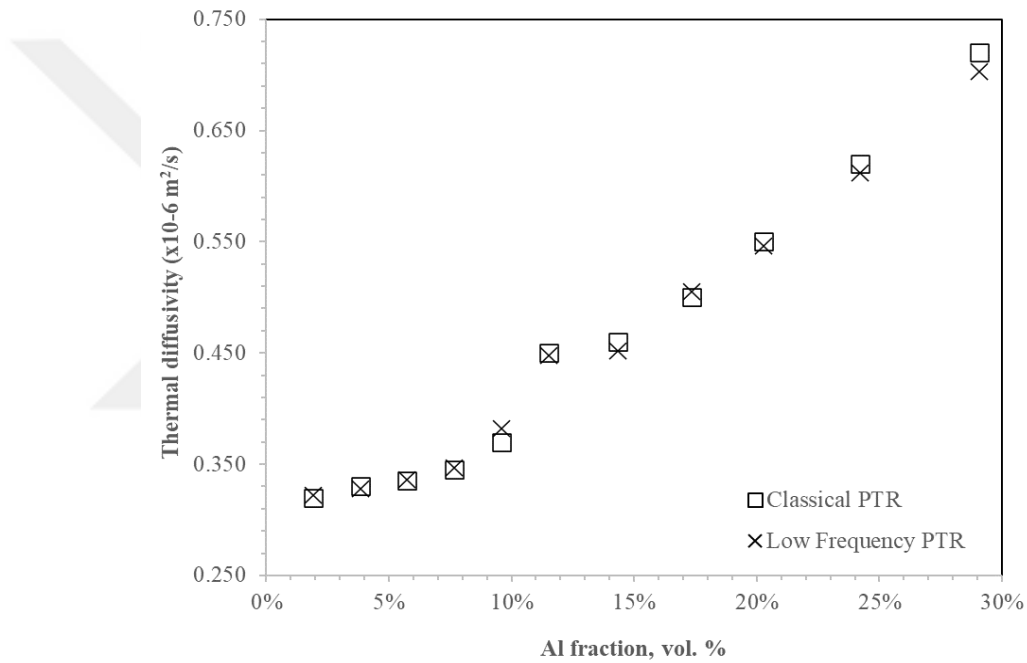


Figure 5.10 Experimental measurement of thermal diffusivity of HDPE reinforced with Al nanoparticles according to Al volume fraction.

5.5 Calibration of PTR Signal

In this section, primary sources of uncertainty are identified, and a comprehensive summary of how each contributes to the overall uncertainty is provided in Table 1. Sample thickness is measured by micrometer at five different points of the sample. Measurement results indicate that the surface roughness is found as 9, 7 and 15

micrometers for M12-MWCNT, M58-MWCNT and Al filled HDPE samples, respectively.

Frequency uncertainty is controlled by a frequency counter (Goodwill Instek, YFC8131H), and it has been observed that there is no oscillation at output frequency, and a stable frequency response is obtained. Providing the measuring range at low frequencies positively affects obtaining this stable behavior.. By evaluating the measuring range of the frequency counter device, the frequency uncertainty is accepted as 0.00005 Hz. Since the measurement at the lowest frequency in the system was performed at 0.1Hz, the uncertainty is noted as 0.005%.

From the experimental tests, it is found that measured phase values of both lock-in and photodetector could generate uncertainty, which is caused by mainly step delay of the chopper, especially for low frequency. It causes undesired fluctuation of phase lag. As recommended in the study of Wang (2019), phase difference can be detected by blocking the probe laser to the photodetector. It is found that phase difference is a maximum of 0.5° fluctuations between 0.1 and 10Hz. Although laser diode temperature is controlled by a thermoelectric cooler, a low level of voltage fluctuations (<1.2%) is observed on the laser power meter, which is caused by which is attributed to electrical signal interference (power supply and cable connections).

Consequently, the overall uncertainty of the α measurement of the sample is within 5%, and the sample thickness causes the majority of uncertainty.

Table 5.1 Uncertainty Sources

Input Parameter		Uncertainty
Sample Thickness	M12-CNT/HDPE	2.4%
	M58-CNT/HDPE	2.2%
	Al/HDPE	3.4%
Phase Measurement		0.5°
Frequency Uncertainty		0.005%
Heating Laser Diode		1.2%

5.6 Conclusions

A modified low frequency photothermal radiometry with back detection configuration is developed. The new experimental setup includes a laser diode beam, operating with the thermoelectric cooler, to carry out excitation on the sample's surface. The range of modulation frequency is ensured by an optical chopper. The IR signal of the measurement sample is collected by an IR lens and focused on a thermopile sensor, which is utilized for the detection process. Then the signal of the thermopile sensor, including phase and amplitude values, was sent to a lock-in for the processing and analysis of the PTR signal.

To obtain the validation of the experimental setup, we compared the experimental results obtained with the modified low-frequency PTR method to those acquired using the classical PTR method on HDPE nanocomposites filled with MWCNT and Al. According to test results, the overall difference between the two methods is less than $\pm 3\%$.

The overall uncertainty of the experimental setup is within 5%. The primary uncertainty source contains sample thickness. Other components of uncertainty include experimental electric noise, frequency error and heating beam of the laser diode.

CHAPTER SIX

THERMAL CHARACTERIZATION OF EPDM COMPOSITES

6.1 Introduction

This chapter examines EPDM composites reinforced with GnPs and CB fillers and their hybrid combinations of various loadings. EPDM has many advantages, including low cost, high elasticity, easy processing and corrosion resistance. However, it is known that neat EPDM has low thermal conductivity. In light of advancements in material technology, thermal management is critical to work stability and the long service life of electronic equipment. In general, the local temperature rise, and the low thermal conductivity are negative factors for the service life and safety of EPDM-based materials (Ma et al., 2019). Thus, significant efforts have been carried out to discover the potential of conductive EPDM-based composites to improve their application areas. A better thermal conduction mechanism can be provided by the conductive filler addition.

The experimental results performed with modified low frequency PTR are presented. The size effect (specific surface area and lateral size) of GnPs filler and hybridization effects between CB and GnPs on the thermal conductivity of the EPDM composites are investigated. This chapter is also related to our study published in *Diamond and Related Materials* (2023) as *A comprehensive study on the thermal and electrical conductivity of EPDM composites with hybrid carbon fillers* (Koca et al., 2023).

6.2 EPDM/GNPs Composites

Figure 6.1 shows the relative thermal conductivity (k_e/k_m) of EPDM nanocomposites reinforced with G1, G2, G3 and G4 fillers. Regardless of the filler size, the thermal conductivity of EPDM nanocomposites increases with increasing GnP loading due to the high thermal conductivity of GnPs fillers. The relative thermal conductivity enhancement is superior for the G1-based EPDM composite than for

those with G2, G3 and G4 at all loadings. The thermal conductivity of neat EPDM is $0.19 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. With the increase in GnPs loading up to 20 phr, the EPDM/G1 sample shows a 94 % enhancement when compared with pure EPDM, to $0.37 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, while G2, G3 and G4 show enhancements of 46 %, 45 % and 40 %, respectively. Measurement thermal diffusivity values and relative thermal conductivity results of EPDM/GnPs composites are provided in Table A6.1 and A6.2 in the Appendix.

In comparison, the obtained results show that GnPs fillers with higher lateral size can provide up to 38 % higher enhancement than those with lower lateral size. This conclusion is compatible with previous reports (Evgin et al., 2020; Shtein et al., 2015; Kim et al., 2015) that investigated different GnP sizes. The lateral size and specific surface area of GnPs fillers considerably affect the thermally conductive network chain formed in the EPDM composite.

In theory, a larger lateral size of the GNPs is advantageous for decreasing phonon scattering between the matrix and filler interface and therefore enhancing the thermal conductivity (Huang et al., 2020; Burger et al., 2016). As specified by earlier studies (Jang et al., 2022; Kim et al., 2015; Zhao et al., 2022), GnPs with smaller lateral sizes produce more interfacial thermal boundary resistance (TBR) between the GnPs filler and EPDM matrix. TBR was ascribed to the low thermal conductivity of composites by hindering phonon transport between filler and matrix.

The EPDM nanocomposites containing 1 phr loading of GnPs exhibit a lower thermal conductivity than the neat EPDM. As specified by Huang et al. (2018), a filler network is not formed at low filler loading, and TBR between GnPs fillers and matrix results in a low k . Moreover, the EPDM molecules wrapping around the GnPs fillers could induce strain and shape change, thus decreasing the thermal conductivity of the GnPs fillers (Huang et al., 2018; Zhang et al., 2014)

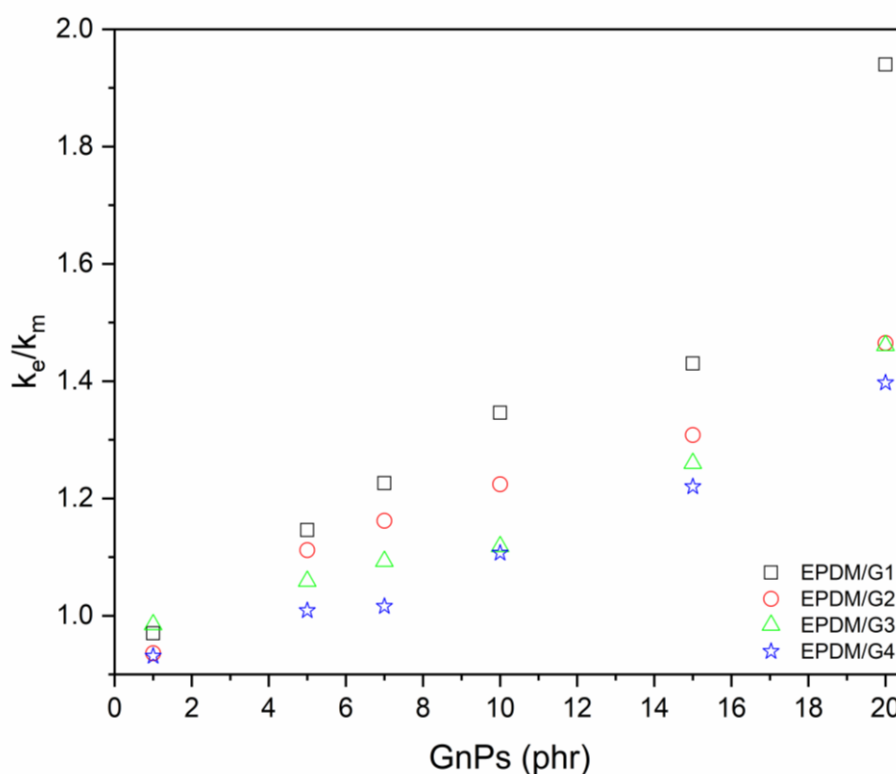


Figure 6.1 Relative thermal conductivity of the EPDM composites according to phr of GnPs loadings.

6.3 EPDM/GNPs-CB Hybrid Composites

In the selection of hybrid nanocomposite materials, G1 filler was chosen since it has the highest thermal conductivity among the EPDM/GnPs composites measurements. Figure 6.2 demonstrates the relative thermal conductivity (k_e/k_m) of the EPDM matrix reinforced with CB20/G1 and CB50/G1 hybrid fillers as a function of G1 phr loading. The EPDM/CB20 and EPDM/CB50 samples exhibited thermal conductivity of 0.277 and 0.298 W/mK, which are 47 % and 59 % higher than the neat EPDM. Measurement thermal diffusivity values and relative thermal conductivity results of EPDM/Hybrid composites are provided in Table A6.3 and A6.4 in the Appendix.

CB fillers improve the thermal conductivity of EPDM and exert substantial phonon heat conduction due to their crystallite structure of graphite. With a higher loading of CB, the number of long filler chains increases, and a 3D network of CB chains in the

matrix is constructed, which leads to thermal conductivity enhancement (Song et al., 2019).

Despite the high thermal conductivity of GnPs and CB, the thermal conductivity of the EPDM composites enhanced less than anticipated. The reason is the high TBR, which leads to lower thermal conductivity by playing a vital role in hindering phonon conduction between the carbon fillers and the matrix (Kim et al., 2015).

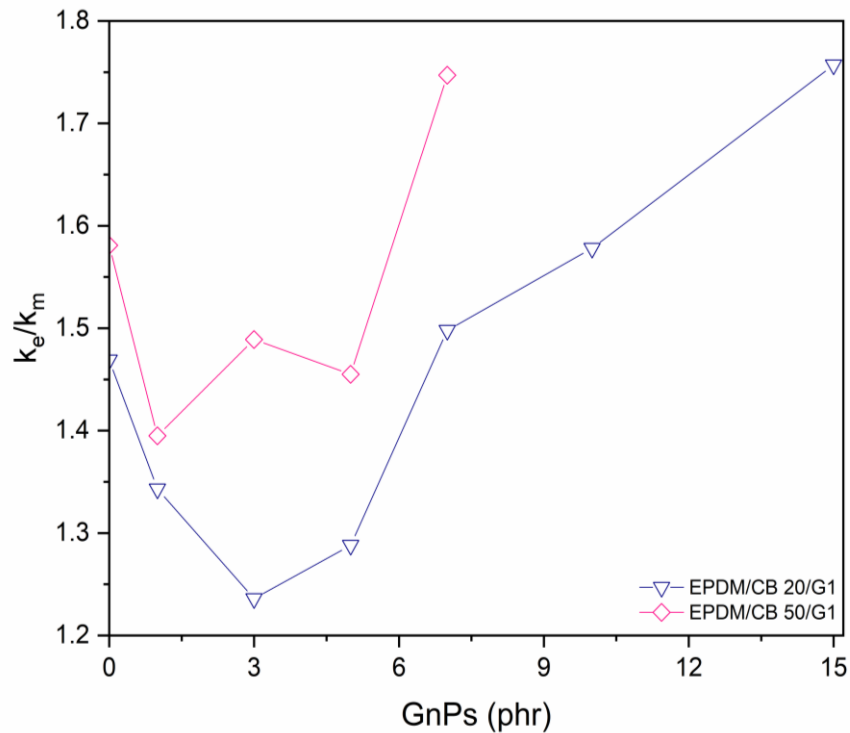


Figure 6.2 Relative thermal conductivity of EPDM/hybrid composites according to GnP loadings.

The hybridization of G1 and CB exhibits both synergistic and no synergistic effects influencing thermal conductivity. The formation of a filler network connection by nano-bridges through the use of carbon hybrid fillers plays a significant role in synergistic enhancement behavior (Jang et al., 2021).

Huang et al. (2018) classified the polymer composites reinforced with hybrid fillers into four cases according to different filler network structures. (1) Both fillers uniformly dispersed without forming a network due to a low filler loading (without

network); (2) one filler forms a network while the other filler remains dispersed uniformly (no synergistic effect, single network); (3) while one of the hybrid fillers uniformly dispersed, the other filler bridges them together to create a network (synergistic effect, single network); (4) Both types of fillers form networks and dual networks are cross-linked (synergistic effect, dual network). According to thermal conductivity results, case 2 and case 3 can be observed for G1 filler loading up to 5 and higher than 5 phr, respectively. This determination is also supported by SEM analyses in the previous sections.

Compared with the thermal conductivity of the EPDM/CB composites, it has been indicated that no synergistic effect is comprised by adding up to 5 phr G1 nanoplatelets to hybrid composites. As mentioned by Yu et al. (2008), an optimum loading ratio of hybrid fillers does not always provide maximum thermal conductivity, but a higher loading of hybrid fillers may cause the synergistic effect of hybrid fillers.

The thermal conductivity of the EPDM/CB50 and EPDM/CB20 composites is decreased by 12 % and 16 % because of the addition of 1 phr and 3 phr G1 nanoplatelets loadings, respectively. This decrease in thermal conductivity is probably because the loading of GnPs is inadequate to ensure a good dispersion and form a conductive path between CB and GnPs fillers. No synergistic effects are due to the increase of the TBR caused by the low loading of GnPs, which could not act as a nano-bridge. The high TBR is due to higher phonon scattering between the EPDM matrix and GnPs fillers, thus leading to a decrement in thermal conductivity (Kim et al., 2015; Kim et al., 2014).

The synergistic effect emerges at 7 phr G1 nanoplatelet loading for CB50/G1 and CB20/G1. The samples of EPDM/CB50 containing 7 phr G1 and EPDM/CB20 containing 15 phr G1 have 75 % and 76 % higher thermal conductivity than the neat EPDM, respectively. Taking into consideration the EPDM composites with a single GnPs filler, conductive networks are formed with the contact between nanoplatelets. With the hybridization, both fillers are attached to each other's surface, resulting in the formation of additional conductive pathways. On the other hand, GnPs fillers can

reduce the agglomeration of CB fillers to form a more conductive network since they can also act as spacers (Valentini et al., 2015). As seen in Figure 4 and SEM images (Figure 4.3-d), GnPs improve the dispersion of CB and act as a conductive bridge when GnPs filler with 7 phr loading is added.

6.4 Conclusions

In this chapter, the thermal conductivity of EPDM nanocomposites reinforced with graphene nanoplatelets filler, carbon black filler and their hybrid combinations are investigated. According to the obtained results, GnPs with larger lateral sizes can provide up to 38 % higher thermal conductivity improvement than GnPs with smaller lateral sizes.

Hybrid fillers have both positive and no synergistic effects on the thermal conductivity of EPDM polymer, and no synergistic effect occurs by adding up to 5 phr of G1 filler to hybrid composites. A synergistic effect is achieved at a G1 loading of 7 phr for both CB20/G1 and CB50/G1. EPDM/CB20 and EPDM/CB50 samples with 7 phr of G1 have thermal conductivity values that are 76 % and 75 % higher compared with the thermal conductivity of the pure EPDM, respectively.

The use of hybrid carbon fillers has promising importance for developing conductive EPDM composites. Composites containing 50 phr CB and 7 phr GnPs loadings have improved thermal conductivity. They could potentially be evaluated in cable engineering, actuators and electromagnetic radiation shielding in which thermal management is important to high work stability and long service life of electronic equipment. These materials offer potential for thermal interface adhesives requiring thermally conductive properties, thanks to high GnPs loading (>15 phr), provided they are electrically insulating.

CHAPTER SEVEN

CONCLUSIONS & FUTURE WORKS

7.1 Conclusions

In this work, a modified modulated PTR method with a low-frequency operating range and back detection configuration is developed to specially obtain the thermal diffusivity of the polymer composites. Since polymer composites are favorable samples for PTR measurements thanks to their strong IR emissivity, they allow obtaining thermal diffusivity at low excitation power and low frequency range during measurements. In this context, the capabilities of the PTR were evaluated, and application changes were made in the sub-equipment used for excitation, modulation and detection processes compared to the classical PTR. From the main findings, we may conclude that:

- The overall uncertainty of the experimental setup is 5%. The main uncertainty source is related to sample thickness. Other components of uncertainty include experimental frequency error, electric noise and heating beam of the laser diode.
- To validate the experimental setup, we compared the experimental results obtained with the modified low-frequency PTR method to those acquired using the classical PTR method on HDPE composites reinforced with MWCNT and Al nanofillers. According to test results, the overall difference between the two methods is less than +/- 3%.

Using the developed low frequency PTR method, the thermal diffusivity of EPDM nanocomposites reinforced with graphene nanoplatelets filler, carbon black filler and their hybrid combinations are measured. The relative thermal conductivity of EPDM composites was calculated from the obtained thermal diffusivity, and the theoretical density and specific heat capacity values were determined by mixing law theory. Based on the results and observations, the following findings can be asserted:

- GnPs with larger lateral sizes can ensure up to 38 % higher thermal conductivity enhancement than GnPs with smaller lateral sizes because they are advantageous for decreasing phonon scattering between matrix and fillers in the interface.
- The thermal conductivity of the EPDM composites reinforced with CB and GnPs hybrid fillers show improvement less than anticipated because of the high thermal boundary resistances.
- The combination of G1 and CB exhibits both positive and no synergistic effects on the thermal conductivity, and no synergistic effect occurs by adding up to 5 phr of G1 to hybrid composites compared with the thermal conductivity of the EPDM/CB composites.
- A synergistic effect is obtained at a G1 loading of 7 phr for CB50/G1 and CB20/G1. EPDM/CB50 and EPDM/CB20 samples with 7 phr of G1 have thermal conductivity values of 75 % and 76 % higher than neat EPDM, respectively.

7.2 Future Works

Future research is still needed to advance the field of photothermal radiometry, and the following recommendations may serve as a starting point for future studies.

- The low melting temperatures of phase change materials pose a challenge for measuring their thermophysical properties using photothermal methods that involve laser excitation. Thanks to using a laser diode at low excitation power, thermal characterization of phase-change materials can be performed with developed modified low frequency PTR.
- To simplify the experimental system by reducing the number of required equipment, a TTL input can be used for direct modulation of laser diodes. This approach yields a square-wave modulation of the laser alternating between the off state and full power.

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APPENDICES

APPENDIX 1: NOMENCLATURE

r_0	: Laser spot size, m
f_0	: Detector radius, m
C	: Volumetric heat capacity, $\text{J}\cdot\text{m}^{-3}\cdot\text{K}^{-1}$
c_p	: Specific heat capacity, $\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$
m	: Slope
z_0	: Surface impedance
e	: Thermal effusivity, $\text{J}\cdot\text{m}^{-2}\cdot\text{s}^{-1/2}\cdot\text{K}^{-1}$
S_{PTR}	: PTR Signal
x	: Position, m
c	: Confidence level
r_{xy}	: Pearson's correlation coefficient
r_t	: Critical value
t	: Time
I_0	: Laser light intensity, $\text{W}\cdot\text{m}^{-2}$
H	: Overall heat transfer coefficient, $\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$
T	: Temperature, $^{\circ}\text{C}$
Bi	: Biot number
k	: Thermal conductivity, $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
d	: Thickness, m
A	: Arbitrary constant
B	: Arbitrary constant
C_1	: Radiation constant, $\text{W}\cdot\mu\text{m}^4\cdot\text{cm}^{-2}$
C_2	: Radiation constant, $\mu\text{m}\cdot\text{K}$
f	: Frequency, Hz
z	: Specific thermal impedance, $\text{m}^2\cdot\text{K}\cdot\text{W}^{-1}$
phr	: Parts per hundred rubber
h	: Heat transfer coefficient, $\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$
M	: Frequency dependent equivalent of Bi-number

GREEK SYMBOLS

α	: Thermal diffusivity, $\text{m}^2 \cdot \text{s}^{-1}$
ε	: Emissivity
μ	: Thermal diffusion length, m
β	: Optical absorption coefficient, m^{-1}
ω	: Angular modulation frequency
σ_{SB}	: Stefan-Boltzmann constant, $\text{W} \cdot \text{cm}^{-2} \cdot \text{K}^{-4}$
λ	: Wavelength (μm).
τ	: Nondimensional thermo-optical parameter
φ	: Phase
σ	: Complex thermal wave vector
α_p	: Level of significance

ABBREVIATIONS

PTR	: Photothermal Radiometry
PT	: Photothermal
PPE	: Photopyroelectric
AOM	: Acousto-optical Modulator
BD	: Back Detection
FD	: Front Detection
PA	: Photoacoustic
PBD	: Photothermal Beam Deflection
LFT	: Laser Flash Technique
PR	: Photothermal Reflectance
IR	: Infrared Radiation
HDPE	: High Density Polyethylene
CNT	: Carbon Nanotube
SWCNT	: Single Wall Carbon Nanotube
MWCNT	: Multi Wall Carbon Nanotube
ISF	: Interstitial Fluid
WM	: Wavelength Modulated
GnPs	: Graphene Nanoplatelets
CB	: Carbon Black

EPDM	: Ethylene Propylene Diene Monomer
vol.	: Volumetric
wt.	: Weight
NR	: Natural Rubber
TMTD	: Tetra-methyl Thiuram Disulfide
SEM	: Scanning Electron Microscopy
TBR	: Thermal Boundary Resistance
PLLA	: Poly L-lactide
PANI	: Polyaniline
PLA	: Polylactic acid
PBS	: Polybutylene succinate
GO	: Graphene Oxide

SUBSCRIPTS

<i>conv</i>	: Convection
<i>rad</i>	: Radiation
<i>m</i>	: Matrix
<i>f</i>	: Filler
<i>dc</i>	: Continued
<i>ac</i>	: Alternative

APPENDIX 2: PTR RESULTS

Table A3.1. Experimental amplitude and phase values of EPDM composites containing 20 phr G1 filler

Frequency (Hz)	Amplitude (V)	Phase (°)
0.10	0.0029120	-60.25
0.12	0.0028563	-71.06
0.20	0.0023894	-91.88
0.27	0.0019021	-107.68
0.42	0.0013034	-134.35
0.50	0.0011205	-145.52
0.63	0.0008707	-154.20
0.79	0.0006516	-168.16
1.00	0.0005038	-180.47
1.25	0.0003874	-194.56
1.63	0.0002479	-212.02
2.00	0.0001738	-233.22
2.50	0.0001166	-256.77
3.16	0.0000708	-272.90
4.00	0.0000486	-295.77
5.00	0.0000346	-314.44
6.30	0.0000215	-348.38
8.00	0.0000142	-379.95
10.00	0.0000103	-415.83

Table A3.2. Experimental amplitude and phase values of EPDM composites containing 15 phr G1 and 20 phr CB fillers

Frequency (Hz)	Amplitude (V)	Phase (°)
0.10	0.0041304	-153.91
0.12	0.0039704	-164.66
0.20	0.0032575	-188.59
0.27	0.0027792	-205.14
0.42	0.0019472	-226.54
0.50	0.0016115	-239.34
0.63	0.0012624	-252.55
0.79	0.0009751	-267.38
1.00	0.0007048	-281.79
1.25	0.0005121	-297.39
1.63	0.0003511	-317.86
2.00	0.0002379	-336.70
2.50	0.0001414	-360.95
3.16	0.0000935	-384.26
4.00	0.0000594	-405.80
5.00	0.0000348	-435.16
6.30	0.0000196	-468.84
8.00	0.0000118	-501.21
10.00	0.0000074	-539.24

Table A3.3. Critical values of Pearson's correlation coefficient (c =level of confidence, α_p =level of significance and $n-2$ =degrees of freedom)

c	90%	95%	99%	99.9%
α_p	0.1	0.05	0.01	0.001
($n-2$)				
1	0.988	0.997	0.99988	1
2	0.9	0.95	0.99	0.999
3	0.805	0.878	0.95874	0.991
4	0.729	0.811	0.9172	0.974
5	0.669	0.755	0.87453	0.951
6	0.622	0.707	0.834	0.925
7	0.582	0.666	0.798	0.898
8	0.549	0.632	0.765	0.872
9	0.521	0.602	0.735	0.847
10	0.497	0.576	0.708	0.823
11	0.476	0.553	0.684	0.801
12	0.458	0.532	0.661	0.78
13	0.441	0.514	0.641	0.76
14	0.426	0.497	0.623	0.742
15	0.412	0.482	0.606	0.725
16	0.4	0.468	0.59	0.708
17	0.389	0.456	0.575	0.693
18	0.378	0.444	0.561	0.679
19	0.369	0.433	0.549	0.665
20	0.36	0.423	0.537	0.652
25	0.323	0.381	0.487	0.597
30	0.296	0.349	0.449	0.554
35	0.275	0.325	0.418	0.519
40	0.257	0.304	0.393	0.49
45	0.243	0.288	0.372	0.465
50	0.231	0.273	0.354	0.442
60	0.211	0.25	0.325	0.408
70	0.195	0.232	0.302	0.38
80	0.183	0.217	0.283	0.357
90	0.173	0.205	0.267	0.338
100	0.164	0.195	0.254	0.321

Table A5.1. Thermal diffusivity measurements of HDPE nanocomposites reinforced with M12 and M58 MWCNT performed with modified low frequency PTR

vol% MWCNT	Thermal Diffusivity ($\times 10^{-6} \text{ m}^2/\text{s}$)	
	M12/HDPE	M58/HDPE
2%	0.278	0.228
4%	0.315	0.262
6%	0.338	0.277
8%	0.370	0.308
10%	0.471	0.353

Table A5.2. Thermal diffusivity measurements of HDPE/Al Nanocomposites performed with modified low frequency PTR

vol% Al	Thermal Diffusivity ($\times 10^{-6} \text{ m}^2/\text{s}$)
	Al/HDPE
2%	0.322
4%	0.328
6%	0.336
8%	0.347
10%	0.382
12%	0.448
14%	0.452
17%	0.505
20%	0.546
24%	0.612
29%	0.703

Table A6.1. Thermal diffusivity of EPDM/GnPs Nanocomposites

GnPs phr	Thermal Diffusivity ($\times 10^{-6} \text{ m}^2/\text{s}$)			
	EPDM/G1	EPDM/G2	EPDM/G3	EPDM/G4
1	0.099	0.096	0.101	0.095
5	0.117	0.114	0.108	0.103
7	0.126	0.119	0.112	0.104
10	0.138	0.126	0.115	0.114
15	0.147	0.135	0.130	0.126
20	0.200	0.151	0.151	0.144

Table A6.2. Relative thermal conductivity of EPDM/GnPs Nanocomposites

GNP phr	Relative Thermal Conductivity (k_e/k_m)			
	EPDM/G1	EPDM/G2	EPDM/G3	EPDM/G4
1	0.970	0.936	0.985	0.931
5	1.146	1.112	1.059	1.009
7	1.226	1.162	1.093	1.016
10	1.346	1.224	1.118	1.107
15	1.430	1.308	1.260	1.220
20	1.940	1.465	1.461	1.397

Table A6.3. Thermal diffusivity of EPDM/Hybrid composites

G1 phr	Thermal Diffusivity ($\times 10^{-6} \text{ m}^2/\text{s}$)	
	EPDM/CB20/G1	EPDM/CB50/G1
0	0.152	0.167
1	0.139	0.147
3	0.128	0.157
5	0.134	0.154
7	0.156	0.185
10	0.164	-
15	0.183	-

Table A6.4. Relative thermal conductivity of EPDM/Hybrid composites

G1 phr	Relative Thermal Conductivity (k_e/k_m)	
	EPDM/CB20/G1	EPDM/CB50/G1
0	1.469	1.581
1	1.343	1.395
3	1.236	1.489
5	1.288	1.455
7	1.498	1.747
10	1.578	-
15	1.757	-