ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

INVESTIGATION OF MECHANICAL, THERMAL AND FLAME RETARDANT PROPERTIES OF GLASS FIBER REINFORCED PBT AND PBT/PET BLENDS

M.Sc. THESIS

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

CAM ELYAF KATKILI PBT VE PBT/PET HARMANLARININ MEKANİK, TERMAL VE ALEVLENMEYİ GECİKTİRİCİLİK ÖZELLİKLERİNİN İNCELENMESİ

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JUNE 2018

Selin PORTAKAL, a M.Sc student of ITU Graduate School of Science Engineering and Technology Student ID 515141041, successfully defended the thesis entitled "Investigation of Mechanical, Thermal and Flame Retardant Properties of Glass Fiber Reinforced PBT and PBT/PET Blends", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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Date of Submission : 4 May 2018
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To my mother,

FOREWORD

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May 2018

Selin PORTAKAL
Chemical Engineer

TABLE OF CONTENTS

Page

ABBREVIATIONS

AlO(OH)	**:** Aluminium Oxide Hydroxide – Boehmite
Al_2O_3	**:** Aluminium Oxide
AlPi	**:** Aluminium Phosphinate
AlPi – Et	**:** Aluminium diethylphosphinate
AlPi – H + RXP	**:** Resorcinol-bis (di-2,6-xylyl phosphate)
APP	**:** Ammonium Polyphosphate
ATH	**:** Aluminum Trihydroxide
BDO	**:** 1,4-butanediol
BHET	**:** bis (2-hydroxyethyl) Terephthalate
DEPAL-AlPi	**:** Aluminium diethylphosphinate
DSC	**:** Differential Scanning Calorimetry
EG	**:** Ethylene Glycol
FR	**:** Flame Retardant
GF	**:** Glass Fiber
GWFI	**:** Glow Wire Flammability Index
GWIT	**:** Glow Wire Ignition Temperature
HB	**:** Horizontal Burning
HDT	**:** Heat Distortion Temperature
LOI	**:** Limiting Oxygen Index
MC	**:** Melamine Cyanurate
MFI	**:** Melt Flow Index
MPP	**:** Melamine Polyphosphate
NIST	**:** National Institute of Standards and Technology
NR	**:** No Rate
PBT	**:** Polybutylene Terephthalate
PET	**:** Polyethylene Terephthalate
PMMA	**:** Poly(methyl methacrylate)
REACH	**:** Registration, Evaluation, Authorization and Restriction of Chemical Substances
SEM	**:** Scanning Electron Microscopy
TEM	**:** Transmission Electron Microscopy
TGA	**:** Thermal Gravimetric Analysis
TPA	**:** Terephthalic Acid
TiO_2	**:** Titanium Dioxide
ZnPi	**:** Zinc bis-(diethylphosphinate)

SYMBOLS

T_g	: Glass Transition Temperature
T_m	: Melting Temperature
L_0	: Gauge Length
T_o	: Onset Temperature
T_p	: Peak Temperature
T_d	: Starting Thermal Degradation Temperature
T_m	: Melting Temperature
X_c	: Degree of Crystallinity
T_i	: Starting Thermal Degradation Temperature
T_f	: Final Thermal Degradation Temperature
ΔH_m	: Melting Enthalpy
ΔH_c	: Crystallization Enthalpy

LIST OF TABLES

Page

LIST OF FIGURES

Page

INVESTIGATION OF MECHANICAL, THERMAL AND FLAME RETARDANT PROPERTIES OF GLASS FIBER REINFORCED PBT AND PBT/PET BLENDS

SUMMARY

Engineering plastics are used more and more areas in a wide spread manner. Especially, need of special performance characteristics, engineering plastics are come to mind. These special characteristics can be defined as high mechanical properties, high abrasion resistance, high electrical and thermal resistance, improved fire retardant performance. Plastics are used in different significant areas such as aeronautics and space, construction, defense industry, automotive, electrical and electronical industry etc. Improvement of mechanical, thermal and fire retardant performance of these engineering plastics, become more of an issue. In order to reach these desirable performance characteristics, manufacturers use reinforcement agents and additives. Glass fibers are commonly used to support polymeric structure with the purpose of obtain stiffness, strength and flexibility. Glass fiber reinforced engineering plastics have also varied fire behavior depend on resins which are used. Previous studies show that scientists had preferred halogenated flame retardants because of their outstanding fire retardant performance in case of fire. By the reason of legislative restrictions (such as REACH), environmental and health considerations, halogen free flame retardant additives have become more and more important. Also, high temperature stable mineral fillers are used to improve thermal properties. The combination of halogen free flame retardants and mineral fillers, give a new impulse to fire retardant performance of engineering plastics. This combination also reduces the cost of high fire retardant performance plastics. Poly(butylene terephthalate) (PBT) is preferred among engineering plastics with its high dimensional stability, low moisture absorption, productivity and fast cycle time characteristics. However, glass fiber reinforced PBT grades have preferred due to modified mechanical properties. Glass fiber reinforced PBT/PET blends have desirable properties such as glossy surface appearance, high rigidity, high temperature and strength properties. Additionally, the most important characteristic of glass fiber reinforced PBT/PET blends is good cost-performance ratio. After the restriction of halogenated based flame retardant, halogen free high performance phosphorus based flame retardant additives are preferred to use in engineering plastics.

In this study, samples were prepared by using co-rotating twin screw extruder and they were shaped by injection moulding machine. A halogen free phosphorus based flame retardant additive which is called aluminium diethyl phosphinate is used as main flame retardant. This halogen free phosphorus based flame retardant is also called DEPAL and especially identified as AlPi – Et in scientific researches. Two aluminium based mineral filler are used as a co-flame retardant which has the same chemical structure but they have different average particle size and specific surface area. In first stage of

experiment, Actilox B60, which its particle size is 1.2 μm, aluminium based mineral filler is used as co-flame retardant. In second stage of experiment, Actilox B30, which its particle size is 2.3 μm, aluminium based mineral filler is used as co-flame retardant. This aluminium based mineral flame retardants are boehmite originated and its chemical formula is AlO(OH). All samples contain totally 20% flame retardant additives except control sample. The samples were extruded with different matrices which are neat PBT, glass fiber (GF) reinforced PBT and GF reinforced PBT/PET blend. In order to determine optimum combination of main flame retardant/co-flame retardant, five different ratios are selected. In first stage of the experiment, Actilox B60 is used and these main flame retardant/co-flame retardant ratios are aligned as 20% DEPAL/0% Actilox B60; 15% DEPAL/5% Actilox B60; 10% DEPAL/10% Actilox B60; 5% DEPAL/15% Actilox B60 and 0% DEPAL/20% Actilox B60. In second stage of experiments, samples were prepared with Actilox B30 as co-flame retardant and the main flame retardant/co-flame retardant ratios are 20% DEPAL/0% Actilox B30; 15% DEPAL/5% Actilox B30; 10% DEPAL/10% Actilox B30; 5% DEPAL/15% Actilox B30 and 0% DEPAL/20% Actilox B30.

Structural properties of samples were evaluated by measurements of density and melt flow index (MFI). In order to obtain mechanical properties of samples; stress at break, tensile modulus, strain at break and Izod impact (+23 °C and -30 °C) values are calculated. Thermal properties of samples were investigated by heat distortion temperature (HDT), thermal gravimetric analysis (TGA) and differential scanning calorimeter (DSC) analysis. Flame retardant performance of the samples were obtained by UL 94, glow wire ignition temperature and glow wire flammability index tests.

In consequence of all experiments; Sample 27, which is contained 5% DEPAL/15% Actilox B30 in 20% GF reinforced PET/PBT blend matrix, is given the best mechanical, thermal and fire retardant performance results.

CAM ELYAF KATKILI PBT VE PBT/PET HARMANLARININ MEKANİK, TERMAL VE ALEVLENMEYİ GECİKTİRİCİLİK ÖZELLİKLERİNİN İNCELENMESİ

ÖZET

Son yıllarda, özellikle yüksek performans kriterlerine ihtiyaç duyulan alanlarda mühendislik plastiklerinin kullanımı gitgide artmıştır. Bu performans özelliklerine örnek olarak; gelişmiş mekanik özellikler, yüksek aşınma dayanımı, termal ve elektriksel dayanıklılık ile gelişmiş yanmazlık özellikleri gösterilmektedir. Plastikler uzay ve havacılık, inşaat, savunma sanayi, otomotiv, elektrik ve elektronik gibi stratejik öneme sahip birçok farklı sektörde kullanılmaktadır. Bu sebeple de mühendislik plastiklerinin mekanik, termal ve yanmazlık özelliklerinin geliştirilmesi önem arz etmektedir. İstenen bu yüksek performans kriterlerine ulaşmak için birçok araştırmacı ve üretici, takviye ajanları ile katkılar kullanmaktadır. Cam elyaf genel olarak esneklik, dayanıklılık ve sertliğin sağlanması amacıyla polimerik yapıya takviye için kullanılır. Cam elyaf takviyeli plastikler, kullanılan reçineye göre farklı yanma davranışları sergilemektedir. Daha önce yapılan çalışmalarda, bilim insanları, yanma durumunda gösterdikleri üstün performanstan dolayı halojenli alev geciktiricileri kullanmayı tercih etmişlerdi. Ancak halojenli alev geciktiricilerinin yanma esnasında çıkarmış oldukları zehirli gazlar, çevre ve sağlık üzerinde yarattığı olumsuz etkiler göz önünde bulundurularak yasal kısıtlamaların oluşturulmasını (REACH) mecbur kılmıştır. Ayrıca plastiklerin termal özelliklerinin geliştirilmesi için yüksek sıcaklıklarda kararlılığını koruyan mineral katkılar kullanılmaya başlanmıştır. Halojensiz alev geciktiriciler ve mineral katkıların bir arada kullanılması ise mühendislik plastiklerinin alev dayanımı üzerine yeni bir bakış açısı kazandırmıştır. Bu katkı maddelerinin bir arada kullanılması performansı olumlu yönde etkilediği gibi maliyeti de düşürücü bir etki göstermiştir.

Poli(bütilen tereftalat) (PBT) yüksek boyutsal kararlılığı, yüksek nem direnci, prodüktivitesi ve hızlı çevrim süresi sayesinde mühendislik plastikleri arasında sıkça tercih edilmektedir. Ancak geliştirilmiş mekanik özellikleri göz önünde bulundurulduğunda cam elyaf takviyeli PBT çeşitlerinin endüstride çok daha yoğun olarak kullanıldığını söyleyebiliriz. Cam elyaf takviyeli Poli(bütilen tereftalat) /Poli (etilen tereftalat) (PBT/PET) harmanlarının da parlak yüzey görünümü, yüksek sertlik, mukavemet ve yüksek sıcaklık dayanımı gibi özellikleri endüstride tercih sebebi olarak gösterilmektedir. Ancak cam elyaf takviyeli PBT/PET harmanlarının kullanılmasındaki en önemli sebeplerden biri PET'nin PBT'ye oranla daha düşük fiyata sahip olması ve buna bağlı olarak da yüksek fiyat/performans yüzdesinin elde edilmesidir. Halojen bazlı alev geciktiricilerin kullanımının kısıtlanması ardından, halojensiz fosfor bazlı alev geciktirici katkılar mühendislik plastiklerinde yüksek alev dayanımı sağladığı için kullanılmaya başlanmıştır.

Bu çalışmada tüm numuneler aynı yönlü çift vidalı ekstrüder kullanılarak hazırlanmış ve enjeksiyonlu kalıplama ile de şekillendirilmiştir. Ana alev geciktirici katkı olarak halojensiz fosfor bazlı alüminyum dietil fosfinat kullanılmıştır. Bu katkının ticari ismi

DEPAL olarak geçmekle birlikte, bilimsel çalışmalarda daha çok AlPi – Et olarak tanımlandığı görülmüştür. Çalışmada yardımcı alev geciktirici olarak aynı kimyasal yapıdaki fakat parçacık boyutu ve spesifik yüzey alanı farklı iki çeşit alüminyum bazlı mineral katkı kullanılmıştır. Deneyin ilk aşamasında parçacık büyüklüğü 1,2 μm, ticari adı Actilox B60 olan mineral katkı; deneyin ikinci aşamasında ise parçacık büyüklüğü 2,3 μm, ticari adı Actilox B30 olan mineral katkı kullanılmıştır. Bu katkı bilimsel çalışmalarda boehmite olarak adlandırılır ve kimyasal formülü AlO(OH)'tir. Saf PBT olarak hazırlanan kontrol numunesi dışındaki tüm numuneler %20 alev geciktirici katkı içermektedir. Diğer tüm numuneler 3 ayrı matriste ekstrüde edilmiştir. Bu matrisler saf PBT, cam elyaf takviyeli PBT ve cam elyaf takviyeli PBT/PET harmanı olarak sıralanmaktadır. Esas alev geciktirici ve yardımcı alev geciktiricinin optimum oranının belirlenmesi için her matriste 5 ayrı oranda deneme yapılmıştır. Deneylerin ilk aşamasında mineral katkı olarak Actilox B60 kullanılmış ve ana alev geciktirici/yardımcı alev geciktirici oranları şu şekilde belirlenmiştir: %20 DEPAL/%0 Actilox B60; %15 DEPAL/%5 Actilox B60; %10 DEPAL/%10 Actilox B60; %5 DEPAL/%15 Actilox B60 ve %0 DEPAL/%20 Actilox B60. Deneylerin ikinci aşamasında mineral katkı olarak Actilox B30 kullanılmış ve ana alev geciktirici/yardımcı alev geciktirici oranları ise şu şekilde belirlenmiştir: %20 DEPAL/%0 Actilox B30; %15 DEPAL/%5 Actilox B30; %10 DEPAL/%10 Actilox B30; %5 DEPAL/%15 Actilox B30 ve %0 DEPAL/%20 Actilox B30.

Hazırlanan örneklerin yapısal özellikleri yoğunluk ve erime akış indisi (MFI) ölçülerek değerlendirilmiştir. Örneklerin mekanik özelliklerinin belirlenmesi amacıyla ise çekme modülü, çekme mukavemeti, kopmadaki uzama ve iki farklı sıcaklıkta (+23 ^{o}C ve -30 ^{o}C) Izod darbe mukavemeti ölçümleri yapılmıştır. Termal özellik incelemesi ise yük altında bozunma sıcaklığı (HDT), termal gravimetrik (TGA) ve diferansiyel taramalı kalorimetre (DSC) analizleri ile yapılmıştır. Örneklerin yanma performansı da UL 94 yanmazlık testi, kızgın tel alevlenebilirlik indeks testi (GWFI) ve kızgın tel ile tutuşma sıcaklığı (GWIT) ölçümü ile belirlenmiştir.

Örneklerin yoğunluk ölçümleri sonucunda en yüksek yoğunluk değerini deneyin ilk aşamasında cam elyaf katkılı PBT/PET harmanına ağırlıkça %20 Actilox B60 eklenen 16 numaralı örnekte, ikinci aşamasında ise cam elyaf katkılı PBT/PET harmanına ağırlıkça %20 Actilox B30 eklenen 28 numaralı örnekte ölçülmüştür. Deneyin ilk aşamasında cam elyaf takviyesiz PBT matrisinde Actilox B60 miktarı artmasıyla yoğunluk değerinin de oransal olarak arttığı gözlenmiştir. Cam elyaf takviyeli PBT matrisi ve cam elyaf takviyeli PBT/PET harmanına aynı oranlarda Actilox B60 eklenmesi yoğunluğun aynı trendle artmasını sağlamıştır. Deneyin her iki aşamasında da beklenildiği üzere en yüksek yoğunluk değerleri, cam elyaf takviyeli PBT/PET harmanına yalnızca %20 oranında mineral bazlı yanmaz katkının eklenmesi ile elde edilmiştir.

Deneyin her iki aşamasında da erime akış indisi incelendiğinde 3 farklı matrise de yalnızca %20 oranında halojensiz fosfor bazlı alev geciktirici katkının eklenmesi akışı kolaylaştırıcı bir etki yaratırken yalnızca mineral bazlı alev geciktirici katkıların eklenmesi düşük oranda da olsa akışı zorlaştırmıştır. Saf PBT'ye %20 oranında cam elyaf takviyesi yapılması beklenildiği üzere akış hızını yarı yarıya düşürmüştür. Aynı oranlarda yanmaz katkı içeren cam elyaf takviyeli PBT/PET harmanı ile cam elyaf takviyeli PBT karşılaştırıldığında ise PET'nin akış hızını arttıran bir etki yarattığı görülmüştür. Actilox B60 ve Actilox B30 katkıların 3 farklı matrise aynı oranlarda ve ayrı ayrı eklenmesiyle elde edilen sonuçların hemen hemen aynı olduğu gözlemlenmiştir. PBT matrisine ağırlıkça %5 DEPAL ve %15 Actilox B60

katkılarının eklenmesiyle elde edilen 4 numaralı örnek ile PBT matrisine ağırlıkça %5 DEPAL ve %15 Actilox B30 eklenen 19 numaralı örnek akış hızları en yüksek olan örnekler olarak belirlenmiştir.

Örneklerin mekanik özellikleri incelendiğinde; çekme mukavemeti ölçümlerinde yalnızca ağırlıkça %20 DEPAL içeren 1 numaralı örneğin mukavemetinin %60 oranında düşürdüğü; deneyin ilk aşamasında 5 numaralı örnekte kullanılan ağırlıkça %20 Actilox B60'ın ve deneyin ikinci aşamasında 20 numaralı örnekte kullanılan ağırlıkça %20 oranındaki Actilox B30'un çekme mukavemetini değiştirmediği gözlemlenmiştir. Cam elyaf takviyesi örneklerin çekme mukavemetini hemen hemen %100 arttırmıştır. Saf PBT'ye eklenen %20 oranındaki DEPAL'in çekme modülünü %31 oranında arttırdığı hesaplanmıştır. Deneyin ilk aşamasında 5 numaralı örnekte kullanılan ağırlıkça %20 Actilox B60'ın çekme modülünü %50 oranında arttırdığı; deneyin ikinci aşamasında 20 numaralı örnekte kullanılan ağırlıkça %20 oranındaki Actilox B30'un ise çekme modülünü hemen hemen hiç değiştirmediği gözlemlenmiştir. Beklendiği üzere deneyin her iki aşamasında da cam elyaf takviye edilen tüm örneklerin çekme modülü artmıştır. Ayrıca cam elyaf takviyeli PBT/PET matrisine sahip örnekler diğer tüm örneklerden daha yüksek çekme modülü değerine sahiptir. Çekme mukavemetinin cam elyaf takviyeli PBT/PET matrisinde ağırlıkça %20 Actilox B60 içeren 16 numaralı örnekte ve cam elyaf takviyeli PBT/PET matrisinde ağırlıkça %20 Actilox B30 içeren 28 numaralı örneklerde en yüksek, çekme modülünün cam elyaf takviyeli PBT/PET matrisinde ağırlıkça %5 DEPAL ve ağırlıkça %15 Actilox B60 içeren 15 numaralı örnekte ve cam elyaf takviyeli PBT/PET matrisinde ağırlıkça %20 Actilox B30 içeren 28 numaralı örnekte en yüksek ve kopmadaki uzama oranları ise ağırlıkça %20 Actilox B60 içeren 5 numaralı örnekte ve ağırlıkça %20 oranında Actilox B30 içeren 20 numaralı örneklerde en yüksek olduğu gözlemlenmiştir**.** Kopmadaki uzama ölçümleri ayrıca incelendiğinde alev geciktirici katkıların matrise eklenmesi ile değerlerde yüksek oranda bir düşüşün gözlendiği belirlenmiştir. Özellikle cam elyaf takviyeli PBT/PET matrisine yanmaz katkıların eklenmesi ile en düşük kopmadaki uzama oranları elde edilmiştir. Actilox B30 mineral katkı içeren örneklerin kopmadaki uzama oranlarının Actilox B60 mineral katkı içeren örneklere kıyasla daha düşük olduğu gözlemlenmiştir.

23 °C ve -30 °C'larda gerçekleştirilen Izod darbe mukavemeti testlerinde, en yüksek darbe mukavemeti 23 °C'de cam elyaf takviyeli PBT/PET harmanına ağırlıkça %20 DEPAL katkısı eklenen 12 numaralı örnekte, cam elyaf takviyeli PBT/PET harmanına ağırlıkça %20 Actilox B60 eklenen 16 numaralı örnekte ve cam elyaf takviyeli PBT matrisine ağırlıkça %5 DEPAL ile %15 Actilox B30 eklenen 23 numaralı örnekte; -30 °C'de ise cam elyaf takviyeli ağırlıkça %20 DEPAL içeren 7 numaralı örnekte, cam elyaf takviyeli PBT/PET harmanına ağırlıkça %20 DEPAL eklenen 12 numaralı örnekte ve cam elyaf takviyeli PBT matrisinde ağırlıkça %20 Actilox B30 içeren 24 numaralı örnekte ölçülmüştür.

Termal özellikler incelenirken, yük altında bozunma sıcaklığı en yüksek olan örneklerin; cam elyaf takviyeli ağırlıkça %20 DEPAL içeren 7 numaralı örnek, cam elyaf takviyeli PBT matrisinde ağırlıkça %5 DEPAL ile %15 Actilox B60 içeren 10 numaralı örnek ve cam elyaf takviyeli PBT/PET matrisinde ağırlıkça %15 DEPAL ile %5 Actilox B30 içeren 5 numaralı örnek olduğu görülmüştür. DEPAL ve Actilox B60 katkıları yük altında bozunma sıcaklığını arttırıcı yönde etki ederken Actilox B30 ise düşürücü yönde etki etmiştir. Termal gravimetrik analiz sonucunda, eklenen tüm katkıların; saf PBT dışında da kullanılan tüm matrislerin bozunmaya başladığı sıcaklık düşmüştür. En yüksek bozunmaya başlama sıcaklıkları deneyin ilk aşamasında cam

elyaf takviyeli PBT matrisinde ağırlıkça %20 Actilox B60 içeren 11 numaralı örnekte, ikinci aşamasında ise cam elyaf takviyeli PBT matrisinde ağırlıkça %20 Actilox B30 içeren 24 numaralı örnekte ve cam elyaf takviyeli PBT/PET matrisinde ağırlıkça %20 Actilox B30 içeren 28 numaralı örnekte incelenmiştir.

Örneklerin yanma performansı incelendiğinde ise halojensiz fosfor bazlı yanmaz katkının, yanma özellikleri üzerinde olumlu yönde büyük bir etkisi olduğu görülmüştür. Yalnızca mineral bazlı katkıların kullanıldığı örneklerin UL 94 standartlarına uymadığı ve %5 oranında bile fosfor bazlı yanmaz katkı içeren örneklerin UL 94 standardına uygun sonuçlar verdiği görülmüştür. Bu durum mineral bazlı katkıların metal oksit içeriğinden kaynaklanmaktadır.

Kızgın tel tutuşma sıcaklıkları incelendiğinde ise deneyin her iki aşamasında da Actilox B60 veya Actilox B30 mineral bazlı katkıların eklenmesi tutuşma sıcaklığını değiştirmemiştir. En yüksek tutuşma sıcaklıkları; yanmaz katkı içermeyen cam elyaf takviyeli 6 numaralı örnekte, cam elyaf takviyeli ağırlıkça %20 DEPAL içeren 7 numaralı örnekte, cam elyaf takviyeli ağırlıkça %15 DEPAL ile %5 Actilox B60 içeren 8 numaralı örnekte ve cam elyaf takviyeli ağırlıkça %10 DEPAL ile %10 Actilox B60 içeren 9 numaralı örnekte olduğu görüşmüştür. Kızgın tel alevlenebilirlik indeksi ölçümlerinde ise yine içinde halojensiz fosfor bazlı yanmaz katkı bulunmayan örneklerin testi geçemediği görülmüştür.

Tüm deneyler sonucunda, %20 cam elyaf takviyeli PBT/PET matrisinde ağırlıkça %5 DEPAL ile %15 Actilox B30 içeren 27 numaralı örnek en iyi mekanik, termal ve yanma performansı sonuçlarını vermiştir.

1. INTRODUCTION

In the 21st century, polymeric materials are commonly used ever more areas in our daily life based on their significant combination of properties such as ease processing and low weight. The widespread usage of polymeric materials has increased the flammability of our environment and fire hazards because of their relatively high combustibility. During the combustion of polymers smoke or toxic fume, which cause loss of life and property, is released therefore governments had legalized to demand the polymeric materials that is especially used in a public situation have to retard flame. Improving the flame retardant properties of polymeric materials is a major challenge for spreading their use to most market areas such as building construction and contents, electrical and electronics, transportation, aerospace. The most well-liked approach for the flame retardation of polymeric materials are adding flame retardant additives to them directly. The addition of flame retardants to the polymer matrix, reduces the mechanical performance than the original polymer and compatibility problems occurs, due to that problems early flame retardant additives were halogen-based. Halogenated molecules which are chloride ion (Cl^-) and bromide ion (Br^-) high energy free radicals, were selected for compatibility with the main polymer and their decomposition ranges. In order to enhancing thermal stability from aliphatic chlorine, aliphatic bromine, aromatic chlorine and aromatic bromine for the highest decomposition range, the flame retardant additives would be chosen to couple polymer thermal stability. But, interference flame reactions inhibited oxidation of hydrocarbon and CO to CO_2 conversion and ended up in excessively toxic fire effluent, highly smoky. These significant problems have led to search for alternative flame retardants which are halogen free. Halogen free flame retardants include phosphorus compounds, low melt glasses, metal hydroxides, carbonate fillers, silica nanoparticles, carbon nanotubes [1-6].

Phosphorus compounds consist of the second widest group of flame retardants and proceed the fastest growing as a result of environmental concerns [7]. Halogen free phosphorus based flame retardants depend on metal phosphinate and melamine have

been proved to be as efficient as halogenated flame retardant additives in different polymers. Aluminium diethyl phosphinate is one of the most used halogen free flame retardant additive in different polymer matrix [8].

These metal salts are successfully commercial flame retardants for polyesters. Additionally, the development of low alkaline, high temperature stable, water releasing aluminium based mineral fillers as additives for new generation flame retardants. Aluminum oxide hydroxide (boehmite) is one of the mineral filler which can be combined with aluminium diethyl phosphinate and as a result of the combination better flame retardancy properties are obtained. Using the combination of diethyl phosphinate and boehmite as a co-flame retardant, there are several advantages such as better flowability of the melt, the formation of a durable protection layer during decomposition, high compatibility, improved mechanical performance and improved flame retandancy performance [9-11].

Thermoplastic polyesters, which has importance commercially, are used frequently for insulating parts in different industry. Poly(butylene terephthalate) (PBT) is one of the most used thermoplastic polyester that has several significant properties such as thermal resistance, good dimensional stability, resistance to oil and greases. The skills of PBT, which are especially glass fiber and mineral reinforced grades, to fulfil in high temperature environments can be explained by comparatively high heat deflection temperatures. PBT is rewardingly used in some applications which provide thermal insulation properties besides to mechanical performance, as good as electrical and chemical resistance [12].

Additionally, poly(ethylene terephthalate) (PET) has a significant importance in thermoplastic polyesters. Depending on these properties such as good thermal and mechanical characteristics, excellent chemical resistance, good barrier and optical properties, it is widely preferred to use in various applications [13].

PBT and PET have been commercially existing engineering plastic which are linear aromatic polyesters. They have excellent processing properties, high mechanical characteristics, electrical properties and good chemical resistance together. The crystallization rate of PBT is much faster than crystallization rate of PET due to its longer chain. However, PET has rigid molecules in structure and because of that

crystallization rate is slow. PBT and PET are miscible in the amorphous state and they have single, composition dependent T_g value [14].

In this study; PBT, glass fiber reinforced PBT and glass fiber reinforced PBT/PET blends were prepared by melt extrusion method with the addition of non-halogenated phosphorus based flame retardant (aluminium diethyl phosphinate) and mineral flame retardant (aluminium oxide hydroxide-boehmite) at different ratios. Also, two different kinds of mineral flame retardant was used. The differences between these mineral flame retardants can be explain by variation of particle size distribution and specific surface area. Structural properties of these composites were evaluated by density and melt flow index measurements. Mechanical properties were obtained by determination of strain at break, tensile modulus and stress at break. Heat distortion temperature, differential scanning calorimeter analysis and thermal gravimetric analysis were determined in order to evaluate thermal properties of the composites. Flame retardant properties of the composites were evaluated by determination of UL 94 classification, measurement of glow wire ignition temperature and glow wire flammability index.

2. THEORETICAL PART

2.1 Poly(butylene terephthalate) PBT

Historically, poly(butylene terephthalate) (PBT) is one of the oldest semi-crystalline thermoplastic which belongs to aromatic polyesters family. PBT is used in a broad array of applications which include durable goods such as electronic equipment, household appliances, automotive parts, power tools and medical appliances. Chemical structure of PBT is given in Figure 2.1.

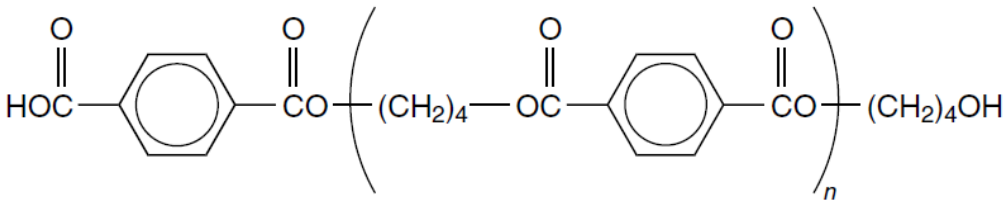

Figure 2.1: Chemical structure of PBT [15].

In 1970 Celanese Corporation produced first PBT resin with a trade name of Celanex. PBT resin is prepared by polycondensation of aliphatic dicarboxylic acids and diols. One of the most significant property of PBT is rapidly crystallization even in a cold mold [15-18].

2.1.1 Synthesis of PBT

PBT can be produced by reacting 1,4-butanediol (BDO) with terephthalic acid (TPA) in the presence of transesterification catalyst. BDO is produced by Reppe process where uses acetylene and natural gas. Large volume PET production processes have led to obtain low-cost terephthalic acid making process. Also, tetraalkyl titanates can be defined as the most generally used catalysts for PBT production. Methanol and water are by-products of PBT polymerization reaction. Polymerization reaction of PBT is shown in Figure 2.2 [15,17].

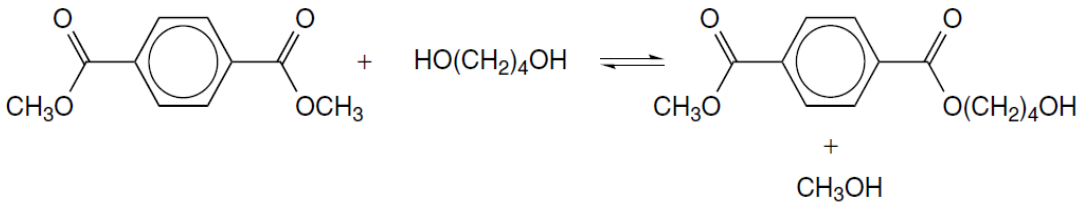

Figure 2.2: Polymerization reaction of PBT [15].

2.1.2 Properties of PBT

PBT displays highly crystalline morphological properties and it has good chemical and wear resistance at room temperature. PBT is qualified by wide range of significant properties, such as: good elongation, high strength and modulus. It has a glass transition temperature (T_g) is between 30-50 °C and a melting temperature (T_m) range of 222-232 °C, depending on its type. Actually, the glass transition temperature of PBT depends on the degree of crystallinity which is about 35-40 %. Also, PBT has excellent electrical properties [15-18].

2.2 Poly(ethylene terephthalate) (PET)

In 1942, first PET resin was synthesized by J. Rex Whinfield and W. Dickson and first commercially PET resin was produced by Imperial Chemical Industries Ltd. under the trade name of Terylene in 1953. PET resin is made by step-growth polycondensation of ethylene glycol (EG) and terephthalic acid (TPA). PET is one of the most used semi-crystalline thermoplastic polyester in packaging, fibers and engineering plastics area. Also blow-molded PET bottle is main usage area of this polymer. Chemical structure of PET is given in Figure 2.3. [15-19].

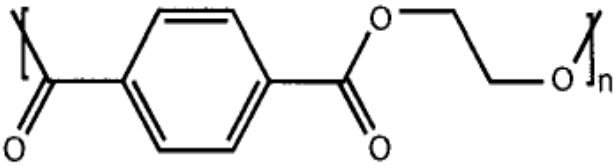

Figure 2.3: Chemical structure of PET [17].

2.2.1 Synthesis of PET

PET can be produced by reaction of pure terephthalic acid (TPA) and ethylene glycol (EG) in the presence of antimony trioxide catalyst which is most commonly used. In PET synthesis reaction, first product is a monomer of bis(2-hydroxyethyl)

terephthalate (BHET) mixed with oligomers and then the mixture reacts excess ethylene glycol. Synthesis reaction of PET is shown in Figure 2.4.

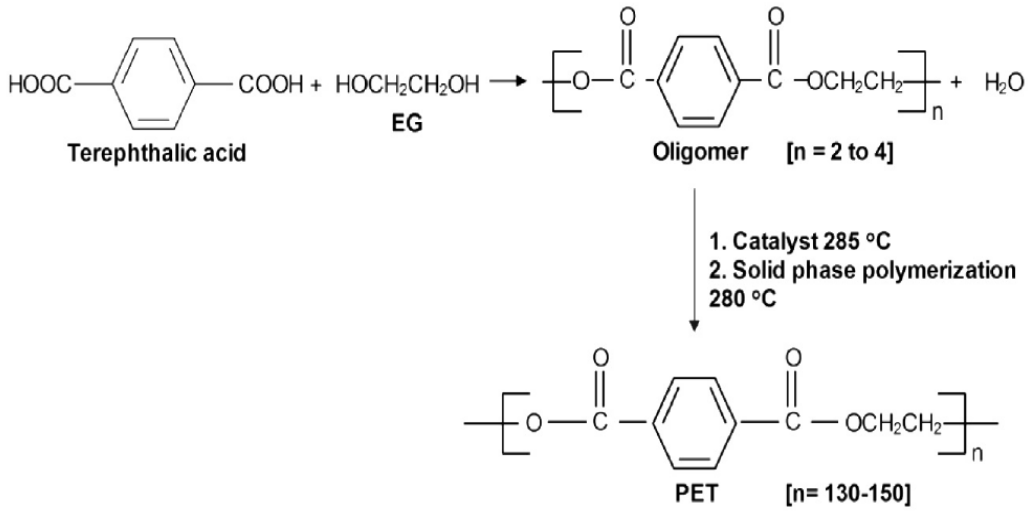

Figure 2.4: Synthesis reaction of PBT [20].

2.2.2 Properties of PET

PET, which is in purest form, has an amorphous morphology. However, if it is modified by additives, it shows crystalline properties and PET is defined as semi-crystalline polyester. When PET heated, it can be stretched either one direction or two directions. The melting temperature of PET depends on the degree of crystallinity. A high degree of heat treated PET samples can have 280 °C T_m value [16,21].

2.3 PBT Polymer Blends

Polymer blends can be defined as two or more different polymers which have varied physical properties are mixed homogenously to enhance physical properties of polymers. Thermodynamic miscibility is one of the most significant part of the mixing different polymers.

Polymer blends have to be full miscible due to phase separation problems. Low melt viscosity, melt stability, processability, thermal performance, cost effectiveness and mechanical properties of PBT, can be shown as inducement of preference.

2.3.1 PBT/PET blends

PBT-PET blends are commercially used in glass fiber reinforced. The features of glass fiber reinforced PBT-PET blends, which are more attractive in comparison of glass

fiber reinforced PBT homoploymer, include high rigidity and strength, high temperature properties and good surface appearance. Good cost/performance ratio is obtained from PBT/PET blends, depending on usage of PET resin, which is cheaper than PBT resin. Also crystallization rate of PET decreases while blended with PBT [17].

2.4 Glass Fibers

Glass fibers are the most common multiple industrial materials which are called reinforcing fibers. Softening temperature of glass fibers are between 650 °C and 970 °C, depending on compositions. Determining thermal properties of fibers, there are two significant factors which are fiber length and diameter distributions. Glass fibers are divided into two main categories that are the low cost general-purpose and premium special-purpose fibers. Also, the reinforcing fibers act as a binder in matrices [22-24].

2.4.1 Glass fiber reinforced polymers

Fiber-reinforced materials are used in polymeric matrices to improve dimensional stability, chemical resistance, insulating properties and reduce cost. E-glass and S-glass type fibers generally used as fiber-reinforced materials in polymeric matrices. E-glass type fibers are used widespread and they have the lowest cost among of all available glass fiber reinforcing agents commercially. Associated with the use of glass fibers in polymer matrices, there are some disadvantages also. Such as higher density, abrasion processing tools, higher processing temperature [22, 25].

2.5 Flammability of Polymers

The usage of plastics is widely increased more and more in buildings, electronic equipment, automobiles, household appliances etc. Plastic materials have several advantages, which are low cost, processability, easy shaping for using instead of other engineering materials in industry. However, they tend to be the most flammable and ignite easily with a flame. For this reason, flammability characteristics of plastics must be known before using in high fire risk area and identified which characteristics should be modified [26, 27].

2.5.1 Burning process of polymers

As is known, polymers are large macromolecules which consisting of large number of repeating units. The binding of these repeating units; gases and volatile liquids are held together with backbone of the polymer. These gases and volatiles create combustible mixtures in the presence of air and readily ignite. Ignition takes place two different types which are autoignition and flash point. Autoignition can be defined as the temperature that achieve sufficient activation energy of combustion and flash point can be defined as combustion occurs at a room temperature with an external source such as flame or spark. According to fire three angle; fuel, heat and oxygen is required to obtain combustion. In polymer combustion reaction; fuel is supplied by combustible volatiles, heat is supplied by an external sources and oxygen is supplied by ambient air. In Figure 2.5 the combustion cycle of polymers is shown.

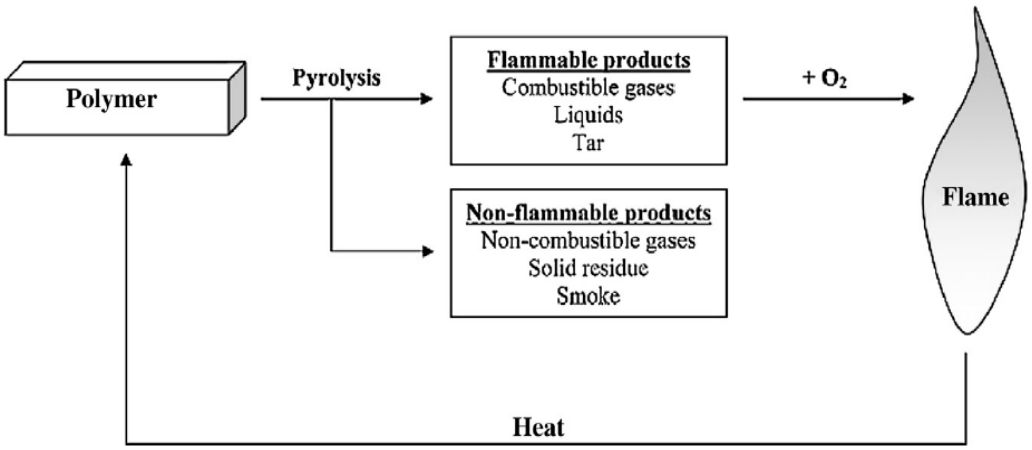

Figure 2.5: The combustion cycle of polymers [29].

Polymer combustion can be split into two main categories which are physical and chemical processes. In Figure 2.6 physical and chemical processes in the polymer combustion is shown horizontally. On the left side of the Figure 2.6; physical, on the right side of the Figure 2.6 chemical processes are shown. Physical combustion process involves energy transport by convection and radiation between the mesophase and flame; vaporization of pyrolysis gases and conduction into the solid. Chemical combustion processes involve thermal degradation of the polymer, mixing of the volatile pyrolysis products with air, combustion of the fuel and air mixture in the combustion zone [28-31].

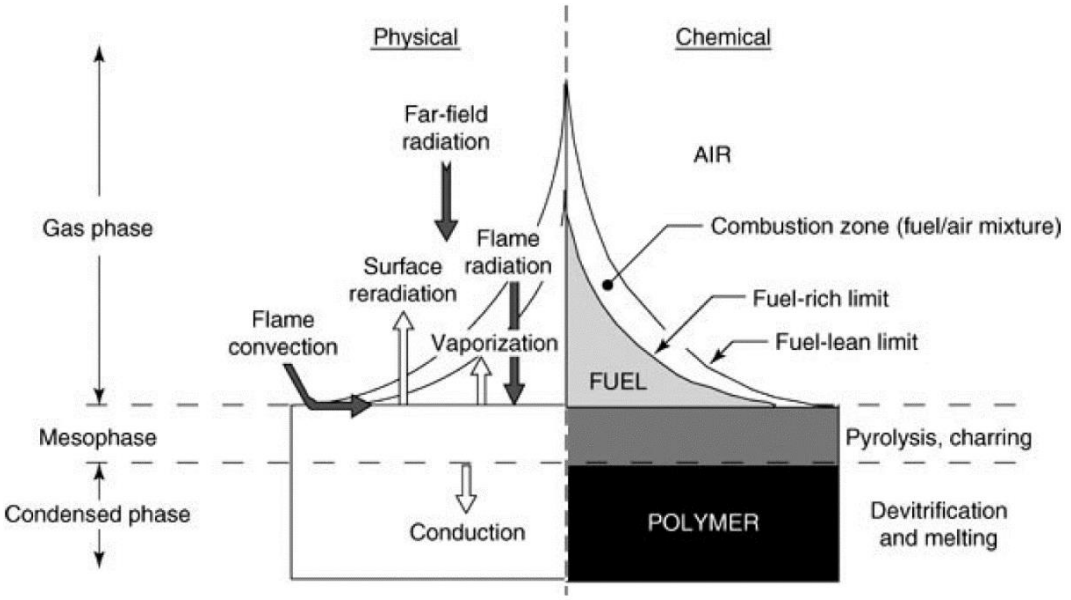

Figure 2.6: Physical and chemical processes in the flaming combustion of polymers [28].

2.5.2 Fire behavior of solid polymers

During the development of a fire, several phases such as ignition, steady burning and unsteady burning are observed respectively in polymers.

2.5.2.1 Ignition

Ignition can be defined as initiation step of combustion with fuel source and oxygen from ambient air. When the lower flammability limit is achieved, autoignition is occurred or material is ignited with an external flame or spark.

In order to identify ignition of polymers two main criteria, which are thermal and chemical, should be examined. Chemical criteria for ignition can be defined as a critical mass flux or a critical heat release rate. At ignition, critical mass flux value is changed according to polymer which is used, because of lower flammability limit of their pyrolysis products. Thermal criteria of ignition can be defined as a surface temperature near the thermal decomposition temperature is needed to start the fuel generation process. Ignition thermal theory assumes that at ignition process the surface temperature is a characteristic property of the polymer [28, 29].

2.5.2.2 Steady and unsteady burning

Ignition is sustained and the rate of burning achieved a constant value, heat release rate and temperature are at their prime, a fully developed fire is expressed. For the entire

test, an average heat release rate is used, or some heat release rate interval can be used. Unsteady burning, it is also called transient ignition, is important related to flammability tests [28, 29].

2.6 Flame Retardant Additives

Flammability is the major challenging of polymeric materials. In order to reduce combustibility of polymeric materials, flame retardant additives are widely used in construction, electronics, household appliances, transportation industry etc. Between 1960s and 1970s fires became more common because of the increment of using polymeric materials in different industries. For flame retardant solutions, a basic event and demands timeline is given in Table 2.1.

Table 2.1: The events and demands that can be addressed with fire retardant solutions [34].

Decade	Event	Demand
1960s	Widespread availability of cheap polymer products – more serious fires	Reduced ignitability
1970s	Smoke becomes a major obstacle to escape	Reduced smoke
1980s – 1990s	Development of cone calorimeter (and emphasis on peak heat release rate, rather than ignitability)	Reduced peak heat release
	Increase in deaths from smoke inhalation	Reduced fire toxicity
2000s	Halogen FRs found across the ecosystem	Halogen-free fire retardants
2010s	Climate change and other environmental concerns become mainstream	Sustainable flame retardants

Halogenated flame retardants, phosphorus based flame retardants and mineral flame retardants are most commonly used [31,34-35].

2.6.1 Halogenated flame retardants

Depending on type of halogen which is used in polymeric matrix, the effectiveness of halogenated flame retardant additive can vary. Fluorinated type compounds are thermally steadier than most polymers below the distortion temperature of polymeric materials and they do not release halogen radicals. Iodine based and fluorine based compounds are not used generally because they cannot interfere with the combustion process of polymers. Iodinated compounds release halogenated species during the combustion process of polymers. Chlorine and bromine species can be easily released because of the low bonding energy with carbon atoms [6].

2.6.2 Phosphorus based flame retardants

The aim of using phosphorus compounds in flame retardancy had been in oxygen involving char-forming polymers, sort of polyesters, polyurethanes etc., which were flow in oxygen functionality on the polymer behaves like phosphorus acids, lead to char [33]. The char is hard to ignite, it behaves like a barrier between polymer and flame, it restricts oxygen access and it decreases the heat generation rate [36]. The variety of phosphorus based flame retardant additives are highly widespread, containing red phosphorus, phosphine oxides, phosphonates, phosphates and phosphinates [6]. These additives generally act in the condensed phase by changing the pyrolytic path of the polymeric material and decreasing the value of gaseous combustibles [35].

The most significant attitudes were based on compounds which are inorganic and organic compounds that involves phosphorus. In recent years, metal phophinates pertain to a novel class of phosphorus flame retardants which are improved and commercialized [37]. Aluminium diethylphosphinate (AlPi-Et) appertains to a new group of non-halogenated flame retardants. Flame retardancy effect of aluminium diethylphosphinate is depend on flame inhibition via the release of phosphorus species in the gas phase and the formation of an aluminium phosphate and carbonaceous char in residue [38].

2.6.2.1 Intumescent flame retardants

In order to protect coatings, fabrics and wood from fire hazardous, intumescent flame retardants are used as additives. In case of thermal degradation, intumescent flame retardants behave like an insulating barrier and decreasing heat transfer area between the polymer surface and the heat source. During the process the theme of intumescence endurances the form of enlarge carbonized layer on the surface of the polymer. Generally, intumescent flame retardant systems need three main components which are an acid source, a carbonizing agent and a blowing agent [6].

2.6.3 Mineral flame retardants

Mineral flame retardant additives are one of the most significant types of flame retardant additives which provide structural entirety and reinforcement. They represent also an alternative to halogen free flame retardants. Mineral flame retardant additives are much more difficult to merge into a polymer matrix at a necessary level to reach

the required quantity of flame retardancy than halogenated flame retardants. All mineral fillers, such as nanoclays, zinc borates and zirconium phosphates, act at the condensed phase, they are diluting the flammable polymer samples, forming barriers to mass and heat transfer and reduce mass and heat loss rate. Additionally, mineral fillers include also mineral flame retardants and they provide fire retardancy via endothermic decomposition at the condensed phase, releasing inert gas and leaving a solid residue. This type of flame retardants include aluminum trihydroxide, magnesium oxide and aluminum oxide hydroxide which are commonly used metal hydroxides [34].

2.6.3.1 Aluminium trihydroxide

Aluminum trihydroxide (ATH or $Al(OH)_3$) is one of the most used flame retardant on the market in a consequence of the necessary of high loadings to reach significant fire retardancy level in polymer composites and its low cost in contrast to other types of metal hydroxide. The decomposition onset temperature is between 180 and 200 °C for aluminum trihydroxide [34]. When ATH is heated, it release water and this increases the overall endothermicity of the flame retardant polymer and generates water vapour that dilutes the flame [29].

2.6.3.2 Magnesium hydroxide

Magnesium hydroxide is less used in contrast to ATH but it works as the same way. The most important different between magnesium hydroxide and aluminum trihydroxide is the decomposition onset temperature which is between 300 °C and 320 °C for magnesium hydroxide [34].

2.6.3.3 Aluminium oxide hydroxide (boehmite)

Boehmite AlO(OH) have recently shown potential as flame retardant additives which act in the gas phase as free radical trap. It is used heat absorber since its endotherm and heat capacity contribution is too small. AlO(OH) is an intermediate decomposition product of aluminum trihydroxide [34]. Boehmite is an approximation of mineral filler wards engineering plastics are shown possible, based on low alkaline, high temperature stable properties. Boehmite shows high performance properties via combination of phorsphorus and nitrogen flame retardants. High spesific surface boehmite is generally used as co-flame retardant and it improves the mechanical properties of the compound. Using boehmite minerals as a co-flame retardant supports

the phase separation between the polymer matrix and the mineral filler, also reduce the content of by-products which are aggressive [11].

2.7 Flammability Test Methods of Polymer

Flammability tests are defined as test methods to characterize the behavior of polymers that exposed to a small heat sources such as glow wire for a short period of time. During exposure, fail or pass criteria are depend on ignition of the samples, formation of flaming droplets, sustained flaming or smoldering after heat source is removed [26].

2.7.1 UL 94

The UL 94 tests method is designed by Underwriters Laboratory Inc. for evaluating flammability of plastic materials which used in appliances and other devices. The UL 94 tests are largely used in academic researches and industry. This test measures how long plastic sample, at specified dimensions, burns after exposure to flame and response to this ignition source (a match or a candle). The UL 94 test standard has several different test methods such as two horizontal, three vertical burning tests and a radiant panel flame spread test. Test samples can be oriented in horizontal or vertical. Two sets of five test samples are used and these samples can be molded 0.8, 1.6 and 3.2 mm thick depending on the desired use of the material. Vertical burning test is most common used method. The test sample, which measuring 12.7 cm in length, is mounted vertically and held from the top. A thin layer of cotton is placed 30.5 cm below the test sample to catch any molten drops that can be ignite the cotton. The burner barrel is positioned 9.5 mm below the bottom end of the test samples. The Bunsen methane burner flame, which is about 19 mm high, is applied at bottom of a total of five test samples twice for 10 seconds. The UL 94 vertical burning test method is shown in Figure 2.7. The burning time is recorded after each application of flame and used for calculations. Depending on calculation results, the total burning time for each samples and absence or presence of molten drops, the test sample is classified V0, V1 and V2 rate.

A V0 rate is defined as when the five test samples extinguish in less than 10 seconds after each flame application. The average burning time for 5 samples should not be longer than 5 seconds and there should not be any molten drips that ignite the cotton where bottom of the samples. The sample afterflame plus afterglow time must not go over 30 seconds.

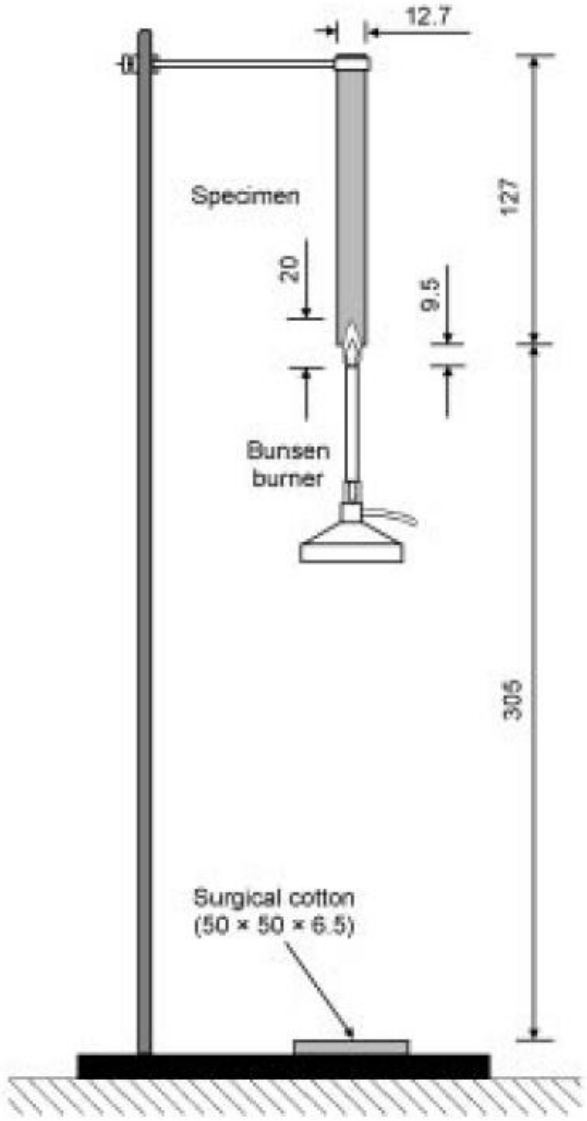

Figure 2.7: UL 94 vertical burning test [29].

A V1 rate can be defined as when the five test samples extinguish in less than 50 seconds after each flame application. The average burning time for 5 samples should not be longer than 25 seconds and there should not be any molten drips. The sample afterflame plus afterglow must not go over 60 seconds.

A V2 rate can be defined as if it corresponds the burning time criteria of V1 rate or V0 rate however the classification type has molten drips which can ignite the cotton. Also if test sample either self-extinguish before a 2.5 cm credentials or burn at a rate of less than 4 cm per minute for test samples of 0.3 to 1.3 cm thickness, or less than 7.5 cm per minute for test specimens less than 0.3 cm thick [24, 26-31].

If the test sample is totally consumed with a flame, sample is noted “No Rate (NR)” which is mean out of spec.

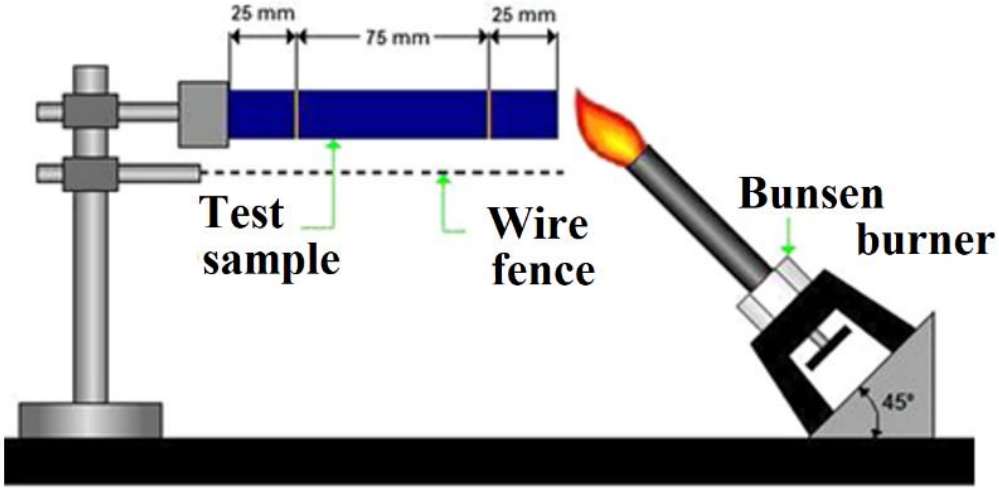

Figure 2.8: UL 94 horizontal burning test [39].

In UL 94 horizontal burning (HB) test specified that the test sample was placed in a horizontal position and aim to burn at a rate less than identified at UL 94 HB standard. A test sample is positioned at 45° in horizontal position. The flame is applied 30 seconds or until the flame achieved the 1 inch to the end of the test sample. If the test sample stops burning before the flame sprawls to the 4 in mark, the time of combustion and the damaged length between these two marks were recorded. The UL 94 horizontal burning test method is shown in Figure 2.8 [39].

2.7.2 Glow wire tests

At glow wire tests high temperature heated hairpin-shaped resistance wire that is tamped, slide rig is used, for 30 seconds against the test sample and after that pulled it back. The glow wire temperature is measured at which the test sample on contact and 30 seconds after released. The glow wire ignition temperature is can be defined as the wire temperature where the test sample is ignited with a flame of 5 seconds duration or further. The glow wire flammability index can be defined as the temperature the temperature at which the flames burn for less than 30 seconds. The glow wire test apparatus are shown in Figure 2.9 [33].

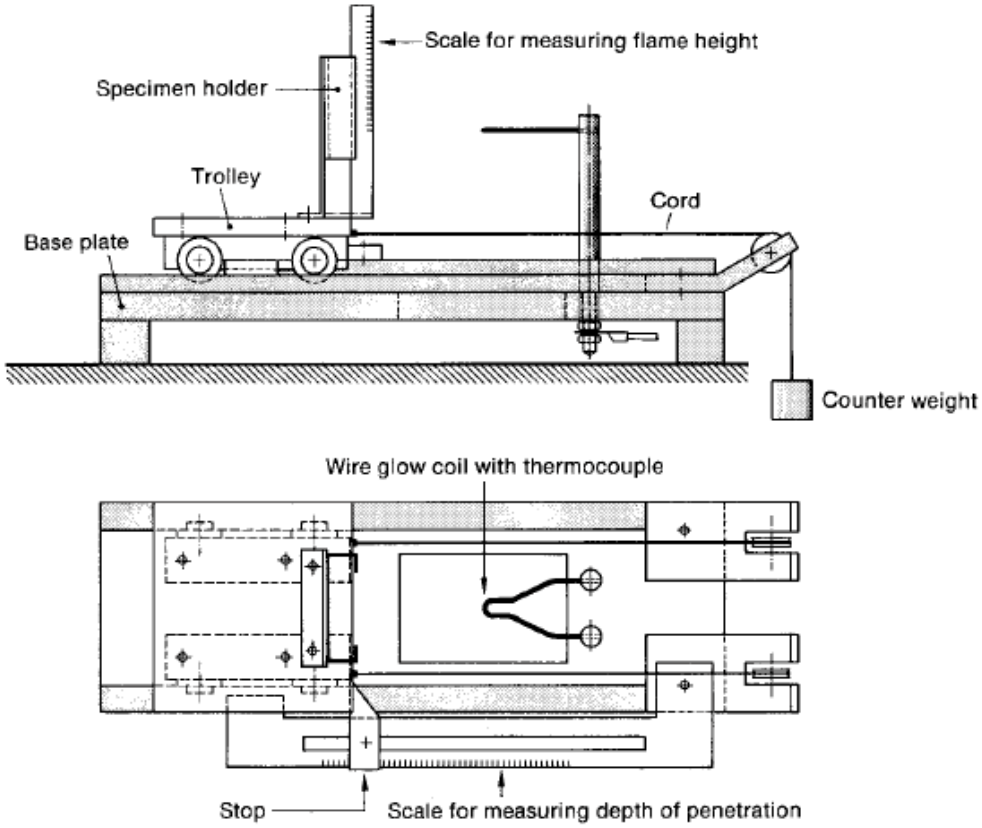

Figure 2.9: Glow wire test apparatus [28].

2.7.3 Limiting Oxygen Index (LOI)

One of the oldest flammability test method is limiting oxygen index test which is used especially determine the minimum amount of oxygen in an oxygen/nitrogen mixture which supports flaming combustion. The LOI test does not supply trustworthy sign of the test sample performance in case of real fires. Three test samples that its dimensions almost 100 x 65 x 3 mm are used in rigid plastic test. One of the LOI test equipment is a glass tube in which the test sample is positioned vertically. The oxygen/nitrogen mixture is forced upward through the glass tube from the bottom. A small candle like flame is applied to the top of the samples to ignite it. If the flame maintains for 3 minutes or spread down the length of the test sample, the test must be repeated at lower oxygen concentration.

If it self-extinguishes, the test must be repeated at higher oxygen concentration. The oxygen concentration is adjusted in this way until the test sample can support combustion. The limiting oxygen index is calculated by LOI=($[O_2]$/($[O_2]$+$[N_2]$)) equation. The limiting oxygen index is a measure of the percentage of oxygen in the flame test atmosphere and the LOI test results are expressed a percentage. In Figure

2.10 schematic view of the limiting oxygen index test apparatus are shown. For instance, a LOI test result of 30 states that 30% of the oxygen/nitrogen mixture is required to be oxygen on the purpose of support continued combustion of the test sample [28-33].

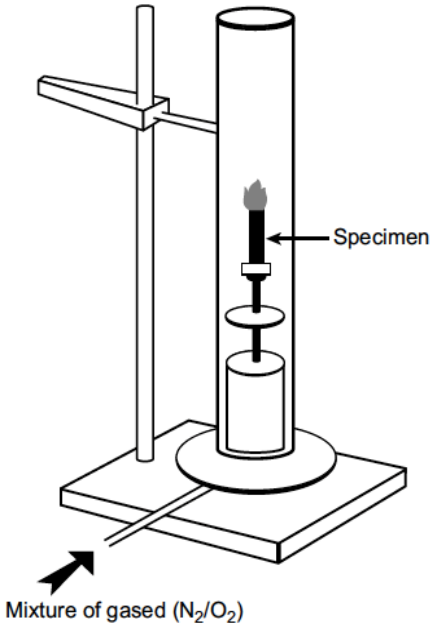

Figure 2.10: Schematic view of the LOI test apparatus [28].

2.7.4 Cone calorimeter

The cone calorimeter test is the bench scale test that was introduced to industry, academic community and R&D by the National Institute of Standards and Technology (NIST).

The cone calorimeter test method is the most advanced method for evaluating plastic samples reaction to real world fire. The cone calorimeter is an oxygen consumption calorimetry which converts the oxygen consumption rates into heat release rates.

It provides also heat release over time, data relevant to flash-over time, smoke release rate, mass loss rate. At the beginning of the test, a square test sample, that its dimensions 10 x 10 cm, is positioned on a load cell allowing the measurement of mass loss rate. The sample surface is exposed to a fixed event heat flux, within the range 0-100 kW/m^2, from a truncated cone radiant electrical heater at a constant rate. The cone radiant electrical heater can be specified representing small fires to fully developed fires. For piloted ignition, an electrical spark is used. From the sample, electrical spark

ignites the pyrolysis gases. The gases are collected by a hood and extracted by an exhaust fan. The heat release rate is calculated by the oxygen consumption which is derived from oxygen concentration. The schematic representation of cone calorimeter apparatus is shown in Figure 2.11. A detailed analysis requires testing at different irradiance levels which can be 25, 35, 50 and 75 kW/m^2. Three test samples should be tested for each heat flux level [28-33].

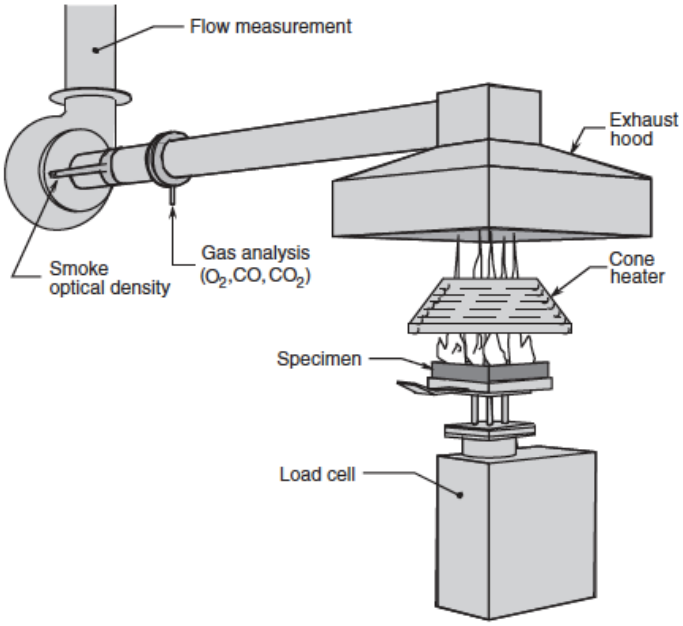

Figure 2.11: Schematic representation of cone calorimeter [30].

2.8 Literature Overview

Laachachi et al. compared boehmite (AlO(OH)) and alumina (Al_2O_3) in the thermal stability and flame retardant properties of poly(methyl methacrylate) (PMMA). In comparison of neat PMMA with PMMA-AlO(OH) and PMMA-Al_2O_3 nanocomposites shows higher fire resistance and thermal stability. 20% AlO(OH)-PMMA and 15% Al_2O_3-PMMA shows greater reduction in peak of heat release rate. On the other hand, more important oxygen barrier effect and insulating effect is investigated by using boehmite. Also, the lowest total smoke released obtained with using AlO(OH). Additionally, in the presence of AlO(OH); the thermal degradation rate is retarded, the accompanying release of water dilutes the fuel supply present in the gas phase [40].

Friederich et al. studied a comparison of metal oxides nano particles in ternary system, which are ammonium polyphosphate (APP), melamine polyphosphate (MPP) and

metal oxide which are alumina and boehmite, was examined in poly(methyl methacrylate), PMMA. In this study they investigated thermal behavior and flame resistance properties of different combinations which are 85% PMMA + 15% APP, 85% PMMA + 15% MPP, 85% PMMA + 15% metal oxide, 85% PMMA + 7.5% APP/7.5% MPP, 85% PMMA +7.5% APP/7.5% metal oxide, 85% PMMA +7.5% MPP/7.5% metal oxide and the last one is 85% PMMA +5% APP/5% MPP/5% metal oxide. Thermogravimetric analysis was done by TGA, thermal diffusivity was measured by laser flash analysis, flammability properties were measured by cone calorimeter and pyrolysis combustion flow calorimetry is used for characterization. The addition of 15% metal oxides to PMMA, metal oxides delayed the starting degradation temperature due to limitation of mobility polymer chain. The TGA curve shape changed in case of using APP. Inversely, replacement of MPP or APP with metal oxides, thermal stability is increased. The metal oxides reinforced the barrier effect by limiting the polymer chain mobility and also the increment of viscosity value, decreased the gases release. The combination of MPP, APP and boehmite (AlO(OH)) or alumina (Al_2O_3) lead to an important improvement of the thermal stability. The thermal analysis show that especially boehmite, MPP and APP combination has the best result. The fire retardancy properties of two different metal oxides are examined by cone calorimeter and also several parameters were measured at the same time such as time of flame out, smoke emission, mass loss etc. The longest combustion time is obtained 85% PMMA + 7.5% MPP/7.5%AlO(OH) and 85% PMMA +5% APP/5% MPP/5% AlO(OH) and the lowest were obtained PMMA containing boehmite combined with APP and/or MPP. In case of combination of boehmite and phosphorus based flame retardant, barrier effect is occurred by a chemical way. At the end of this study, in case of using boehmite nano particles in ternary system better flammability properties are obtained. In consequence of crystallization reaction, AlO(OH) based ternary system release low amount of CO which means that combustion was nearly completed however inversely Al_2O_3 based ternary systems present incomplete combustion reaction. In conclusion, AlO(OH) based systems show better flammability properties than Al_2O_3 based systems, also the best synergy effect on the heat release rate is obtained 85% PMMA + 7.5% APP/7.5% AlO(OH) [41].

Köppl et al. investigated comparison of morphological, mechanical, rheological and flammability properties of halogen free additives aluminium diethylphosphinate

(AlPi – Et) and a mixture of aluminium phosphinate (AlPi) and resorcinol-bis(di-2,6-xylyl phosphate) (AlPi-H + RXP) are used in neat poly(butylene terephthalate) and 30 % glass fiber reinforced poly(butylene terephthalate). The morphology of the samples was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and microcomputertomographt (μ-CT). The crystallinity analysis of samples was done by differential scanning calorimetry (DSC). The rheological behaviour of these samples were investigated by stress controlled mechanical-dynamic rheometer. The flammability characteristics of samples were assessed by UL 94 test and limiting oxygen index (LOI). Last the mechanical testing were performed by using tensile and Charpy impact testing machine. The particle morphology of AlPi-Et and AlPi-H + RXP comprise of agglomerates with a size of 10-100 μm and 5-50 μm respectively. These systems show a similar nanocomposite-like morphology. The agglomerates of the AlPi-H + RXP has a slightly lower median length, which around 30 μm, than AlPi-Et, that is around 35 μm. when the flame retardant concentration is increased to 20%, they observed the same agglomerate size but a total number of agglomerates is increased. The glass fiber reinforced PBT composites with AlPi-H + RXP shows a relative poor fiber-matrix adhesion conversely AlPi-Et PBT composite shows strong fiber-matrix adhesion. If the flammability properties of glass fiber (GF) reinforced PBT is compared the neat PBT, glass fiber compress the melt flow and dripping. Also, the LOI value of GF reinforced PBT is lower than neat PBT. AlPi-Et flame retardant additive were performed better flame retardant properties than AlPi-H + RXP for GF reinforced PBT under the special conditions of LOI. The UL 94 characterization of both flame retardant additives are similar. But AlPi-Et flame retardant additive was slightly better than AlPi-H + RXP. As it was expected GF reinforced PBT shows better tensile strength properties and tensile modulus almost four times. In comparison of the addition AlPi-Et leads to a lower impact and tensile strength properties than the addition of AlPi-H + RXP to the GF reinforced PBT. At the end of this study, they investigated the addition of AlPi-based flame retardant additives in both neat PBT and GF reinforced PBT, leads to a desirable flame retardant properties and significant decrease of stress and elongation at break of the samples [42].

A study done by Gallo et al. looked at the PBT nanocomposites in combination with aluminium phosphinate and halogen free flame retarded PBT. The composite was

prepared with the melt processing method. Thermal analysis of the composites was done by TGA, the flammability properties of composites were investigated by UL 94 test and cone calorimetry. They used three different metal oxides such as Aluminium diethyl phosphinate (AlPi), titanium dioxide (TiO_2) and nanometric aluminium oxide (Al_2O_3). Flame retardancy mechanism of halogen free PBT were determined for AlPi in combination with different nanometric metal oxides. PBT/AlPi composites has higher fire resistance in UL 94 test, cone calorimeter test and increase the limiting oxygen index (LOI) value. The addition of other metal oxides particles to the PBT/AlPi composites, UL 94 classification and the LOI value were not changed significantly however the cone calorimeter test result is restricted under forced flaming special conditions. The addition of metal oxide particles to PBT/AlPi (10 weight%) composites, V-0 classification is obtained. But they obtained the same classification result that using 20 weights% PBT/AlPi. At the end of this study, they realized a good dispersion of nanometric metal mineral fillers into the PBT shows desirable fire retardant performance [43].

Braun et al. investigated pyrolysis and flammability properties of glass fiber reinforced poly(butylene terephthalate) with two different metal phosphinates without and with melamine cyanurate (MC). 30 wt.% glass fiber reinforced PBT and 20 wt.% flame retardants which include 13.3 wt.% metal phosphinate/6.7 wt.% MC. These metal phosphinates were aligned aluminium diethyl phosphinate (AlPi) and Zinc bis-(diethylphosphinate) (ZnPi). Thermal analysis was done by using TGA and infrared spectrometer. Fire behaviour is determined by using a pyrolysis combustion flow calorimeter, UL 94 and limiting oxygen index (LOI). Residue analysis is measured by wavelength dispersive X-Ray fluorescence and scanning electron microscopy. GF reinforced PBT with AlPi and MC that performed V-0 rate in UL-94 and LOI of 44%. Conversely, GF reinforced PBT with ZnPi that performed horizontal burning (HB) rate in UL-94 and LOI of 27%. In the presence of the AlPi polyester decomposition is impressed because of the subsequent formation of AlPi-terephthalate. While the aluminium salts react with the polymer matrix, part of zinc salts vaporized in addition to the formation of ZnPi-terephthalate. Under the flame conditions, AlPi and ZnPi behave same way and an increased peak of heat release rate and mass loss while the amount of residue is increased. At the end of this study, GF reinforced PBT with AlPi has better UL-94 classification from the GF reinforced PBT with ZnPi. The analysis

of residue, for AlPi containing GF reinforced PBT, find out trace amount carbonaceous char that is like and adhesive between the glass fiber however the residue analysis of ZnPi containing GF reinforced PBT, carbonaceous char is not found [44].

Zhang et al. investigated the flame retardancy mechanism of poly(ethylene terephthalate)/boehmite nano composites and also investigated of its thermal stability. Combustion behaviour and flammability properties were calculated using limiting oxygen index (LOI) and cone calorimeter. Thermal behaviour and pyrolysis were assessed using TGA and gas chromatography-mass spectrometry and also using scanning electron microscopy combustion residues were examined. Pure PET and PET/oehmite nanocomposite were prepared in situ. First of all, esterification reaction was occurred and then AlO(OH) sol is added. After that polycondensation is completed. Via addition of small amount of AlO(OH) mineral flame retardant, the LOI value of PET is increased significantly. Also cone calorimetry results showed that PET/boehmite nanocomposite has better thermal stability than pure PBT. Pyrolysis, gas chromatography, mass spectrometry result is showed the addition of flame retardancy additives change the pyrolysis process, thick carbon char is occurred, decreased the combustible gas concentration. Additionally, SEM results of the char crusts showed that the PET/boehmite char crust was thicker. At the end of this study, the result of addition of boehmite to pure PET, improved thermal stability and flame retardancy properties were obtained [19].

Guido et al. studied on flame retardancy and thermal stability properties of synthetic boehmite treated polyester fabrics in order to limit melt dripping and achieve desirable thermal stability and flame retardancy. Assessment of morphology of the treated PET fabrics and elemental analysis were done by scanning electron microscopy. Investigation of thermal properties of these PET fabrics, thermos gravimetric analyser is used. The flame retardancy properties of these samples, measured by vertical fabric flammability test. PET fibers are showed regular and smooth morphological properties but treated PET, in the presence of the boehmite particles, show the formation of microaggregates attributable to boehmite nanoparticles. The treatment of PET fabrics with a sol containing boehmite has strongly improved flame resistance, as confirmed by the raise up the final residue and by the dripping wipe out as well. At the end of this study; this halogen free, environmentally flame retardants could usefully move current flame retardant additives [45].

3. EXPERIMENTAL PART

3.1 Materials

3.1.1 Poly(butylene terephthalate) (PBT)

Poly(butylene terephthalate) used in this study with a trade name of Poly(butylene terephthalate) Resin KH2090 that was supplied by YingKou Kanghui Petrochemical Co., Ltd., China. The melt mass flow rate (250 °C/2.16 kg) and melting temperature are 50 g/10 min and 223.5 °C respectively.

3.1.2 Poly(ethylene terephthalate) (PET)

Poly(butylene terephthalate) used in this study with a trade name of ADVANITE™ 23001 that was supplied by SASA Polyester Company, Turkey. The melt volume rate of the PET is 4.5 cm^3/10 min at 250 °C.

3.1.3 Glass fiber

E-type glass fiber was obtained from Nippon Electric Glass Co., Ltd. The filament diameter and the strand length are 10.5 μm and 3 mm respectively.

3.1.4 Aluminium diethylphosphinate (DEPAL)

Aluminium diethylphosphinate (AlPi) used in this study with a trade name of Exolit OP 1230 that was supplied by Clariant. Exolit OP 1230 white, fine grained powder based on an organic phosphinate. It is the first non-halogenated flame retardant and called as DEPAL. The average particle size (D_{50}) and density (at 20 °C) are 20-40 μm and 1.35 g/cm^3 respectively.

3.1.5 Aluminium oxide hydroxide (boehmite)

In this study, two different types of boehmite were used as co-flame retardant. These are Actilox B60 and Actilox B30.

3.1.5.1 Actilox B60

Actilox B60 was obtained from Nabaltec AG, Germany. The average particle size (D_{50}) and specific surface area are 1.2 μm and 5 m^2/g respectively.

3.1.5.2 Actilox B30

Actilox B30 was obtained from Nabaltec AG, Germany. The average particle size (D50) and specific surface area are 2.3 μm and 3 m^2/g respectively.

3.1.6 Lubricant

An ester of mixed montan acid used in this study as a lubricant with a trade name of Licowax OP P that was supplied by Clariant. Its particle size is approximately 61 μm.

3.1.7 Process stabilizer

Hydrolytically stable phosphite used in this study as a processing stabilizer with a trade name of Irgafos 168 that was supplied by BASF. Its melting range is 183-186 °C and density is 1.03 g/cm^3.

3.1.8 Heat stabilizer

Phenolic Primary Antioxidant used in this study as a long-term thermal stabilizer with a trade name of Irganox 1010 that was supplied by BASF. Its melting range is 110-125 °C and density is 1.15 g/cm^3.

3.2 Equipment

3.2.1 Twin screw extruder

Coperion ZSK 26 P 10.6 extruder that is shown in Figure 3.1 was used for sample preperation. This co-rotating twin screw extruder have 1 non-heating zone, which is first zone that connected main feeder, and 10 heating zones. 3 different feeders are connected with the extruder. The main feeder is connected with the first zone and feeding the main polymer matrix to the machine. There are two side feeders on the barrel. First side feeder is on the fourth heating zone and it feeds only powder additives to the mixture. Second side feeder is on the sixth heating zone and it feeds glass fibers to the mixture. Vacuum is applied at the tenth heating zone. L/D ratio of the extruder is 40:1 and maximum screw speed is 1800 rpm. Screw length of the extruder is 1020 millimeters. Screw diameter is 25.5 millimeters and permissible maximum operating pressure is 180 bar. Motor power of vacuum is 0.75 kilowatt, cooling unit is 0.69 kilowatt, pelletizer is 2.2 kilowatt.

Figure 3.1: Co-rotating twin screw extruder.

3.2.2 Injection moulding machine

According to ISO 527 standard, the samples were produced by Arburg Allrounder 320 K 700 – 100 Injection Molding Machine that is shown in Figure 3.2 Technical specifications of the machine are given in Table 3.1.

Table 3.1: Technical specifications of injection molding machine.

Specifications	Value	Unit
Screw Diameter	25	mm
Maximum Injection Pressure	2500	bar
Maximum Volumetric Displacement	49	cm3
Wax. Shot Weight	45	g
Hydraulic Motor Power	15	kW
Maximum Clamping Force	700	kN
Maximum Screw Speed	35	m/min
Screw Back Pressure	350	bar
Plasticizing Capacity	8	kg/h
L/D Ratio	20	

Figure 3.2: Arburg Allrounder 320 K 700-100 injection molding machine.

3.2.3 Density determination

The densities of samples were measured with AND GR200 Analytical Semi-Micro Balance as shown in Figure 3.3

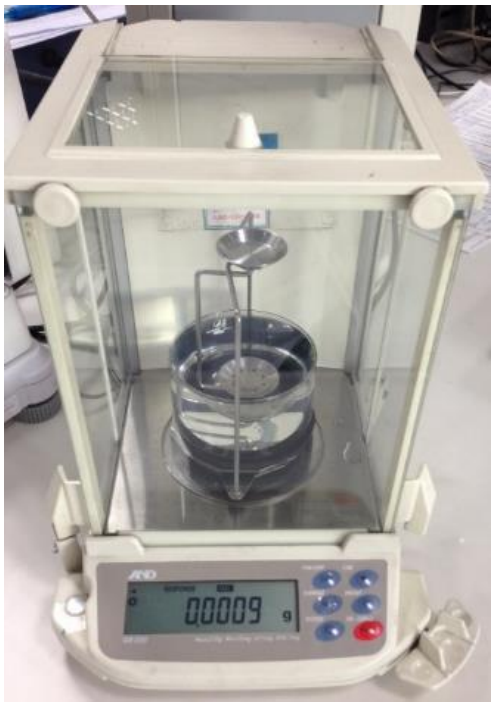

Figure 3.3: Analytical semi-micro balance.

3.2.4 Melt flow index (MFI) equipment

The melt flow index of samples was measured with CEAST MF20 melt flow tester as shown in Figure 3.4. Manual mass selector, which make simpler testing, is also integrated onto the melt flow tester.

Figure 3.4: Melt flow tester.

3.2.5 Tensile test machine

The tensile properties of samples were performed by Zwick Universal Tensile Testing Machine Z050 by 50 kN load cell as load indicator and long stroke extensometer as extension indicator, shown in Figure 3.5.

Figure 3.5: Universal tensile testing machine.

3.2.6 Izod impact test machine

Izod impact strength properties of samples were measured by Ceast Resil Impactor 6957 Izod Impact Test Machine that can be operated between 1 and 50 Joule energy pitch, shown in Figure 3.6.

Figure 3.6: Izod impact test machine.

3.2.7 Heat distortion temperature (HDT) equipment

Heat distortion temperature of samples were measured by Ceast 3P HDT VICAT thermal tester that equipped with three testing station, shown in Figure 3.7.

Figure 3.7: HDT thermal tester.

3.2.8 Differential scanning calorimeter (DSC)

Thermal analyses of samples were done with TA Instruments Q2000 Differential Scanning Calorimeter that is shown in Figure 3.8. Performance specifications of differential scanning calorimeter are given in Table 3.2.

Table 3.2: Performance specifications of DSC.

Performance Specifications of DSC	
Temperature Range	Ambient to 725 °C
With Cooling Accessories	-180 to 725 °C
Temperature Accuracy	± 0.1 °C
Temperature Precision	± 0.01°C
Dynamic Measurement Range	>± 500 mW
Sensitivity	0.2 µW
Indium Height/Width (mW/°C)	60

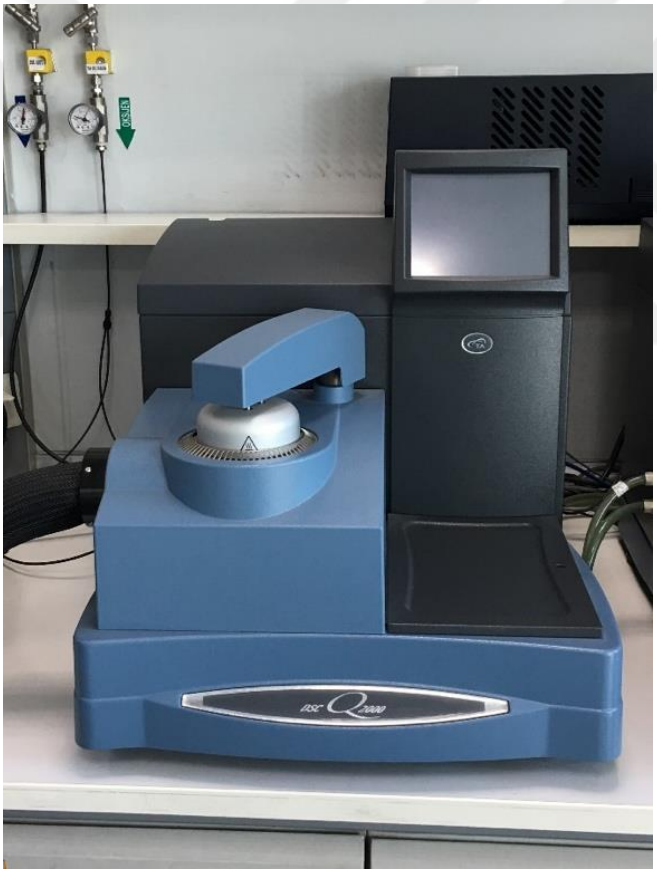

Figure 3.8: Differential scanning calorimeter.

3.2.9 Thermal gravimetric analysis (TGA)

Thermal gravimetric analyses of samples were done with TA Instruments Q500 Thermal Gravimetric Analyzer that is shown in Figure 3.9. Performance specifications of thermal gravimetric analyzer are given in Table 3.3.

Table 3.3: Performance specifications of TGA.

Performance Specifications of TGA	
Maximum Sample Weight	1 g
Weighing Precision	± 0.01 %
Sensitivity	0.1 µg
Controlled Heating Rate	0.01 to 100 °C/min
Temperature Range	Ambient to 1000 °C
Baseline Dynamic Drift	< 50 µg

Figure 3.9: Thermal gravimetric analyzer.

3.2.10 UL 94 test equipment

Flammability specification of samples were measured with CEAST Flammability Meter 6153 which is shown in Figure 3.10. UL 94 method contains two different testing categories which are horizontal and vertical.

Figure 3.10: Flammability meter.

3.2.11 Glow wire test equipment

Glow wire test was carried out by using EMS Glow Wire Test Device GW 2007 test equipment to obtain the fire resistance. In Figure 3.11 glow wire test device is shown.

Figure 3.11: Glow wire test device.

3.3 Experimental Procedure

3.3.1 Samples preparation procedure

Control Sample and 28 test samples were prepared. All samples contains 1% heat stabilizer, 1% process stabilizer and 3% lubricant. For all samples heat stabilizer, process stabilizer and lubricant were neglected and were not used in calculations. The samples were defined 3 different matrices in unreinforced PBT, 20% GF reinforced PBT and 20% GF reinforced PBT/PET blends. Aluminium diethylphosphinate (DEPAL) took on a task main flame retardant additive as non-halogenated phosphorus based flame retardant. As co-flame retardant, 2 different types of aluminium based mineral flame retardant additives were used. These additives were mentioned as Actilox B60 and Actilox B30 with trade name and their average particle size and specific surface areas were different.

As indicated in the Table 3.4, all the samples except Control Sample and Sample 6 20% of flame retardant additives were used in different combinations.

Table 3.4: Formulation of samples.

Sample Numbers	PBT	PET	GF	DEPAL	ACTILOX B60	ACTILOX B30	Explanations
Control Sample	100	-	-	-	-	-	Neat PBT
Sample 1	80	-	-	20	-	-	PBT80 D20
Sample 2	80	-	-	15	5	-	PBT80 D15 A6-5
Sample 3	80	-	-	10	10	-	PBT80 D10 A6-10
Sample 4	80	-	-	5	15	-	PBT80 D5 A6-15
Sample 5	80	-	-	-	20	-	PBT80 A6-20
Sample 6	80	-	20	-	-	-	PBT80 GF20
Sample 7	60	-	20	20	-	-	PBT60 GF20 D20
Sample 8	60	-	20	15	5	-	PBT60 GF20 D15 A6-5
Sample 9	60	-	20	10	10	-	PBT60 GF20 D10 A6-10
Sample 10	60	-	20	5	15	-	PBT60 GF20 D5 A6-15
Sample 11	60	-	20	-	20	-	PBT60 GF20 A6-20
Sample 12	48	12	20	20	-	-	PBT48 PET12 GF20 D20
Sample 13	48	12	20	15	5	-	PBT48 PET12 GF20 D15 A6-5
Sample 14	48	12	20	10	10	-	PBT48 PET12 GF20 D10 A6-10
Sample 15	48	12	20	5	15	-	PBT48 PET12 GF20 D5 A6-15
Sample 16	48	12	20	-	20	-	PBT48 PET12 GF20 A6-20
Sample 17	80	-	-	15	-	5	PBT80 D15 A3-5
Sample 18	80	-	-	10	-	10	PBT80 D10 A3-10
Sample 19	80	-	-	5	-	15	PBT80 D5 A3-15
Sample 20	80	-	-	-	-	20	PBT80 A3-20
Sample 21	60	-	20	15	-	5	PBT60 GF20 D15 A3-5
Sample 22	60	-	20	10	-	10	PBT60 GF20 D10 A3-10
Sample 23	60	-	20	5	-	15	PBT60 GF20 D5 A3-15
Sample 24	60	-	20	-	-	20	PBT60 GF20 A3-20
Sample 25	48	12	20	15	-	5	PBT48 PET12 GF20 D15 A3-5
Sample 26	48	12	20	10	-	10	PBT48 PET12 GF20 D10 A3-10
Sample 27	48	12	20	5	-	15	PBT48 PET12 GF20 D5 A3-15
Sample 28	48	12	20	-	-	20	PBT48 PET12 GF20 A3-20

3.3.2 Samples processing conditions

All samples were processed via co-rotating twin screw extruder and pelletized. The twin screw extruder which have 1 non-heating zone and 10 heating zones. Main feeding was made in the first non-heating zone and PBT, which is the main matrix, was fed into this zone. In the samples which had PBT/PET blend matrix, 80 % PBT and 20 % PET mixed previously and were fed into in first heating zone. Flame retardant additives were fed into side feeder which is connected to fourth heating zone. The glass fiber was fed into second side feeder that is connected to sixth heating zone. All temperature values of heating zones are given in the Table 3.5 Screw speed was chosen as 600 rpm and the vacuum pressure was measured as 1 bar.

Table 3.5: Temperature conditions of extruder.

Heating Zones of Extruder										
Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Zone 7	Zone 8	Zone 9	Zone 10	Zone 11
-	260	250	240	230	220	210	210	200	190	260

3.3.3 Injection moulding machine and process parameters

Injection moulding process was implemented for shaping the samples after extrusion process. The PBT compounds which were in pellet form fed into the injection unit. Molten polymer was pushed into the mold cavity and samples were released from the mold after cooling actualized. The test specimens were produced for tensile tests, Izod impact strength tests, glow wire tests and UL 94 tests. The screw speed was defined as 15 m/min, the back pressure 40 bar and cooling time was 12 seconds.

3.4 Characterization

3.4.1 Structural properties

3.4.1.1 Measurement of density

The densities of samples were determined according to ISO 1183 [46]. At first the samples were weighed in the air and after that they were land in the water to the density measurement kit of AND GR200 Analytical Semi-Micro Balance.

3.4.1.2 Measurement of melt flow index (MFI)

The MFI value of samples were evaluated according to ISO 1133 [47]. The sample was heated in the kilderkin and squeezed with the piston via a standard weight that is 2.16 kg in the equipment. Measurement the weight of polymer in grams after

squeezing it 10 minutes was called melt flow index. Before commencing the test, temperature of the equipment was set to 250˚C.

3.4.2 Mechanical properties

3.4.2.1 Determination of tensile properties

The tensile properties of samples were determined according to ISO 527-1 [48]. Also, according to ISO 527 Type 1A standard, thickness and wideness values of the test specimen were 4 mm and 10 mm respectively. Testing speed was set to 5 mm/min, E mode speed was set to 1 mm/min and gauge length (L_0) was set to 70 mm.

Strain at break, tensile modulus and stress at break values were determined from tensile measurements. The tensile measurements were carried out at standard condition which is 23 ± 2 °C.

3.4.2.2 Determination of Izod impact strength

According to ISO 180, Izod impact strength value of samples were obtained by Ceast Resil Impactor 6957 Izod Impact Test Machine. According to ISO 3167 Type B, the test samples were prepared as 4 x10 x 80 mm^3 dimensions. The test was carried out 3 times and then calculated average value of test results. 2 mm notched samples were used at Izod impact strength test. The notched side of the samples were met to the pendulum of test device [49,50].

3.4.3 Thermal properties

3.4.3.1 Determination of heat distortion temperature (HDT)

The heat distortion temperatures of samples were measured according to ISO 75-1/2. The samples undergo a pre-set penetration under load, while heated into a silicon oil bath. The temperature rate was defined as 120 °C/h, the start temperature and preheating time was 30 °C and 300 s respectively. The cooling temperature was defined as 30 °C [51,52].

3.4.3.2 Differential scanning calorimeter (DSC) analysis

Differential scanning calorimetry is an evaluation method according to ISO 3146, which is a function related between the energy that was given to the reference material and was subject to a controlled temperature sample. DSC curve designated for the characteristic of the ingredients melting point [53].

This evaluation method extends the melting point, glass transition temperature, crystallization temperature spots via convenient peak points. At first, the samples were heated from 25 ˚C to 300 ˚C at 10 ˚C/min under the nitrogen atmosphere, then they were cooled from 300 ˚C to 25 ˚C. After that the same samples were heated from 25 ˚C to 300 ˚C again. In DSC measurement, second heating run is evaluated to remove the thermal history of polymer. In second heating run, the samples show accurate thermal response.

Determination of percent crystallinity of thermoplastics, equation 3.1. is used. In the equation; the heat of melting, ΔH_m and cold crystallization ΔH_c values are determined by integrating areas under the curves. ΔHm° is identified reference value and represent the melting heat of polymer where is 100% crystalline [54].

$$Xc = [(\Delta H_m + \Delta H_c)/(\Delta Hm^{\circ})] \times 100 \quad \textbf{(3.1)}$$

3.4.3.3 Determination of thermal stability by TGA

According to ISO 11358, thermal gravimetric analyses of the samples were done. Thermal gravity analysis is an evaluation method that shows the mass loss via decomposing or draining and the mass gain via oxidation for organic, inorganic and synthetic ingredients. It is also called as a measurement of the composites mass lost related heating. These ingredients were designated by using TA Instruments Q500 TGA between 0-900°C at a 100 °C/min heating rate. During evaluation, nitrogen gas is used as a carrier with a constant flow rate. In thermal gravimetric analysis; starting thermal degradation temperature and final thermal degradation temperature were measured [55].

3.4.4 Flame retardant properties

3.4.4.1 Determination of UL 94 classification

According to UL 94 Standard, the plastic ingredients burning behaviour is analyzed related the flame extend and time. This test was carried out 5 times in 3 different thicknesses of test samples such as 0.75 mm, 1.60 mm and 3.2 mm.

This test could be performed as horizontal and vertical burning. According to UL 94, vertical burning test acceptance criteria are indicated in Table 3.6.

Table 3.6: Acceptance criteria for vertical burning test.

Criteria Conditions	V0	V1	V2
Afterflame time for each individual sample t_1 or t_2	≤ 10 s	≤ 30 s	≤ 30 s
Total afterflame time for any condition set (t_1 plus t_2 for the 5 samples)	≤ 50 s	≤ 250 s	≤ 250 s
Afterflame plus afterglow time for each individual sample after the second flame application (t_2+t_3)	≤ 30 s	≤ 60 s	≤ 60 s
Afterflame or afterglow of any sample up to the holding clamp	No	No	No
Cotton indicator ignited by flaming particles or drops	No	No	Yes

t_1 is defined as afterflame time after first flame application. t_2 is defined as afterflame time after second flame application. t_3 is defined as afterglow time after second flame application [56].

For evaluation of UL 94 classification 5 test specimens were needed. Firstly; disposed a test sample positioned perpendicular to the flame and a cotton was placed under. Then flame height was set 2 cm before the test sample contacted to the flame. After that, the test sample was fit above the blue flame and let the test sample in contact with the flame 10 seconds. Then the burning duration and dropping were evaluated after withdraw the test sample from the flame. Afterwards the flame was blow out, the same procedure was repeated to the test samples and again the burning duration and dropping were evaluated after second 10 seconds. According to UL 94 Standard, this procedure was performed with 5 test specimens.

3.4.4.2 Determination of glow wire ignition temperature

The glow wire ignition temperatures of samples were measured according to IEC 60695-2-13. The GWIT has temperature that is 25 ˚C higher than the maximum test temperature, obtained during the experiment. These samples do not ignite or if sustained and continuous, flaming combustion does not occur longer than 5 seconds for any single flame event and these samples are not completely consumed.

Before commencing the test, Table 3.7 was used to predict initial test temperature interval of the samples.

Table 3.7: Temperature intervals in reference to UL94 classification.

UL 94 Classification of	No Rate					V2		V0	
Samples Temperature (°C)	550	600	650	700	750	800	850	900	960

A set of six test samples, which are 1 mm and 2 mm plaques, were prepared for testing at a chosen temperature. The samples were evaluated to have withstood these tests if there is no ignition or if all the following situations apply;

- The longest sustained and continuous flames or glowing of the sample after remove the glow wire, extinguish within 30 seconds,
- The sample is not totally consumed,
- There is no ignition of the wrapping tissue.

If three test samples were not withstanding above criteria, no need to try higher temperature. If the samples fail to withstand above criteria, the test repeated with new test samples at a test temperature favorably 50 ˚C higher.

After that repeat the test and lower the interval of test temperatures to 25 ˚C in the final approach to obtain the maximum test temperature at which all samples withstand above criteria [57].

3.4.4.3 Determination of glow wire flammability index

The glow wire flammability index of samples was determined according to IEC 60695-2-12. The GWFI is the highest temperature, measured during the experiment, at which the test samples do not ignite or if the samples ignite, extinguishes within 30 s after removal of the glow-wire and is not totally consumed. And the second scope of the experiment, if molten drips occur, do not ignite the wrapping tissue. A set of six test samples, which are 1 mm and 2 mm plaques, were prepared for testing at a chosen temperature that coming from GWIT test results. The samples are evaluated to have withstood these tests if there is no ignition or if all of the following situations apply;

- The longest sustained and continuous flames or glowing of the sample after remove the glow wire, extinguish within 30 s
- The sample is not totally consumed,
- There is no ignition of the wrapping tissue.

If one of the three samples fail to withstand above test criteria, the test was repeated and the temperature favorably 50 ˚C lower. In case of repeat the test, interval of test temperature was reduced to 25 ˚C to obtain the maximum test temperature. If three test samples were not withstanding above criteria, no need to try higher temperature [58].

4. RESULTS AND DISCUSSION

All evaluations were done according to the standards explained in section 3.

4.1 Evaluation of Structural Properties

4.1.1 Measurement of density

According to Table 4.1 and the Figures 4.1 and 4.2 it is observed that increasing the rate of Actilox B60 flame retardant, slightly increases the density of first five samples. In comparison of the density value of Control Sample and Sample 6, which 20% glass fiber reinforced PBT, it is seen that the density value of Sample 6 is expectedly higher than control sample. When the addition of Actilox B60 FR to the glass fiber reinforced PBT and neat PBT are compared, it is observed that they show same tendency where GF reinforced PBT gives a higher density value as for that unreinforced PBT.

Table 4.1: Density test results of samples.

Samples	Density (g/cm^3)	Explanations
Control Sample	1.30	Neat PBT
Sample 1	1.31	PBT80 D20
Sample 2	1.35	PBT80 D15 A6-5
Sample 3	1.39	PBT80 D10 A6-10
Sample 4	1.41	PBT80 D5 A6-15
Sample 5	1.46	PBT80 A6-20
Sample 6	1.45	PBT80 GF20
Sample 7	1.45	PBT60 GF20 D20
Sample 8	1.50	PBT60 GF20 D15 A6-5
Sample 9	1.54	PBT60 GF20 D10 A6-10
Sample 10	1.60	PBT60 GF20 D5 A6-15
Sample 11	1.66	PBT60 GF20 A6-20
Sample 12	1.48	PBT48 PET12 GF20 D20
Sample 13	1.52	PBT48 PET12 GF20 D15 A6-5
Sample 14	1.57	PBT48 PET12 GF20 D10 A6-10
Sample 15	1.62	PBT48 PET12 GF20 D5 A6-15
Sample 16	1.67	PBT48 PET12 GF20 A6-20
Sample 17	1.35	PBT80 D15 A3-5
Sample 18	1.38	PBT80 D10 A3-10
Sample 19	1.43	PBT80 D5 A3-15
Sample 20	1.47	PBT80 A3-20
Sample 21	1.53	PBT60 GF20 D15 A3-5
Sample 22	1.57	PBT60 GF20 D10 A3-10
Sample 23	1.62	PBT60 GF20 D5 A3-15
Sample 24	1.67	PBT60 GF20 A3-20
Sample 25	1.53	PBT48 PET12 GF20 D15 A3-5
Sample 26	1.58	PBT48 PET12 GF20 D10 A3-10
Sample 27	1.61	PBT48 PET12 GF20 D5 A3-15
Sample 28	1.69	PBT48 PET12 GF20 A3-20

Also, GF reinforced PBT/PET blend gives a little bit higher density value with respect to GF reinforced PBT and neat PBT. When the addition of Actilox B60 and Actilox B30 flame retardants are compared, it is observed that they almost show the same trend at all different ratios.

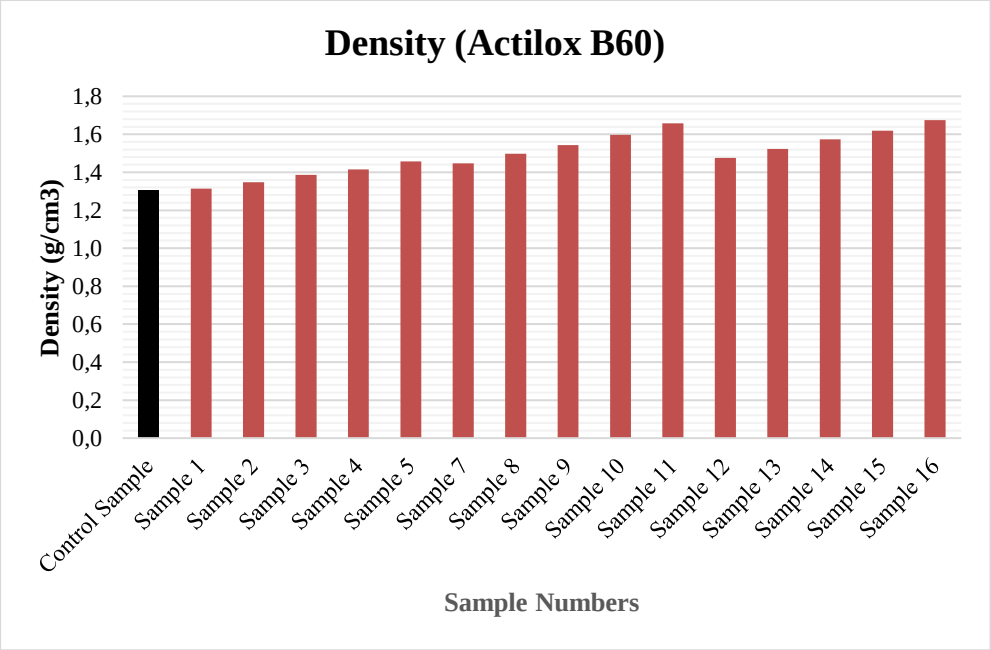

Figure 4.1: Density test results of Actilox B60 additive samples.

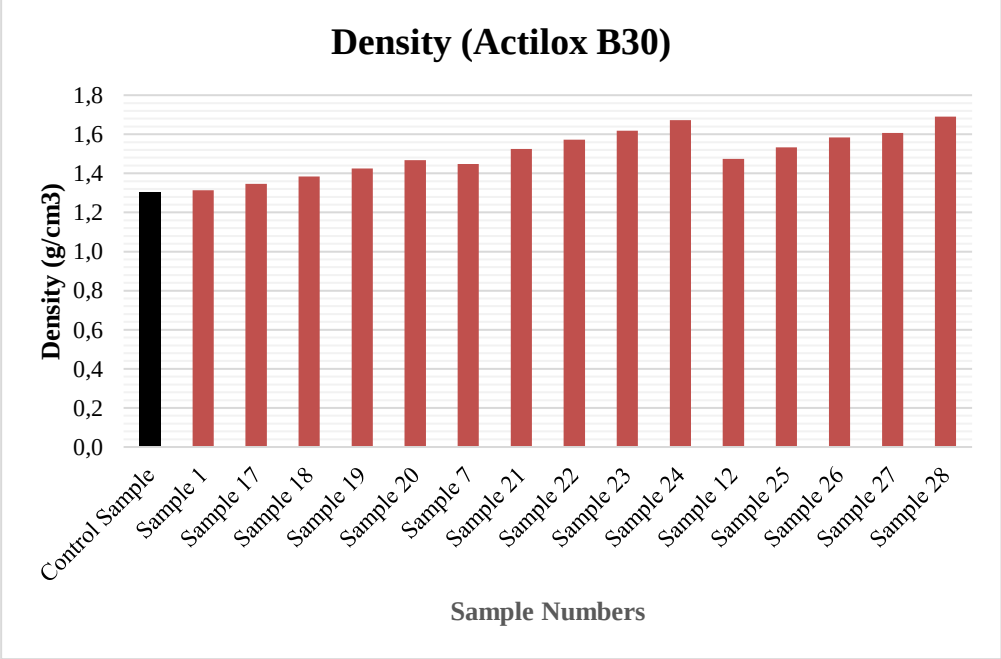

Figure 4.2: Density test results of Actilox B30 additive samples.

4.1.2 Measurement of melt flow index (MFI)

It is clearly observed from Table 4.2 and the Figures 4.3 and 4.4 which shows the effect of phosphorus based flame retardant (DEPAL) adding to the neat PBT, MFI value is increased. MFI values of Sample 2, Sample 3 and Sample 4 are presented in Figure 4.3 and it shows that increasing the amount of Actilox B60 flame retardant, decreases the melt viscosity.

When Sample 1, which only contains 20% DEPAL, and Sample 5, which only contains 20% Actilox B60 are compared, it is observed MFI value of Sample 5 is lower than Sample 1.

Table 4.2: MFI test results of all samples.

Samples	MFI (g/10min)	Explanations
Control Sample	59.9	Neat PBT
Sample 1	69.4	PBT80 D20
Sample 2	67.6	PBT80 D15 A6-5
Sample 3	73.5	PBT80 D10 A6-10
Sample 4	78.7	PBT80 D5 A6-15
Sample 5	56.4	PBT80 A6-20
Sample 6	29.1	PBT80 GF20
Sample 7	34.3	PBT60 GF20 D20
Sample 8	40.2	PBT60 GF20 D15 A6-5
Sample 9	41.3	PBT60 GF20 D10 A6-10
Sample 10	42.7	PBT60 GF20 D5 A6-15
Sample 11	22.9	PBT60 GF20 A6-20
Sample 12	28.9	PBT48 PET12 GF20 D20
Sample 13	39.8	PBT48 PET12 GF20 D15 A6-5
Sample 14	40.7	PBT48 PET12 GF20 D10 A6-10
Sample 15	46.1	PBT48 PET12 GF20 D5 A6-15
Sample 16	46.6	PBT48 PET12 GF20 A6-20
Sample 17	81.7	PBT80 D15 A3-5
Sample 18	75.8	PBT80 D10 A3-10
Sample 19	82.2	PBT80 D5 A3-15
Sample 20	54.0	PBT80 A3-20
Sample 21	40.9	PBT60 GF20 D15 A3-5
Sample 22	44.0	PBT60 GF20 D10 A3-10
Sample 23	53.0	PBT60 GF20 D5 A3-15
Sample 24	32.7	PBT60 GF20 A3-20
Sample 25	37.7	PBT48 PET12 GF20 D15 A3-5
Sample 26	55.1	PBT48 PET12 GF20 D10 A3-10
Sample 27	55.9	PBT48 PET12 GF20 D5 A3-15
Sample 28	48.7	PBT48 PET12 GF20 A3-20

According to Table 4.2 it is determined that the MFI value of 20 % glass fiber reinforced PBT is 58.9 % lower than the neat PBT. From the experimental data, it is also observed that MFI value of glass fiber reinforced PBT is higher than the MFI value of glass fiber reinforced PBT/PET blend. The addition of DEPAL and Actilox B60 flame retardants to glass fiber reinforced PBT, increases the melt viscosity. When the addition of Actilox B60 and Actilox B30 flame retardants are compared, it is

observed that they almost show the same trend where Actilox B30 FR additive gives a higher MFI value with respect to Actilox B60 FR additive.

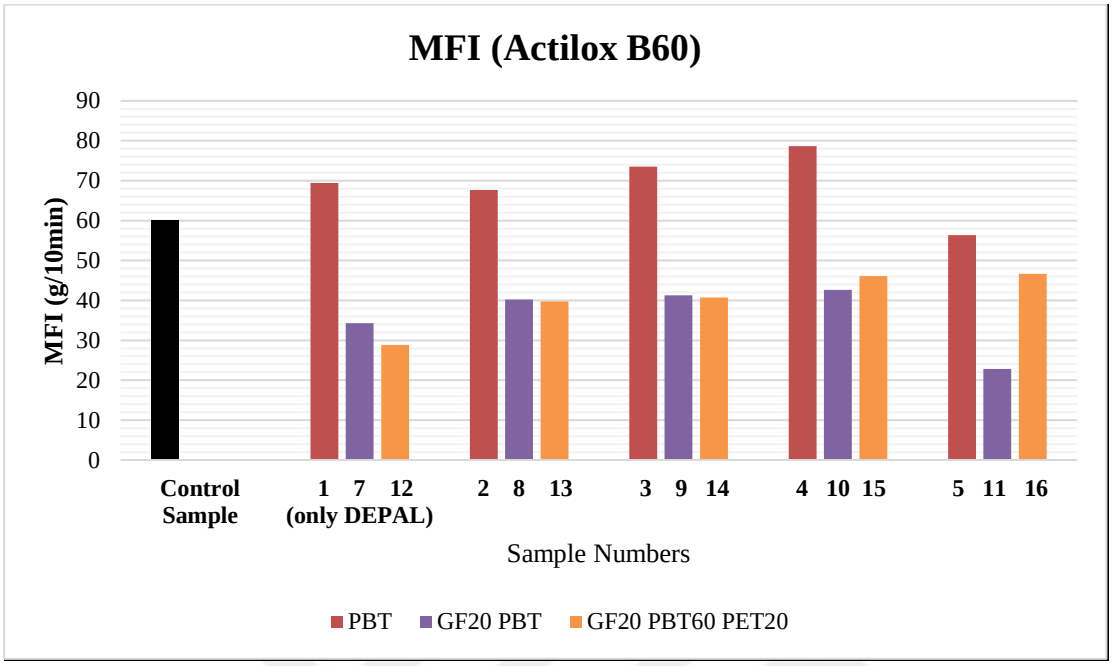

Figure 4.3: Comparative analyses of MFI test results of Actilox B60 samples.

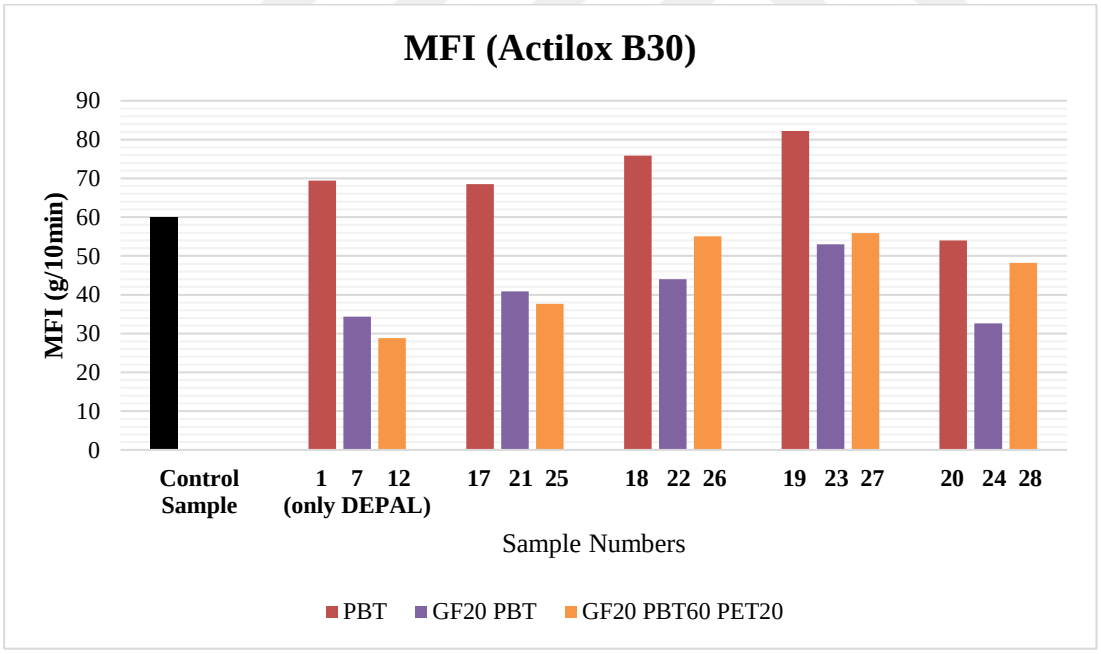

Figure 4.4: Comparative analyses of MFI test results of Actilox B30 samples.

4.2 Evaluation of Mechanical Properties

4.2.1 Tensile properties

According to Table 4.3, it is calculated that Sample 1 which contains only 20% DEPAL additive decreases stress at break as 60%; Sample 5 which contains only 20% Actilox B60 FR additive does not change the stress at break, Sample 20 which contains Actilox B30 FR additive decreases stress at break as 4%. When comparing neat PBT and Sample 6 that contains only 20% GF reinforced PBT, the stress at break increases 105%. While comparing Sample 4 which contains 5% DEPAL and 15% Actilox B60 PBT and Sample 10 which contains same ratio of DEPAL and Actilox B60 according to Control Sample, stress at break of Sample 4 decreases 14% and stress at break of Sample 10 increases 80%. While comparing all samples which contains Actilox B30 at the same ratio according to Control Sample, stress at break of Sample 19 decreases 19% and Sample 23 increases 58%.

Table 4.3: Tensile properties test results of all samples**.**

Samples	Stress at Break (MPa)	Tensile Modulus (MPa)	Strain at Break (%)	Explanations
Control Sample	57 ± 0.3	2080 ± 70	12.5 ± 5.0	Neat PBT
Sample 1	36 ± 0.5	2730 ± 110	3.5 ± 0.2	PBT80 D20
Sample 2	39 ± 0.3	2180 ± 40	3.8 ± 0.2	PBT80 D15 A6-5
Sample 3	44 ± 0.1	3060 ± 190	2.5 ± 0.1	PBT80 D10 A6-10
Sample 4	50 ± 0.2	3030 ± 160	3.5 ± 0.4	PBT80 D5 A6-15
Sample 5	57 ± 0.3	2930 ± 50	4.8 ± 0.4	PBT80 A6-20
Sample 6	117 ± 0.3	7070 ± 90	3.3 ± 0.1	PBT80 GF20
Sample 7	92 ± 1.1	8040 ± 190	2.3 ± 0.1	PBT60 GF20 D20
Sample 8	76 ± 1.3	7400 ± 120	1.8 ± 0.1	PBT60 GF20 D15 A6-5
Sample 9	86 ± 1.4	8000 ± 100	2.0 ± 0.1	PBT60 GF20 D10 A6-10
Sample 10	90 ± 1.1	8280 ± 100	1.7 ± 0.1	PBT60 GF20 D5 A6-15
Sample 11	98 ± 1.5	8990 ± 230	1.7 ± 0.1	PBT60 GF20 A6-20
Sample 12	84 ± 1.8	8520 ± 180	1.6 ± 0.1	PBT48 PET12 GF20 D20
Sample 13	84 ± 0.5	8220 ± 180	1.5 ± 0.1	PBT48 PET12 GF20 D15 A6-5
Sample 14	87 ± 1.4	8000 ± 250	1.6 ± 0.1	PBT48 PET12 GF20 D10 A6-10
Sample 15	81 ± 1.9	9130 ± 80	1.2 ± 0.1	PBT48 PET12 GF20 D5 A6-15
Sample 16	104 ± 1.0	9110 ± 180	1.6 ± 0.1	PBT48 PET12 GF20 A6-20
Sample 17	38 ± 1.1	2250 ± 180	2.2 ± 0.1	PBT80 D15 A3-5
Sample 18	45 ± 0.1	2680 ± 150	2.8 ± 0.5	PBT80 D10 A3-10
Sample 19	48 ± 0.8	2760 ± 220	3.8 ± 0.4	PBT80 D5 A3-15
Sample 20	55 ± 1.3	2930 ± 130	4.0 ± 0.5	PBT80 A3-20
Sample 21	86 ± 1.1	7800 ± 110	1.8 ± 0.1	PBT60 GF20 D15 A3-5
Sample 22	90 ± 2.7	8030 ± 70	2.1 ± 0.1	PBT60 GF20 D10 A3-10
Sample 23	90 ± 1.1	8280 ± 100	1.7 ± 0.1	PBT60 GF20 D5 A3-15
Sample 24	94 ± 0.7	9020 ± 250	1.6 ± 0.1	PBT60 GF20 A3-20
Sample 25	84 ± 1.8	8530 ± 210	1.5 ± 0.1	PBT48 PET12 GF20 D15 A3-5
Sample 26	88 ± 1.3	8150 ± 140	1.4 ± 0.1	PBT48 PET12 GF20 D10 A3-10
Sample 27	76 ± 1.3	8300 ± 110	1.2 ± 0.1	PBT48 PET12 GF20 D5 A3-15
Sample 28	96 ± 1.9	9390 ± 90	1.4 ± 0.1	PBT48 PET12 GF20 A3-20

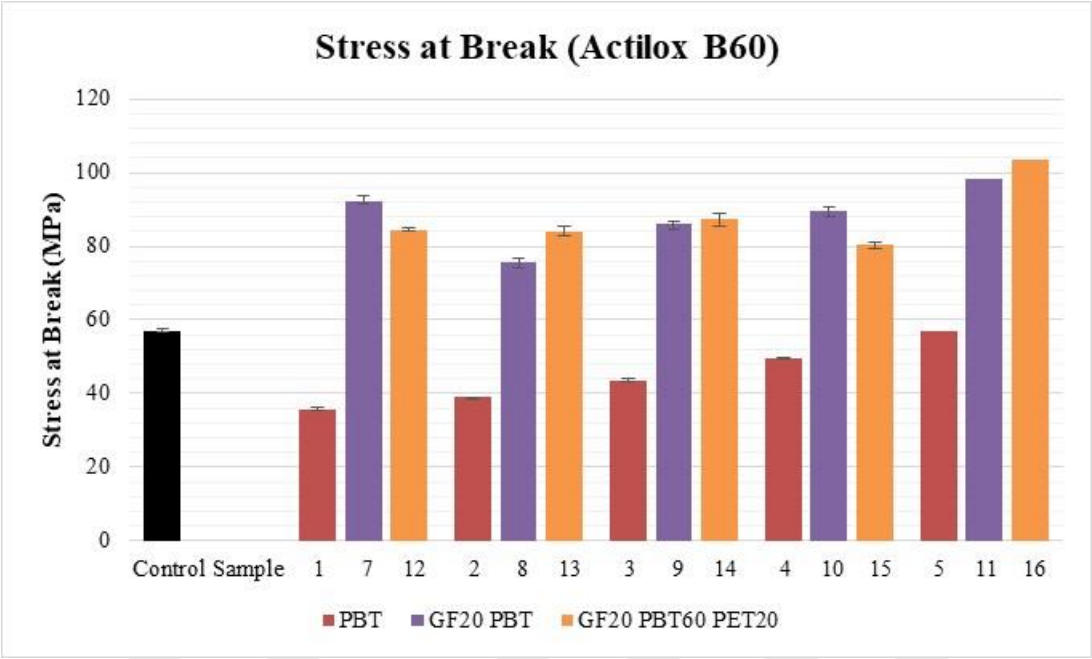

Figure 4.5: Stress at break test results of Actilox B60 samples.

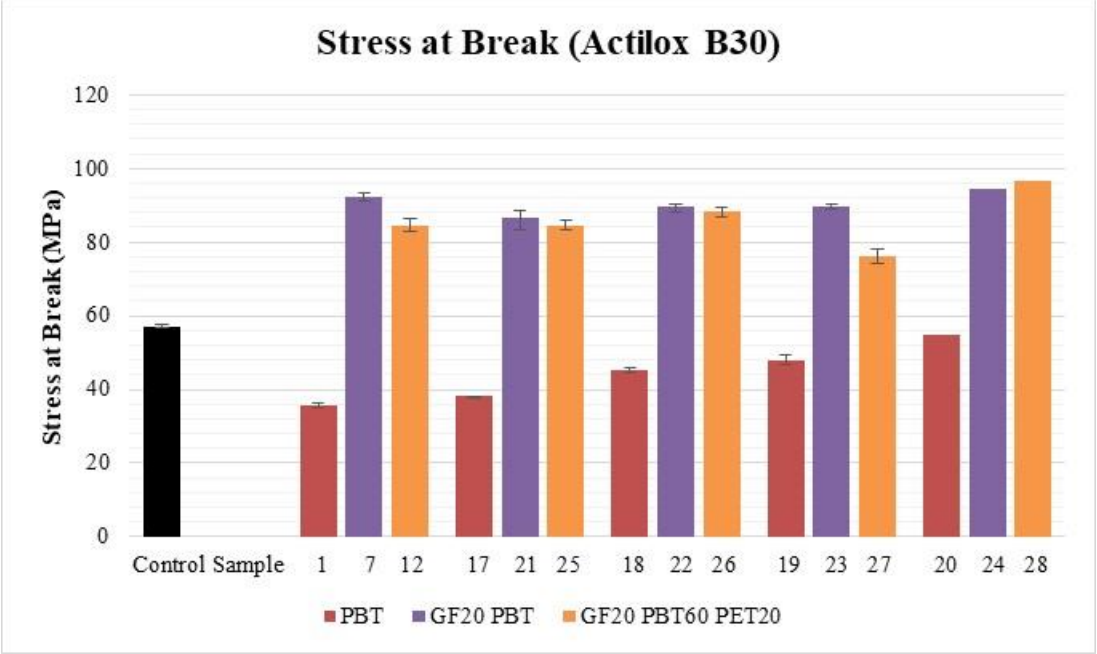

Figure 4.6: Stress at break test results of Actilox B30 samples.

According to Control Sample, while comparing Sample 15 that contains same Actilox B60 ratio of GF reinforced PBT/PET blend the stress break value increases 42% and also for Sample 27 that contains same Actilox B30 ratio of GF reinforced PBT/PET blends' stress at break value increases 33%. According to all calculations while comparing the samples that contains same Actilox B60 rate and same Actilox B30 rate the stress at break results of all samples have almost same trend. According to Table

4.3, Figure 4.5 and Figure 4.6, considering the calculations; adding both Actilox flame retardant additives almost did not change the stress break value. The addition of DEPAL flame retardant additives to all type of matrices, decreases the strain at break value. Also, GF reinforcement is considerably increases the stress at break value.

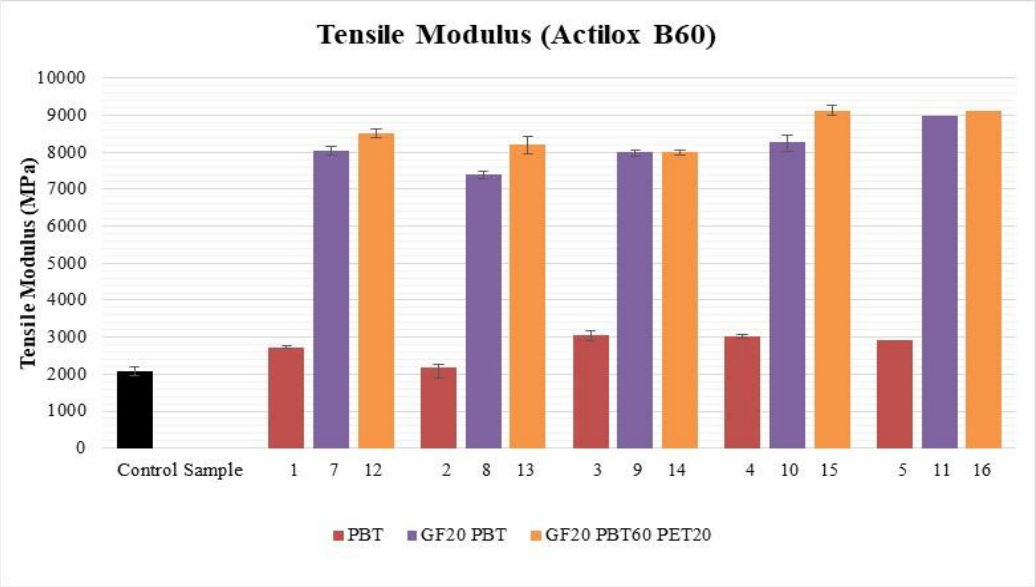

Figure 4.7: Tensile modulus test results of Actilox B60 samples (Sample 1, 7 and 12 contain only DEPAL).

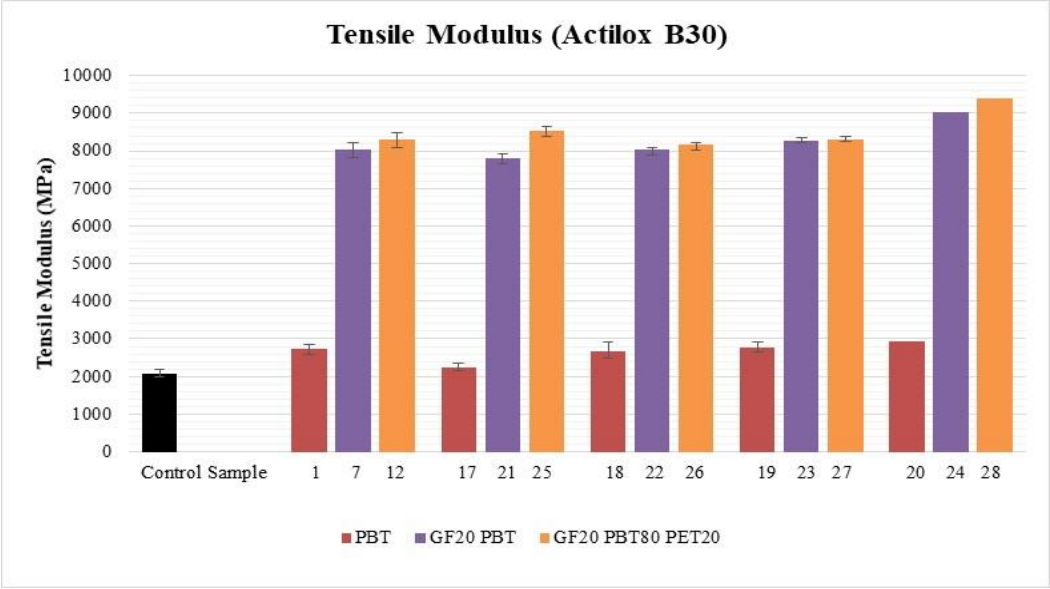

Figure 4.8: Tensile modulus test results of Actilox B30 samples (Sample 1, 7 and 12 contain only DEPAL).

According to Table 4.3, Figure 4.7 and Figure 4.8, while all the results examined, it is seen that all the additives increases the tensile modulus values. From Table 4.3, it is calculated that the Sample 1 which contains only 20% of DEPAL to neat PBT

increases the tensile modulus 31%, the Sample 5 which contains only 20% of Actilox B60 FR increases the tensile modulus 40.7% and the Sample 20 which contains only 20% of Actilox B30 FR increases the tensile modulus 40.6%.

According to Control Sample, comparing Sample 4 which contains 5% DEPAL and 15% Actilox B60 PBT and Sample 10 that contains same ratios of DEPAL and Actilox B60 GF reinforced PBT; it is calculated that the incrementation in tensile modulus for Sample 4 is 45% and for Sample 10 is 297%.

According to Control Sample, comparing the samples which contains same ratios of Actilox B30; it is calculated that the incrementation in tensile modulus for Sample 19 is 32% and for Sample 23 is 300%. According to Control Sample, the incrementation on Sample 15 that contains same ratio of Actilox B60 GF reinforced PBT/PET blend tensile modulus is 340%. Also, the incrementation on Sample 27 that contains same ratio of Actilox B30 GF reinforced PBT/PET blend tensile modulus is 300%. In accordance with all computations; the comparison of the samples that contain Actilox B60 and Actilox B30, it is seen that tensile modulus have almost same trend. It is obvious that GF reinforcement increases the tensile modulus more than FR additives.

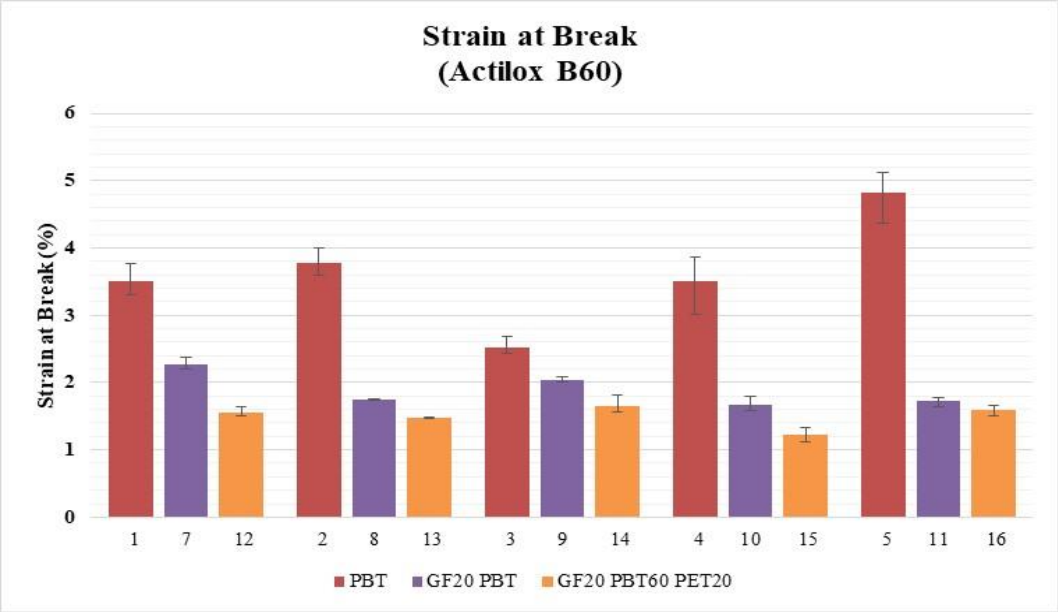

Figure 4.9: Strain at break test results of Actilox B60 samples (Sample 1, 7 and 12 contain only DEPAL).

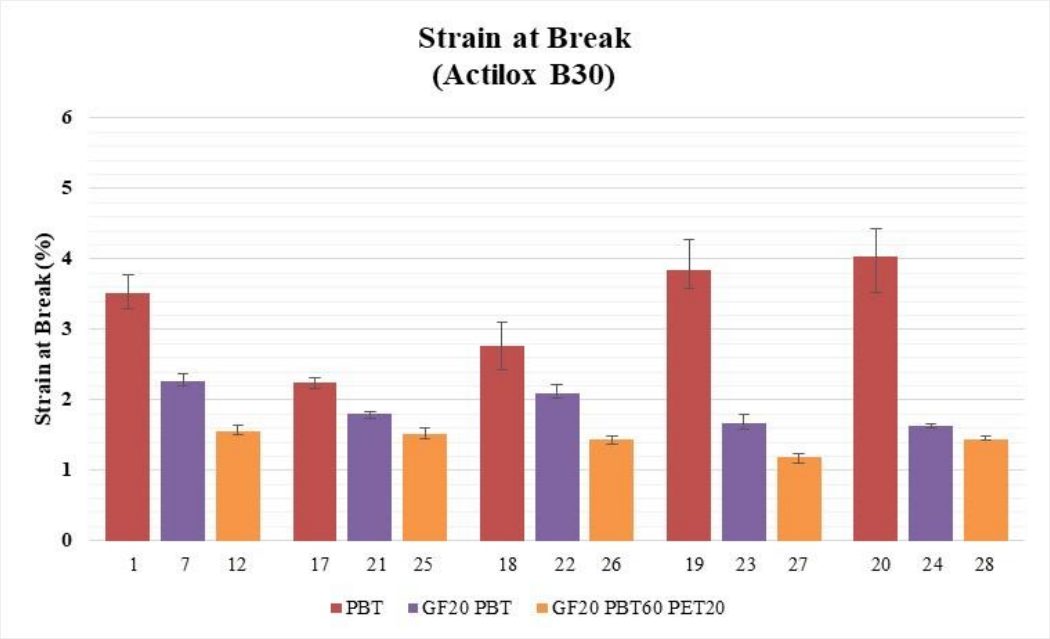

Figure 4.10: Strain at break test results of Actilox B30 samples (Sample 1, 7 and 12 contain only DEPAL).

According to Table 4.3, the addition of 20% DEPAL to the neat PBT (Sample 1), strain at break value is decreased to 12.5% from 3.5% and the reinforcement of 20% GF to neat PBT (Sample 6), strain at break value is decreased to 12.5% from 3.3%. In comparison of strain at break results of Sample 2, which contains 5% Actilox B60 and Sample 17, which contains 5% Actilox B30, it is observed that the strain at break result of Sample 2 is higher than Sample 17, so it shows that Sample 2 is more flexible than Sample 17.

From the experimental data, it is determined that there is no significant difference between Sample 4, which contains 15 % Actilox B60 and Sample 19, which contains 15 % Actilox B30. When the addition of 20 % Actilox B60 FR to neat PBT and the addition of 20 % Actilox B30 are compared, effect of Actilox B30 to strain at break result is higher than the addition of Actilox B60.

Stain at break results for GF reinforced PBT matrix and GF reinforced PBT/PET blend matrix are given Table 4.3, Figure 4.9 and Figure 4.10. GF reinforced PBT matrix is showed slightly high strain at break results compare to GF reinforced PBT/PET matrix at all different Actilox and DEPAL ratios. In general, the addition of Actilox B60 showed slight increase in strain at break compare with the addition of Actilox B30 to all matrix at different rates.

4.2.2 Izod impact properties

Evaluation of Izod impact strength of samples at 23 °C according to Table 4.4, Sample 1 that contains only 20% DEPAL adding to neat PBT decreases the Izod impact strength 150%. Sample 5 that contains only 20% Actilox B60 FR additive decreases the Izod impact strength 60%. Sample 20 that contains only Actilox B30 FR additive decreases Izod impact strength 78%. While comparing neat PBT and Sample 6 that contains only 20% GF reinforced PBT, it is calculated that the Izod impact strength value increases 6%.

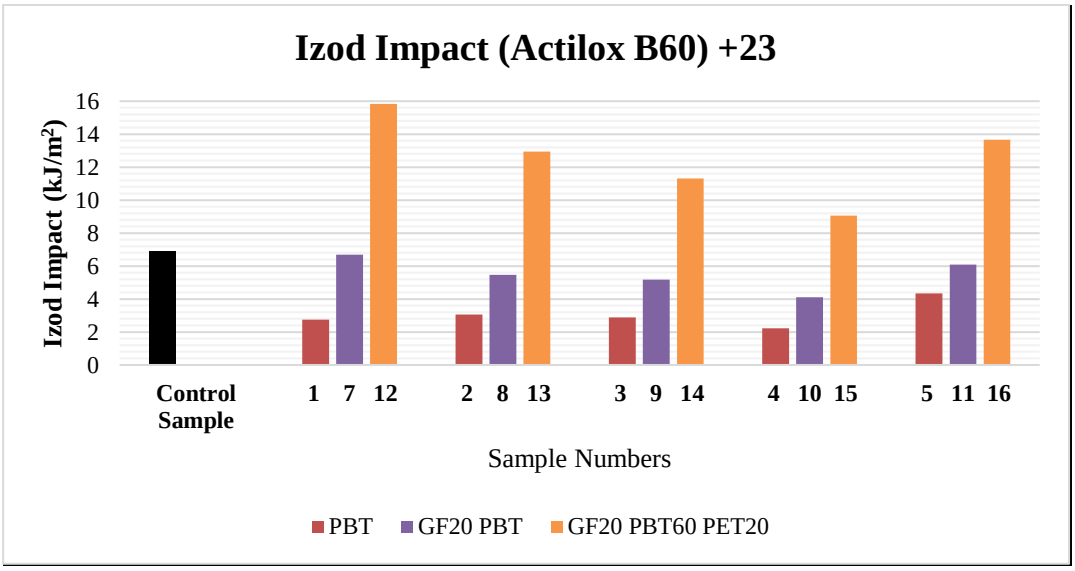

Figure 4.11: Comparative analyses of Izod impact strength (+23 ºC) test results of Actilox B60 samples.

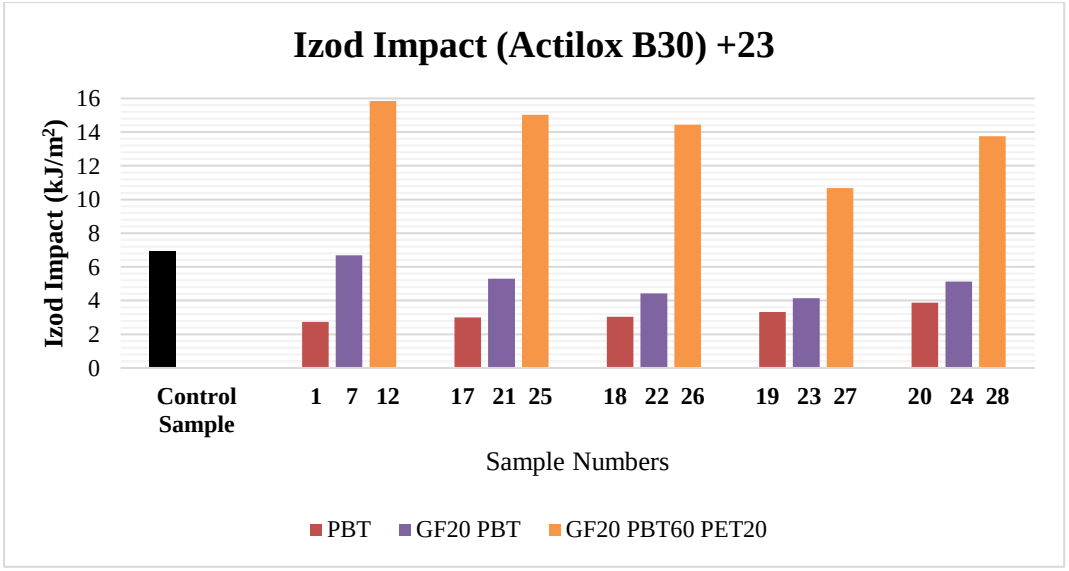

Figure 4.12: Comparative analyses of Izod impact strength (+23ºC) test results of Actilox B30 samples.

According to Control Sample while observing 3 different matrix includes 20% DEPAL additive, it is obvious that Sample 1 which owns only PBT matrix the Izod impact strength value is less as 150%, Sample 7 which owns GF reinforced PBT matrix the Izod impact strength value is less as 3.2%, Sample 12 which owns GF reinforced PBT/PET blend matrix the Izod impact strength value is high as 130%. According to the Figures 4.11 and 4.12, observing samples contains same rates of flame retardant additives in different matrix has same tendency. Considering that all calculations; while comparing the samples that contains same rates of Actilox B60 and Actilox B30, Izod impact strength results have almost same tendency.

Evaluation of Izod impact strength of samples at -30 °C According to Table 4.4, Sample 1 that contains only 20% DEPAL adding to neat PBT decreases the Izod impact strength 74%. Sample 5 that contains only 20% Actilox B60 FR additive decreases the Izod impact strength 15%. Sample 20 that contains only Actilox B30 FR additive decreases Izod impact strength 18%. While comparing neat PBT and Sample 6 that contains only 20% GF reinforced PBT, it is calculated that the Izod impact strength value increases 31%.

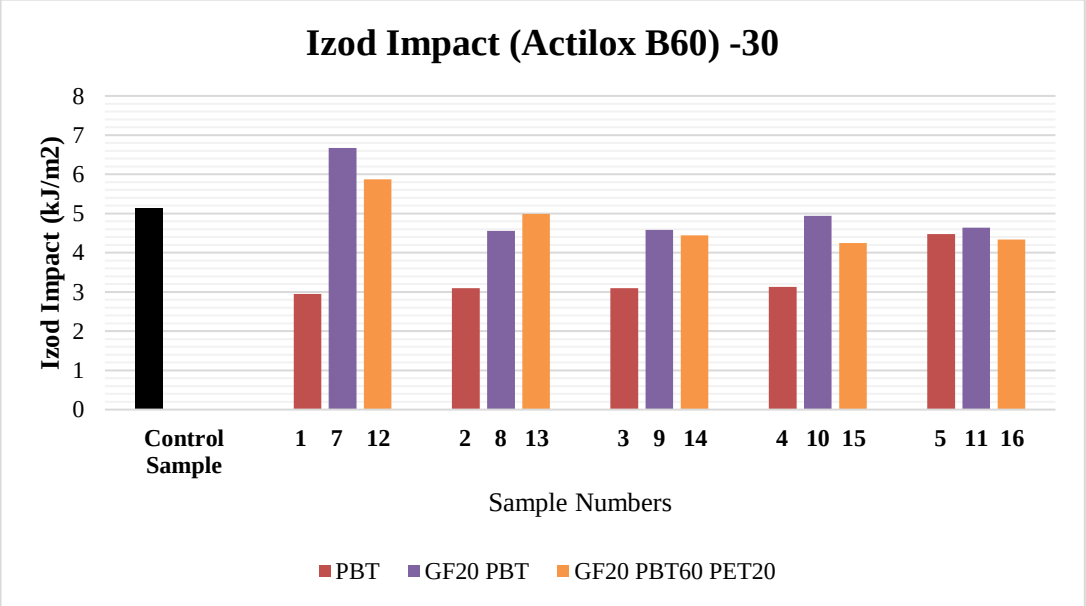

Figure 4.13: Comparative analyses of Izod impact strength (-30 ºC) test results of Actilox B60 samples.

According to Control Sample while observing 3 different matrix includes 20% DEPAL additive, it is obvious that Sample 1 which owns only PBT matrix the Izod impact strength value is less as 74%. Sample 7 which owns GF reinforced PBT matrix the

Izod impact strength value is high as 30%. Sample 2 which owns GF reinforced PBT/PET blend matrix the Izod impact strength value is high as 15%. According to the Figures 4.13 and 4.14 observing samples contains same rates of flame retardant additives in different matrix has same tendency. From all calculations; while comparing the samples that contains same rates of Actilox B60 and Actilox B30, Izod imptact strength results have same tendency. And also it is seen that at -30 ℃, samples that contains Actilox B30 have a little high Izod impact strength.

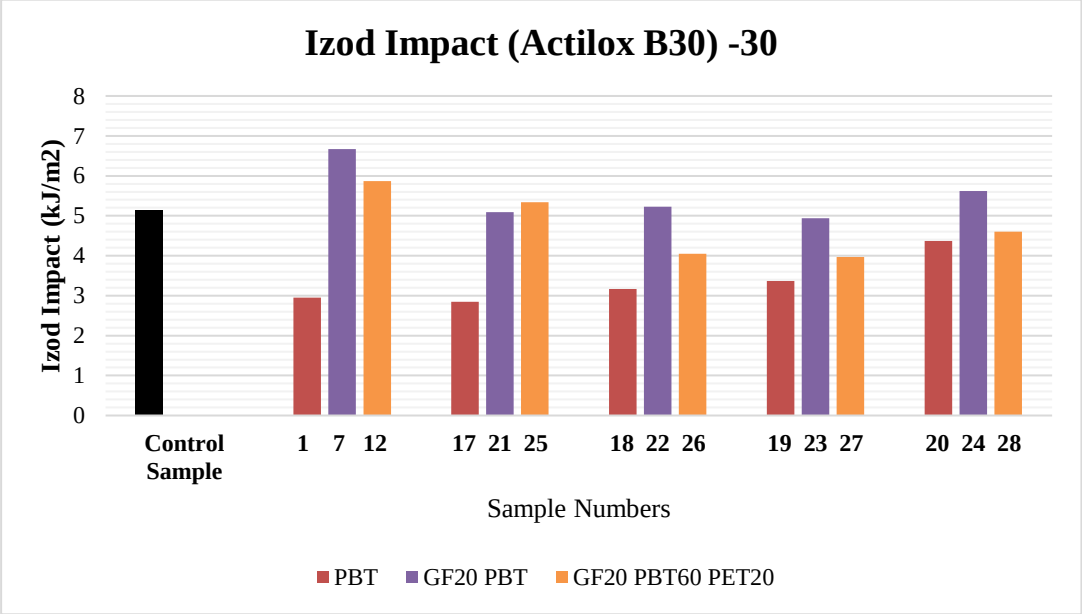

Figure 4.14: Comparative analyses of Izod impact strength (-30 ºC) test results of Actilox B30 samples.

4.3 Evaluation of Thermal Properties

4.3.1 Measurement of heat distortion temperature (HDT)

From Table 4.4 it is shown that the addition of Actilox B60 FR and Actilox B30 FR at all different rate, increases the HDT except Sample 20 which is most probably due to an experimental error.

According to Figure 4.15 when the Actilox B60 FR and DEPAL added to GF reinforced PBT at different ratios, heat distortion temperature is kept at 190 – 200 °C band. Also, when the Actilox B30 FR and DEPAL added to GF reinforced at different ratios, it can be seen in Figure 4.16 has the same heat distortion temperature band. From the experimental data; it is also observed that two different types of Actilox FR additives give almost the same HDT results. Besides, when the Actilox FR and

DEPAL added to GF reinforced PBT/PET blend at different rates, HDT results are kept at 180 – 190 °C range.

Table 4.4: HDT test results of all samples.

Samples	HDT (ºC)	Explanations
Control Sample	61.5	Neat PBT
Sample 1	86.6	PBT80 D20
Sample 2	107.2	PBT80 D15 A6-5
Sample 3	74.3	PBT80 D10 A6-10
Sample 4	74.8	PBT80 D5 A6-15
Sample 5	69.7	PBT80 A6-20
Sample 6	194.7	PBT80 GF20
Sample 7	205.1	PBT60 GF20 D20
Sample 8	188.9	PBT60 GF20 D15 A6-5
Sample 9	196.2	PBT60 GF20 D10 A6-10
Sample 10	200.5	PBT60 GF20 D5 A6-15
Sample 11	192.4	PBT60 GF20 A6-20
Sample 12	189.5	PBT48 PET12 GF20 D20
Sample 13	183.2	PBT48 PET12 GF20 D15 A6-5
Sample 14	181.2	PBT48 PET12 GF20 D10 A6-10
Sample 15	192.2	PBT48 PET12 GF20 D5 A6-15
Sample 16	188.4	PBT48 PET12 GF20 A6-20
Sample 17	74.0	PBT80 D15 A3-5
Sample 18	77.0	PBT80 D10 A3-10
Sample 19	82.9	PBT80 D5 A3-15
Sample 20	50.3	PBT80 A3-20
Sample 21	196.8	PBT60 GF20 D15 A3-5
Sample 22	192.5	PBT60 GF20 D10 A3-10
Sample 23	196.7	PBT60 GF20 D5 A3-15
Sample 24	196.5	PBT60 GF20 A3-20
Sample 25	179.1	PBT48 PET12 GF20 D15 A3-5
Sample 26	178.8	PBT48 PET12 GF20 D10 A3-10
Sample 27	187.3	PBT48 PET12 GF20 D5 A3-15
Sample 28	183.3	PBT48 PET12 GF20 A3-20

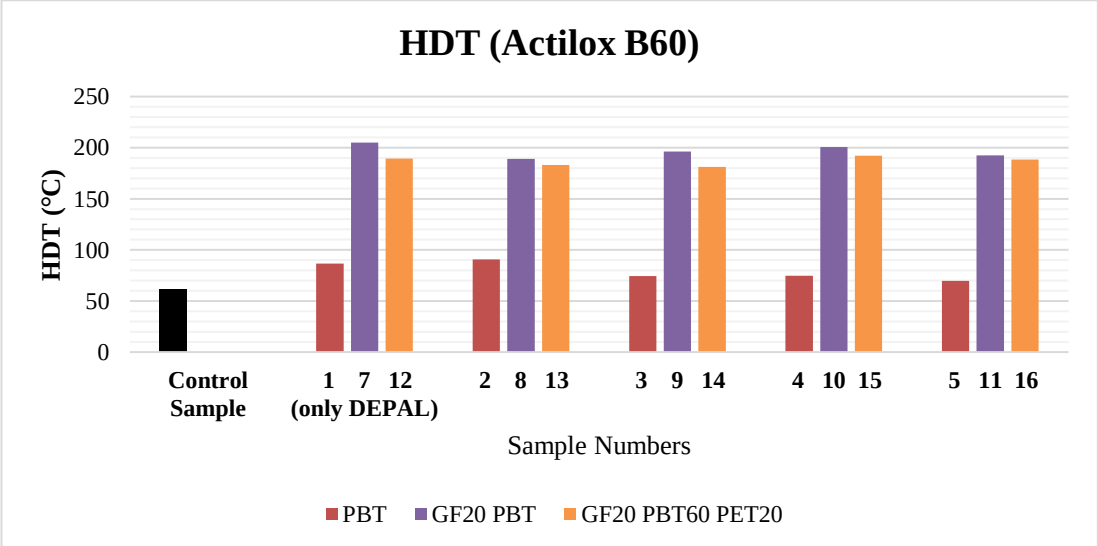

Figure 4.15: Comparative analyses of HDT test results of Actilox B60 samples.

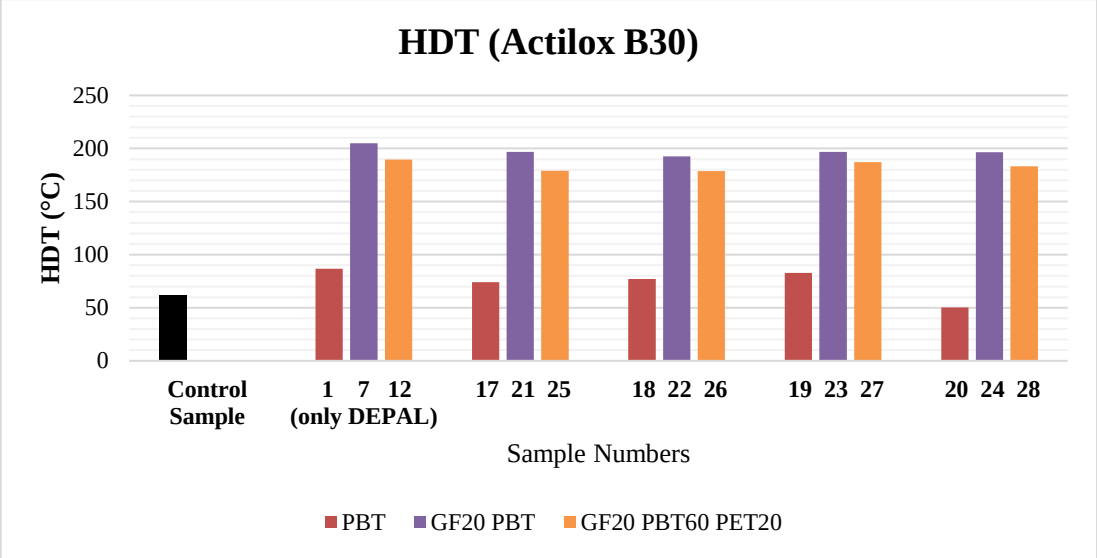

Figure 4.16: Comparative analyses of HDT test results of Actilox B30 sample.

4.3.2 Differential scanning calorimeter (DSC) analysis

Differential scanning calorimeter (DSC) analyses were performed as identified in section 3.4.3.2. The onset and peak temperatures of melting regions, heat of melting, cold crystallization enthalpy are given in Table 4.5. According to these values percent crystallinity of samples were calculated. The addition of 20% phosphorus based flame retardant additive (DEPAL) to the neat PBT (Control Sample), onset temperature is shifted 11°C (Sample 1) and percent crystallinity is determined almost 60%. The addition of 20% glass fiber to the neat PBT onset temperature is increased 19 °C (Sample 6) and percent crystallinity is calculated almost %57. In case of Actilox B60 is added to Control Sample, onset temperature of neat PBT is increased 12 °C and percent crystallinity is obtained 61% (Sample 5); Actilox B30 is added to Control Sample, onset temperature of neat PBT is increased 16 °C and percent crystallinity is determined 57% (Sample 20). Increasing the amount of Actilox B60 or Actilox B30 and decreasing the amount of DEPAL in PBT matrix, the onset temperature is almost remained. The addition of 20% phosphorus based flame retardant additive (DEPAL) to the glass fiber reinforced PBT, onset temperature is shifted 16 °C (Sample 7) and in comparison, of percent crystallinity of Control Sample and Sample 7, almost 50% difference is observed. In case of Actilox B60 is added to GF reinforced PBT, onset temperature is obtained 214 °C and percent crystallinity is obtained 43% (Sample 11); Actilox B30 is added to GF reinforced PBT, onset temperature is obtained 194 °C and percent crystallinity is determined 163% that is must be an experimental error (Sample 24).

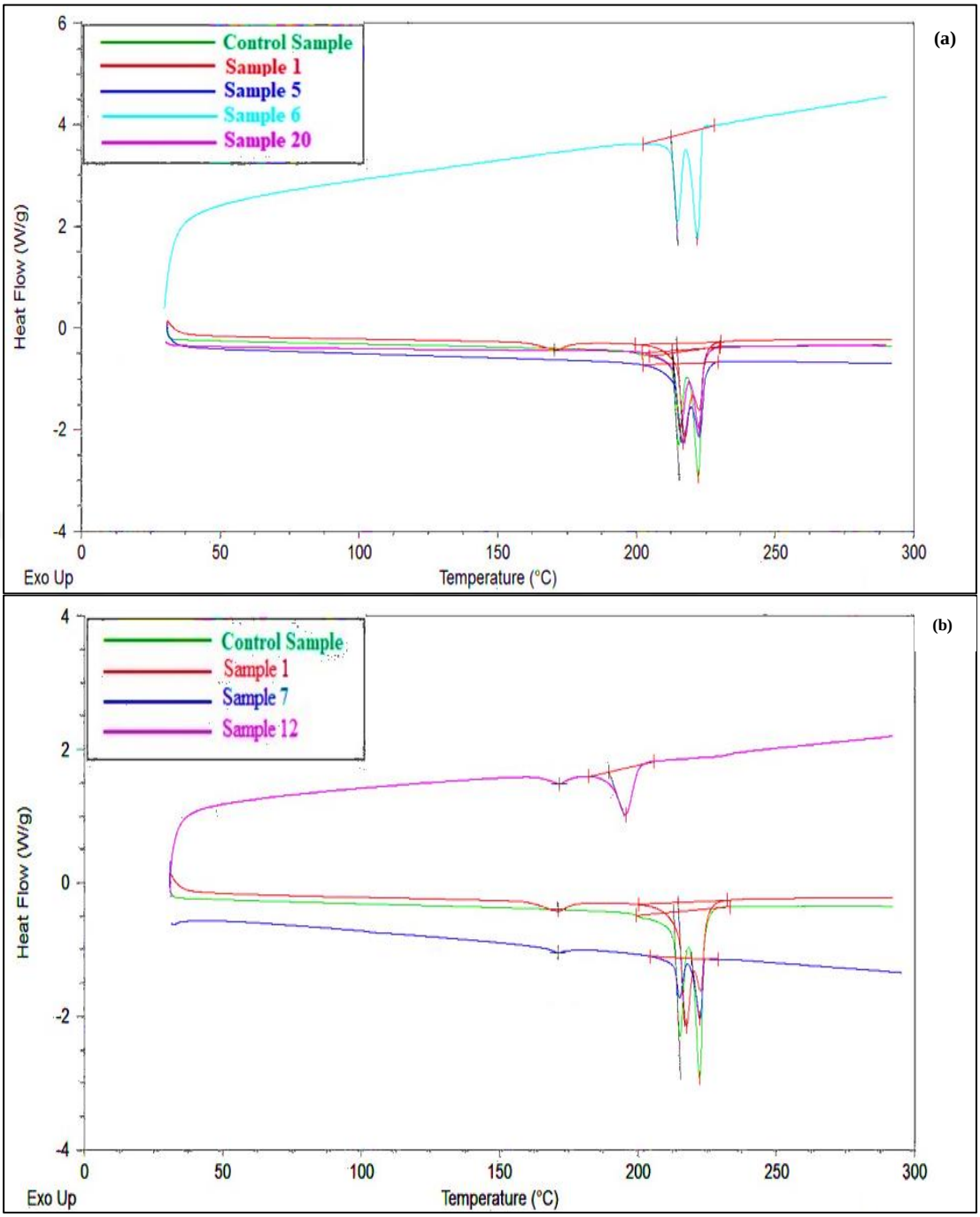

Figure 4.17: DSC curves of **(a)** 20% DEPAL/PBT (Sample 1), 20% Actilox B60/PBT (Sample 5), 20% GF reinforced PBT (Sample 6), 20 % Actilox B30/PBT (Sample 20) and **(b)** 20% DEPAL/PBT (Sample 1), 20% DEPAL/GF reinforced PBT (Sample 7), 20% DEPAL/GF reinforced PBT/PET blend (Sample12).

From Figure 4.17, 4.18 and 4.19 onset temperatures are sharply shifted depend on the addition of all flame retardant additives to PBT/PET blend matrix. The reason of this shifting, PET has smaller onset temperature and crystallization temperature than PBT. Additionally, percent crystallinity is sharply reduced in samples of PBT/PET blend.

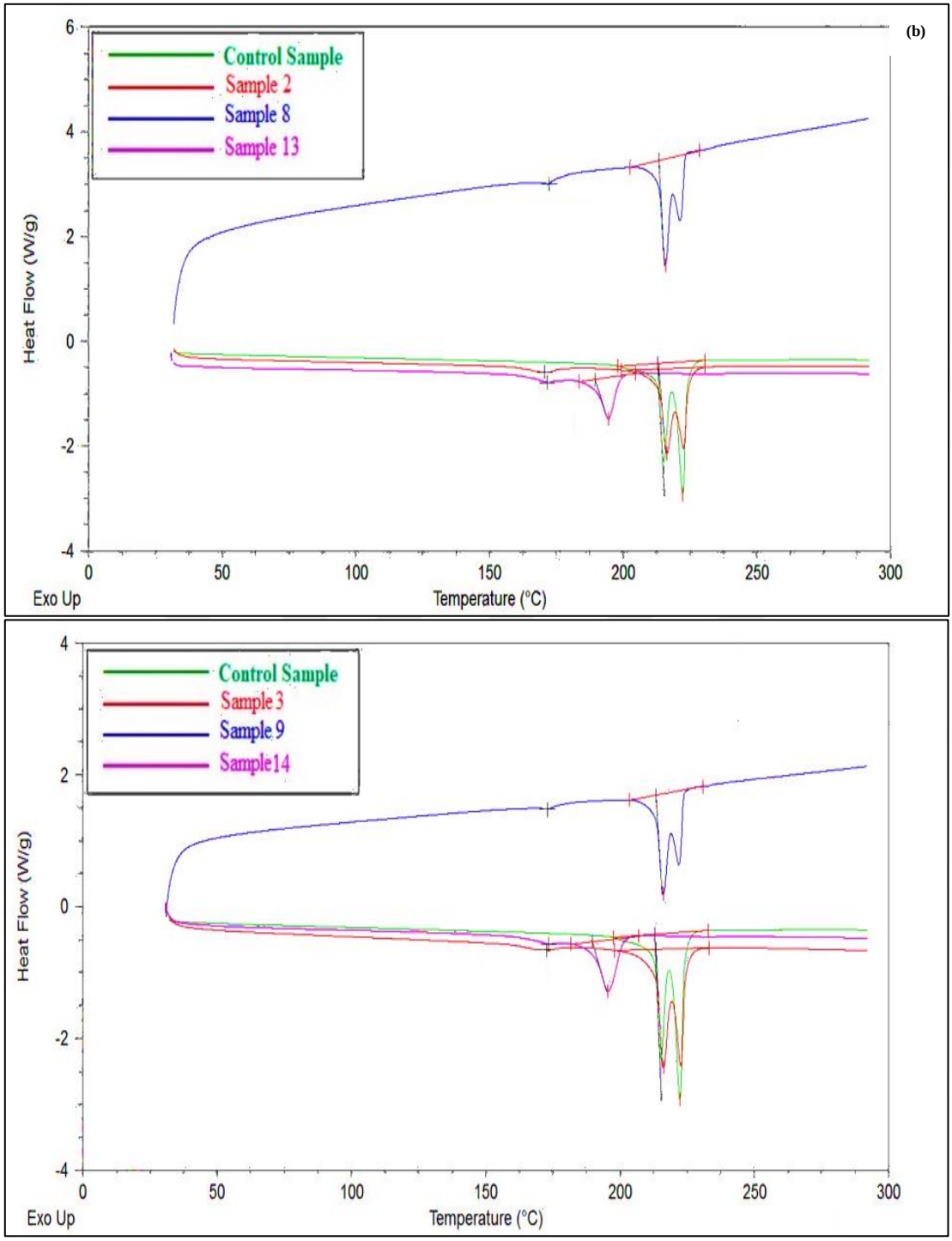

Figure 4.18: DSC curves of **(a)** DEPAL 15%/Actilox B60 5% with different matrices which PBT(Sample 2), GF reinforced PBT(Sample 8), GF reinforced PBT/PET blend (Sample 13) **(b)** DEPAL 10%/Actilox B60 10% with different matrices which PBT(Sample 3), GF reinforced PBT(Sample 9), GF reinforced PBT/PET blend (Sample 14) **(c)** DEPAL 5%/Actilox B60 15% with different matrices which PBT (Sample 4), GF reinforced PBT (Sample 10), GF reinforced PBT/PET blend Sample 15) **(d)** Actilox B60 20% with different matrices which PBT (Sample 5), GF reinforced PBT (Sample 11), GF reinforced PBT/PET blend (Sample 16).

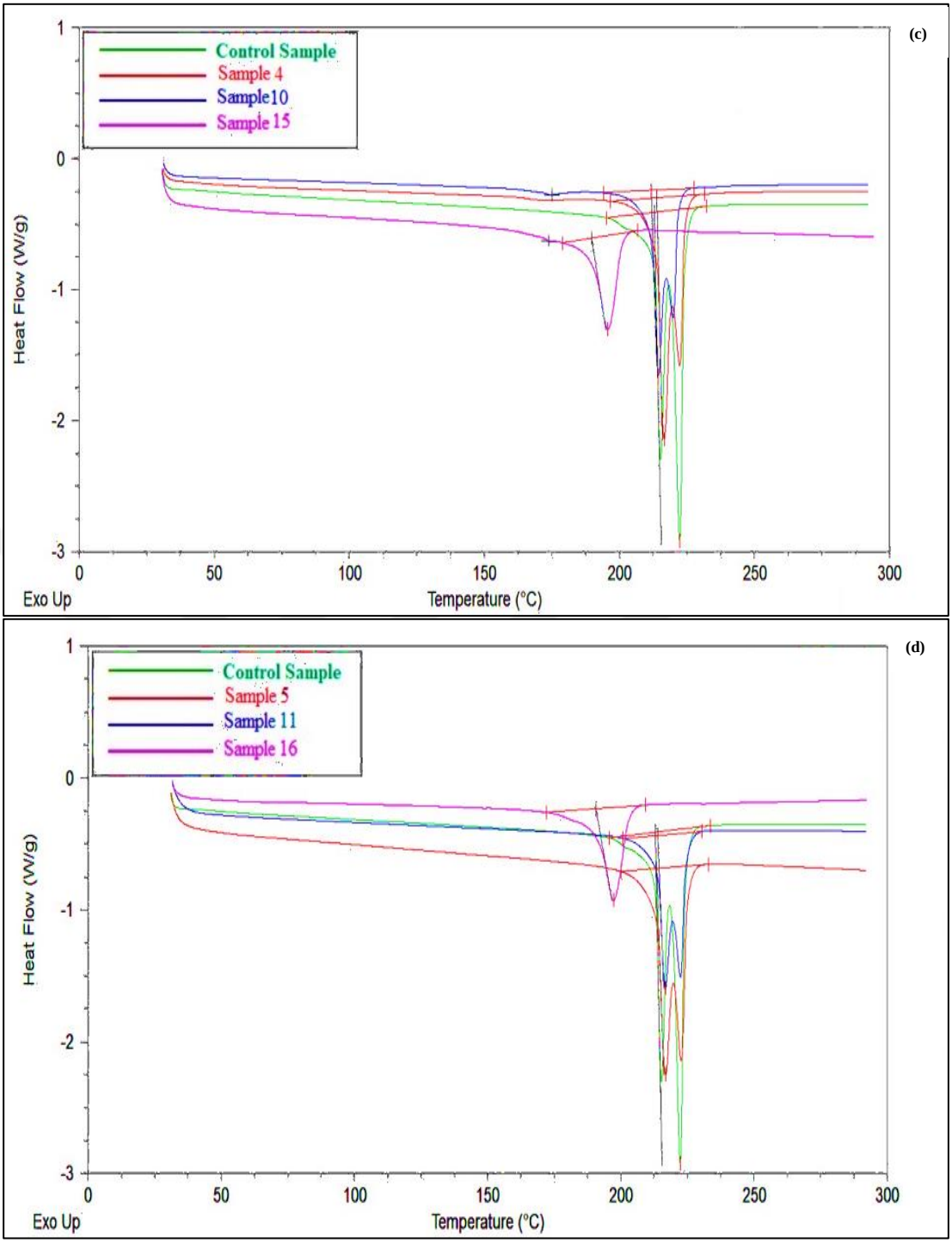

Figure 4.18 (continued): DSC curves of **(a)** DEPAL 15%/Actilox B60 5% with different matrices which PBT (Sample 2), GF reinforced PBT(Sample 8), GF reinforced PBT/PET blend (Sample 13) **(b)** DEPAL 10%/Actilox B60 10% with different matrices which PBT (Sample 3), GF reinforced PBT(Sample 9), GF reinforced PBT/PET blend (Sample 14) **(c)** DEPAL 5%/Actilox B60 15% with different matrices which PBT (Sample 4), GF reinforced PBT (Sample 10), GF reinforced PBT/PET blend (Sample 15) **(d)** Actilox B60 20% with different matrices which PBT (Sample 5), GF reinforced PBT (Sample 11), GF reinforced PBT/PET blend (Sample 16).

In comparison of Sample 2, which is contain 15% DEPAL/5% Actilox B60 in neat PBT; Sample 8, which is contain 15% DEPAL/5% Actilox 60 in GF reinforced PBT and Sample 13, which is contain 15% DEPAL/5% Actilox 60 in GF reinforced PBT/PET blend, the onset temperature of Sample 13 is the smaller than Sample 2 and Sample 8 because of the PET ingredient. However, if we compared the percent crystallinity of these samples, Sample 8 is smaller than Sample 2 and Sample 13.

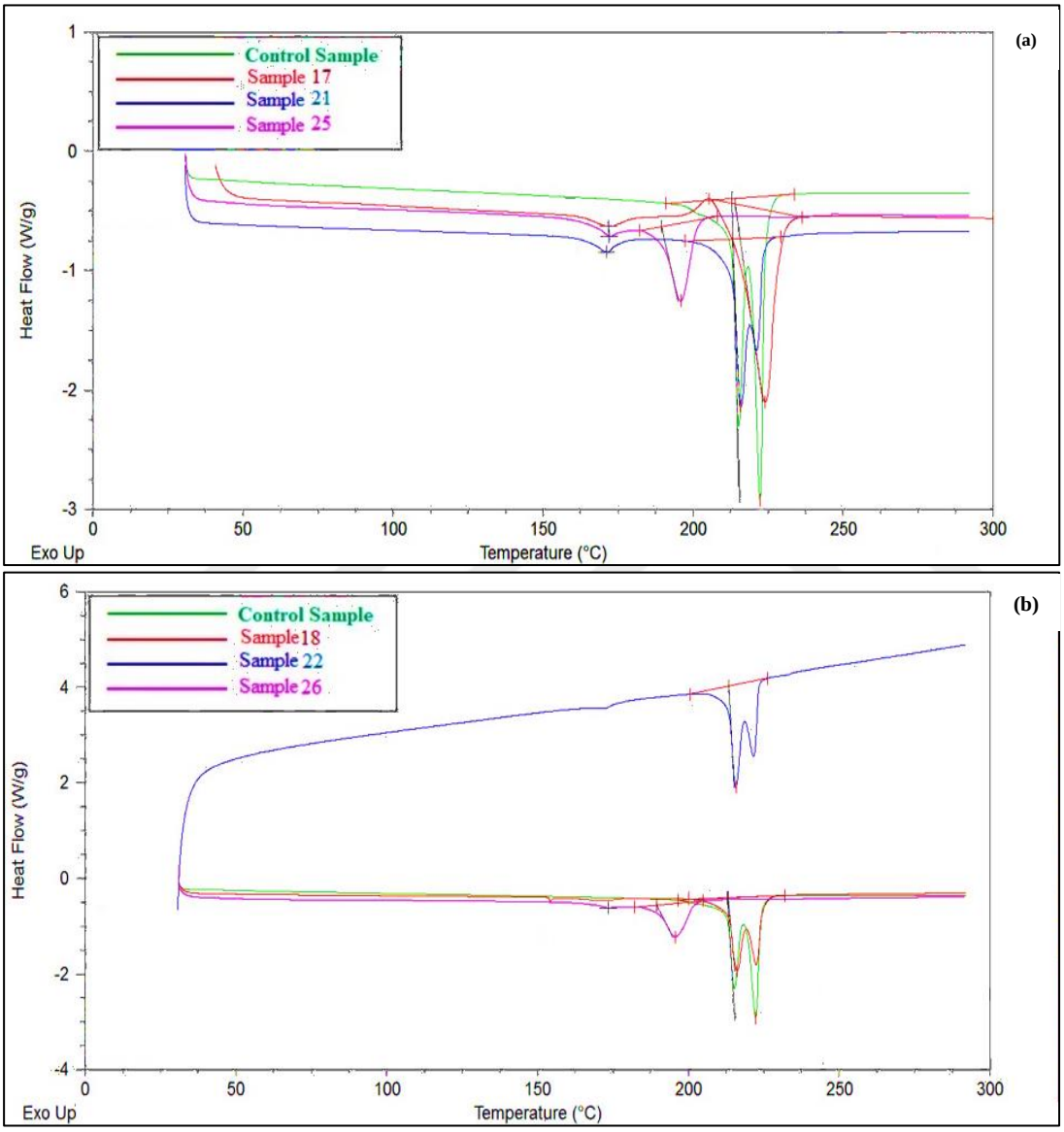

Figure 4.19: DSC curves of **(a)** DEPAL 15%/Actilox B30 5% with different matrices which PBT (Sample 17), GF reinforced PBT(Sample 21), GF reinforced PBT/PET blend (Sample 25) **(b)** DEPAL 10%/Actilox B30 10% with different matrices which PBT (Sample 18), GF reinforced PBT(Sample 22), GF reinforced PBT/PET blend (Sample 26) **(c)** DSC DEPAL 5%/Actilox B30 15% with different matrices which PBT (Sample 17), GF reinforced PBT (Sample 21), GF reinforced PBT/PET blend (Sample 25) **(d)** Actilox B30 20% with different matrices which PBT (Sample 18), GF reinforced PBT (Sample 22), GF reinforced PBT/PET blend (Sample 26).

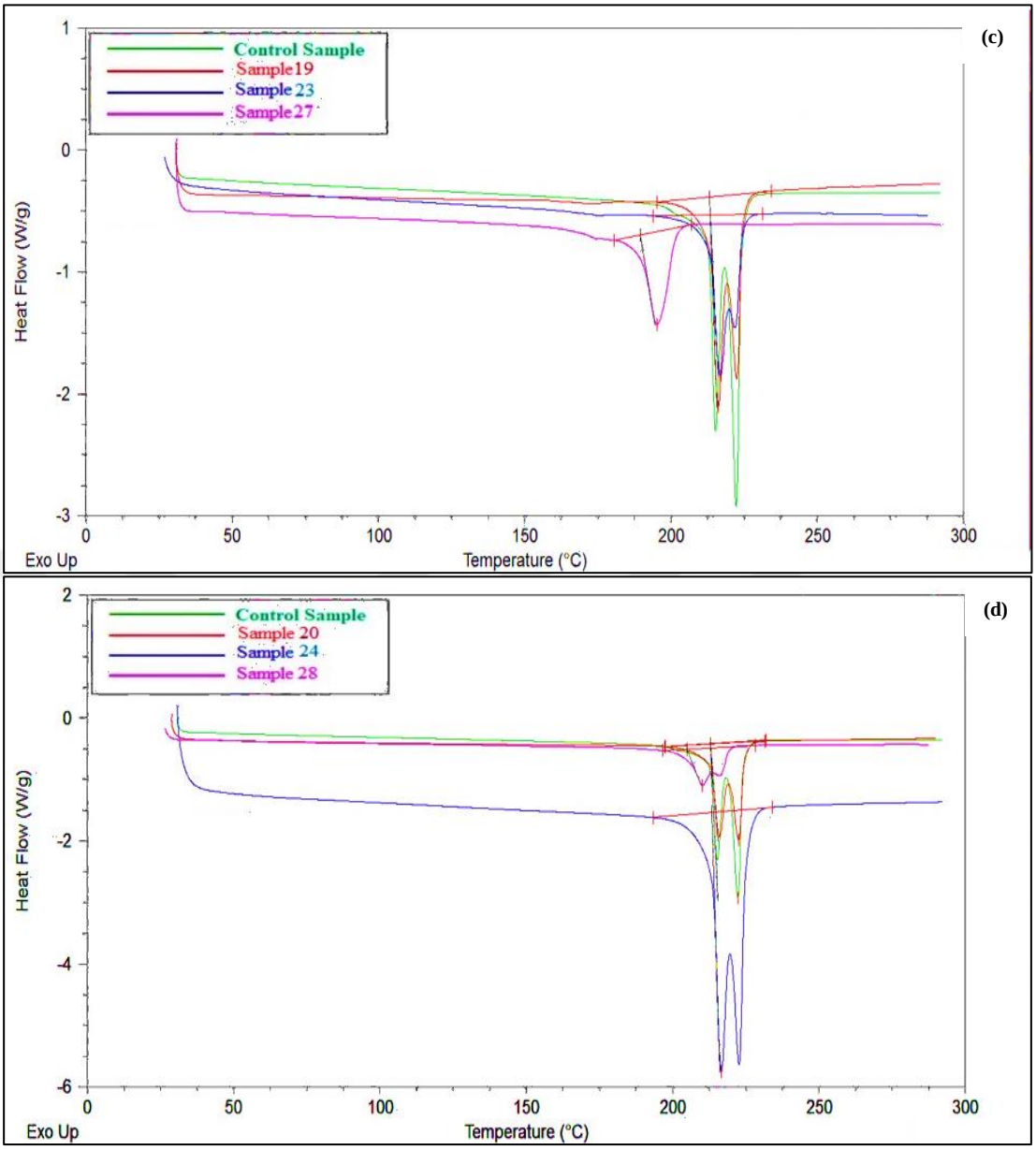

Figure 4.19 (continued): DSC curves of (a) DEPAL 15%/Actilox B30 5% with different matrices which PBT (Sample 17), GF reinforced PBT(Sample 21), GF reinforced PBT/PET blend (Sample 25) (b) DEPAL 10%/Actilox B30 10% with different matrices which PBT (Sample 18), GF reinforced PBT(Sample 22), GF reinforced PBT/PET blend (Sample 26) (c) DSC DEPAL 5%/Actilox B30 15% with different matrices which PBT (Sample 17), GF reinforced PBT (Sample 21), GF reinforced PBT/PET blend (Sample 25) (d) Actilox B30 20% with different matrices which PBT (Sample 18), GF reinforced PBT (Sample 22), GF reinforced PBT/PET blend (Sample 26).

The amount of Actilox B60 is increased in GF reinforced PBT matrix, percent crystallinity is increased gradually. Sample 5, Sample 11 and Sample 16 are compared from Figure 4.18 (d), it is clearly observed that the addition of same amount of flame

retardant to the different matrices, give us the different melting enthalpy and percent crystallinity.

Table 4.5: DSC analysis of samples.

Samples	Onset Temperature (T_o)	Peak Temperature (T_p)	ΔHm (J/g)	ΔHc (J/g)	Xc (%)	Explanations
Control Sample	186	213	47.2	54.43	70.1	Neat PBT
Sample 1	197	215	44.8	41.37	59.4	PBT80 D20
Sample 2	196	213	45.8	42.47	60.9	PBT80 D15 A6-5
Sample 3	194	213	49.4	45.39	65.4	PBT80 D10 A6-10
Sample 4	198	214	42.1	39.98	56.6	PBT80 D5 A6-15
Sample 5	194	213	46.1	42.86	61.4	PBT80 A6-20
Sample 6	205	213	38.6	44.58	57.4	PBT80 GF20
Sample 7	202	219	28.9	29.04	40.0	PBT60 GF20 D20
Sample 8	205	213	37.3	36.44	25.7	PBT60 GF20 D15 A6-5
Sample 9	200	213	33.4	31.31	44.6	PBT60 GF20 D10 A6-10
Sample 10	196	212	31.2	28.73	41.3	PBT60 GF20 D5 A6-15
Sample 11	197	214	32.1	30.68	43.3	PBT60 GF20 A6-20
Sample 12	154	190	15.4	24.25	27.5	PBT48 PET12 GF20 D20
Sample 13	147	189	28.8	22.33	35.5	PBT48 PET12 GF20 D15 A6-5
Sample 14	140	187	25.7	24.86	35.1	PBT48 PET12 GF20 D10 A6-10
Sample 15	161	189	24.1	23.18	32.8	PBT48 PET12 GF20 D5 A6-15
Sample 16	160	190	23.5	24.07	33.0	PBT48 PET12 GF20 A6-20
Sample 17	204	214	49.8	44.72	65.2	PBT80 D15 A3-5
Sample 18	184	213	41.9	38.92	55.7	PBT80 D10 A3-10
Sample 19	190	213	45.1	41.07	59.4	PBT80 D5 A3-15
Sample 20	198	213	41.8	41.22	57.3	PBT80 A3-20
Sample 21	197	213	32.9	30.30	43.6	PBT60 GF20 D15 A3-5
Sample 22	203	213	43.4	40.01	57.5	PBT60 GF20 D10 A3-10
Sample 23	192	213	33.6	30.19	44.0	PBT60 GF20 D5 A3-15
Sample 24	194	213	124.1	112.7	163	PBT60 GF20 A3-20
Sample 25	150	189	15.4	22.95	26.6	PBT48 PET12 GF20 D15 A3-5
Sample 26	156	189	27.3	25.11	36.4	PBT48 PET12 GF20 D10 A3-10
Sample 27	154	189	28.9	25.61	37.9	PBT48 PET12 GF20 D5 A3-15
Sample 28	184	204	21.9	21.26	30.0	PBT48 PET12 GF20 A3-20

Sample 17, Sample 21 and Sample 25 are compared from Figure 4.19 (a), it is observed that the addition of same amount of flame retardants to the different matrices, give us the different melting enthalpy and percent crystallinity. Sample 17 contains 15% DEPAL/5% Actilox B30 in neat PBT, Sample 21 contains 15% DEPAL/5% Actilox B30 in GF reinforced PBT and Sample 25 contains 15% DEPAL/5% Actilox B30 in GF reinforced PBT/PET blend. In comparison of Sample 17, 21 and 25, it is clearly observed that the percent crystallinity value is decreased. In accordance with all observation; the comparison of the samples that contain Actilox B60 and Actilox B30, it is seen that the value of percent crystallinity shows almost same tendency but the samples which contains Actilox B60 have slightly higher crystallinity value.

4.3.3 Thermal gravimetric analysis (TGA)

Under nitrogen atmosphere, thermal gravimetric analysis was performed from room temperature to 900 °C. The results are shown in Fig. 4.20, Figure 4.21 and Fig 4.22. Table 4.6 presents thermal degradation start temperature, final degradation temperature, mass loss at final temperature and residue amount of the samples at 900 °C.

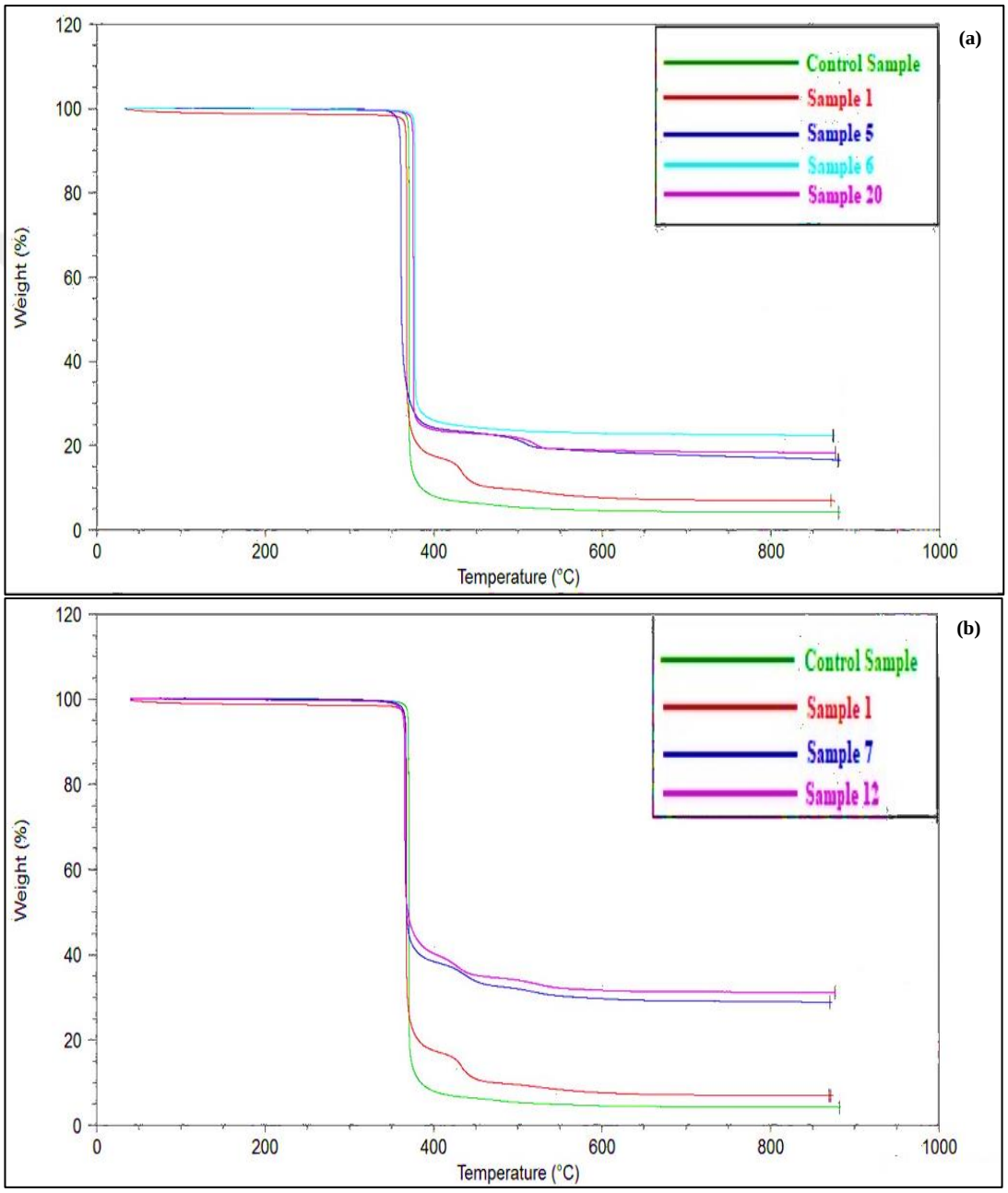

Figure 4.20: TGA curves of **(a)** 20% DEPAL/PBT (Sample 1), 20% Actilox B60/PBT (Sample 5), 20% GF reinforced PBT (Sample 6), 20 % Actilox B30/PBT (Sample 20) **(b)** 20% DEPAL/PBT (Sample 1), 20% DEPAL/GF reinforced PBT (Sample 7), 20% DEPAL/GF reinforced PBT/PET blend (Sample12).

According to Fig. 4.20, Fig 4.21 and Fig 4.22 all curves are shifted lower temperature in comparison of Control Sample. The addition of 20% DEPAL to the neat PBT (Sample 1), aluminum diethyl phosphinate particles lower starting degradation temperature by 4 °C. When added 20% Actilox B60 to neat PBT (Sample 5), decreases the starting degradation temperature by 29 °C and the addition of 20% Actilox B30 (Sample 20), T_i slightly decreases 2 °C.

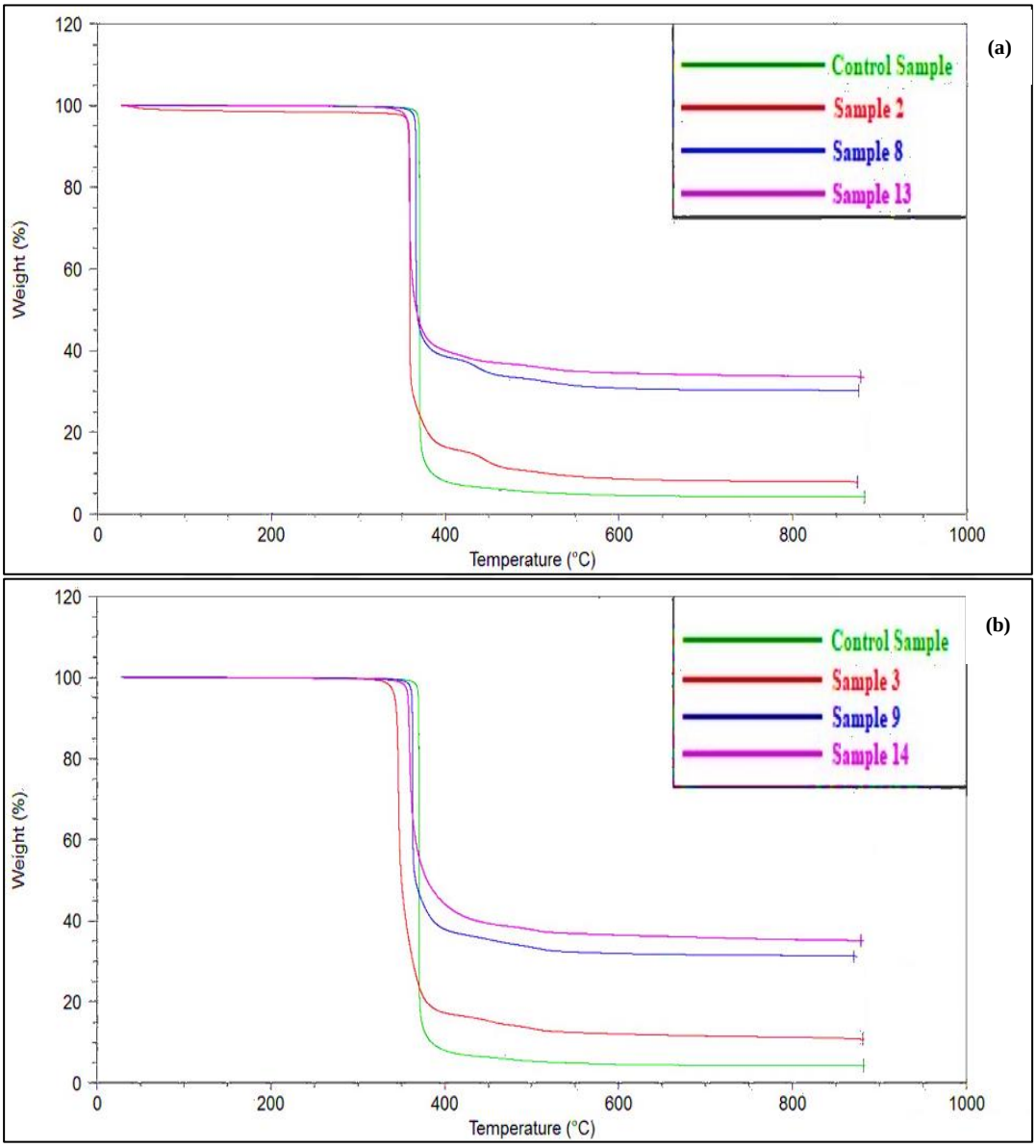

Figure 4.21: TGA curves of **(a)** DEPAL 15%/Actilox B60 5% with different matrices which PBT (Sample 2), GF reinforced PBT(Sample 8), GF reinforced PBT/PET blend (Sample 13); **(b)** DEPAL 10%/Actilox B60 10% with different matrices which PBT (Sample 3), GF reinforced PBT (Sample 9), GF reinforced PBT/PET blend (Sample 14) **(c)** DEPAL 5%/Actilox B60 15% with different matrices which PBT (Sample 4), GF reinforced PBT (Sample 10), GF reinforced PBT/PET blend (Sample 15); **(d)** 20% Actilox B60 in PBT (Sample 5), in GF reinforced PBT (Sample 11), in GF reinforced PBT/PET blend (Sample 16).

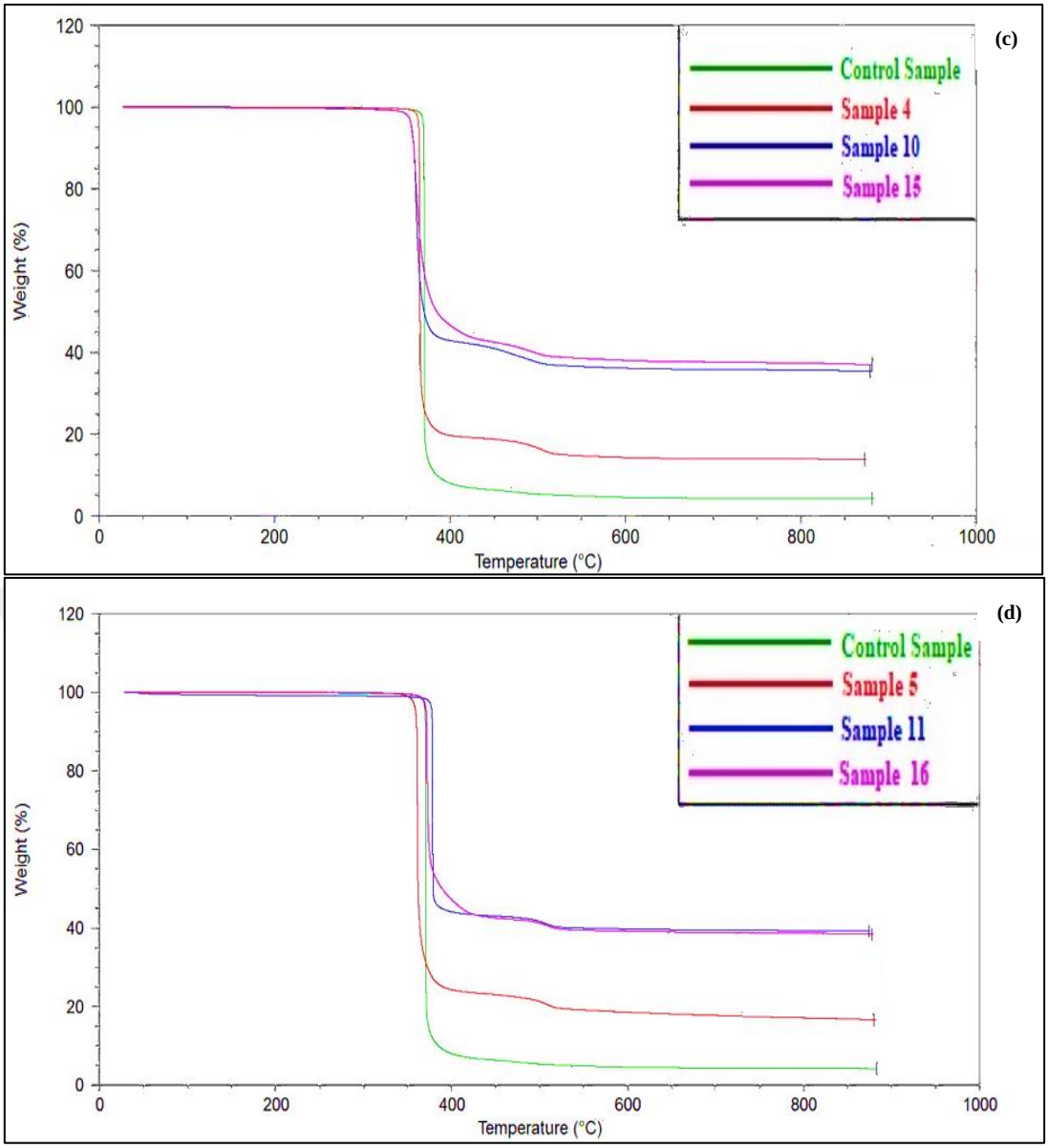

Figure 4.21 (continued): TGA curves of (a) DEPAL 15%/Actilox B60 5% with different matrices which PBT (Sample 2), GF reinforced PBT(Sample 8), GF reinforced PBT/PET blend (Sample 13); (b) DEPAL 10%/Actilox B60 10% with different matrices which PBT (Sample 3), GF reinforced PBT (Sample 9), GF reinforced PBT/PET blend (Sample 14) (c) DEPAL 5%/Actilox B60 15% with different matrices which PBT (Sample 4), GF reinforced PBT (Sample 10), GF reinforced PBT/PET blend (Sample 15); (d) 20% Actilox B60 in PBT (Sample 5), in GF reinforced PBT (Sample 11), in GF reinforced PBT/PET blend (Sample 16).

If we examined the effect of 20% glass fiber to the neat PBT (Sample 6), we can not see a significant change of T_i. However, all additives are improved the thermal stability at weight loss compared by neat PBT. The addition of 20% DEPAL, 20% Actilox B60, 20% Actilox B30 and 20% glass fiber to neat PBT improved the thermal stability at percentage weight loss from 4.2 to 6.9, 16.6, 18.3 and 22.4 respectively. The addition of the same ratio (20%) phosphorus based flame retardant to different matrices which

are neat PBT (Sample 1), GF reinforced PBT (Sample 7) and GF reinforced PBT/PET blend (Sample 12), the value of the residues are 6.9%, 28.8% and 31.1% at 900 °C, respectively.

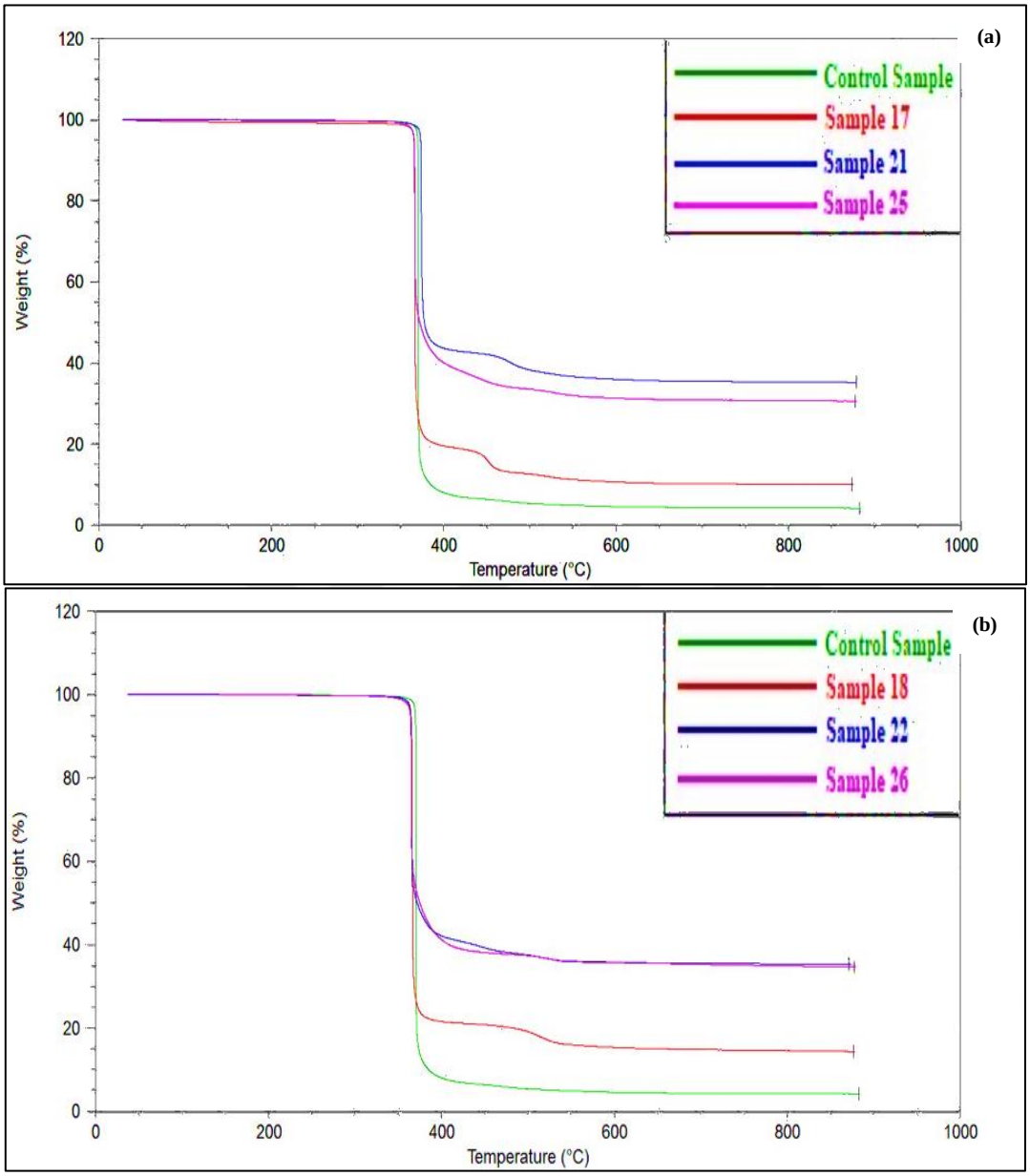

Figure 4.22: TGA curves of **(a)** DEPAL 15%/Actilox B30 5% with different matrices which PBT (Sample 17), GF reinforced PBT (Sample 21), GF reinforced PBT/PET blend (Sample 25) **(b)** DEPAL 10%/Actilox B30 10% with different matrices which PBT (Sample 18), GF reinforced PBT (Sample 22), GF reinforced PBT/PET blend (Sample 26) **(c)** DEPAL 5%/Actilox B30 15% with different matrices which PBT (Sample 19), GF reinforced PBT (Sample 23), GF reinforced PBT/PET blend (Sample 27) **(d)** Actilox B30 20% with different matrices which PBT (Sample 19), GF reinforced PBT (Sample 24), GF reinforced PBT/PET blend (Sample 28).

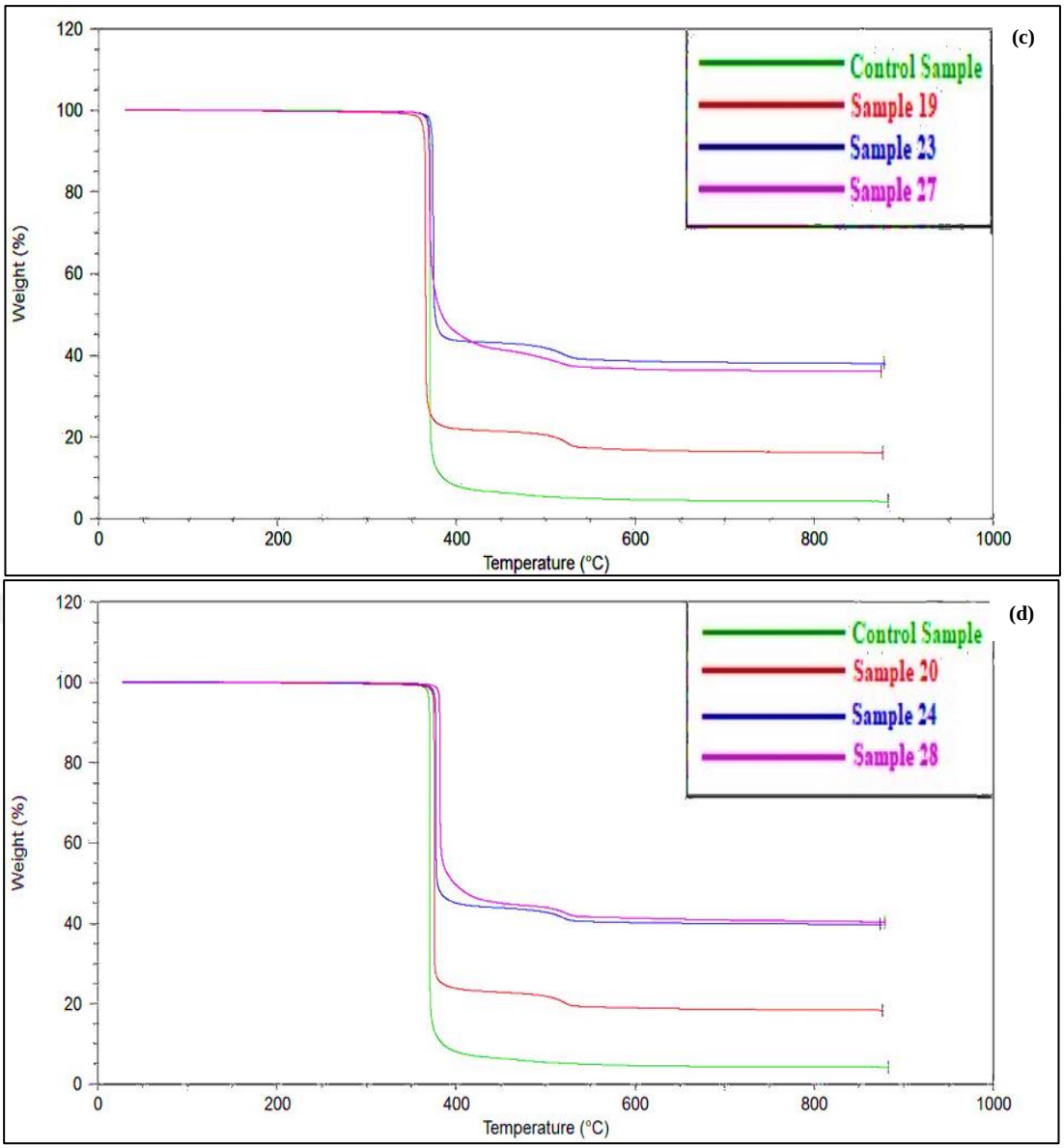

Figure 4.22 (continued): TGA curves of (a) DEPAL 15%/Actilox B30 5% with different matrices which PBT (Sample 17), GF reinforced PBT (Sample 21), GF reinforced PBT/PET blend (Sample 25) (b) DEPAL 10%/Actilox B30 10% with different matrices which PBT (Sample 18), GF reinforced PBT (Sample 22), GF reinforced PBT/PET blend (Sample 26) (c) DEPAL 5%/Actilox B30 15% with different matrices which PBT (Sample 19), GF reinforced PBT (Sample 23), GF reinforced PBT/PET blend (Sample 27) (d) Actilox B30 20% with different matrices which PBT (Sample 19), GF reinforced PBT (Sample 24), GF reinforced PBT/PET blend (Sample 28).

Likewise, 15% phosphorus based flame retardant/5% mineral based flame retardant (Actilox B60) are added to the same matrices which are neat PBT (Sample 2), GF reinforced PBT (Sample 8) and GF reinforced PBT/PET blend (Sample 13), the value of the residues are 7.9%, 30.2% and 33.6% at 900 °C, respectively. According to Figure 4.21 observing the samples that contain same rates of flame retardant additives

in different matrix has the same tendency for Actilox B60. 15% phosphorus based flame retardant/5% mineral based flame retardant (Actilox B30) are added to the same matrices which are neat PBT (Sample 17), GF reinforced PBT (Sample 21) and GF reinforced PBT/PET blend (Sample 25), the value of the residues are 10.1%, 35.2% and 30.6% at 900 °C, respectively. In accordance with all observation; the comparison of the samples that contain Actilox B60 and Actilox B30, it is seen that the value of the residue shows almost same tendency but the samples which contains Actilox B30 have slightly higher thermal stability.

Table 4.6: TGA results of samples.

Samples	T_i	T_f	Mass Loss @T_f (wt.%)	Residue @ 900 °C (wt%)	Explanations
Control Sample	352	403	92	4.2	Neat PBT
Sample 1	348	473	88	6.9	PBT80 D20
Sample 2	337	476	87	7.9	PBT80 D15 A6-5
Sample 3	312	529	87	10.8	PBT80 D10 A6-10
Sample 4	336	543	85	13.9	PBT80 D5 A6-15
Sample 5	323	535	80	16.6	PBT80 A6-20
Sample 6	351	491	76	22.4	PBT80 GF20
Sample 7	336	562	70	28.8	PBT60 GF20 D20
Sample 8	344	576	68	30.2	PBT60 GF20 D15 A6-5
Sample 9	334	539	67	31.3	PBT60 GF20 D10 A6-10
Sample 10	309	540	63	35.4	PBT60 GF20 D5 A6-15
Sample 11	348	602	59	39.2	PBT60 GF20 A6-20
Sample 12	336	565	68	31.1	PBT48 PET12 GF20 D20
Sample 13	323	529	64	33.6	PBT48 PET12 GF20 D15 A6-5
Sample 14	324	522	62	35.1	PBT48 PET12 GF20 D10 A6-10
Sample 15	320	531	61	36.9	PBT48 PET12 GF20 D5 A6-15
Sample 16	343	537	60	38.5	PBT48 PET12 GF20 A6-20
Sample 17	336	479	86	10.1	PBT80 D15 A3-5
Sample 18	334	539	83	14.3	PBT80 D10 A3-10
Sample 19	331	547	82	16.1	PBT80 D5 A3-15
Sample 20	350	551	80	18.3	PBT80 A3-20
Sample 21	345	544	63	35.2	PBT60 GF20 D15 A3-5
Sample 22	336	573	64	35.3	PBT60 GF20 D10 A3-10
Sample 23	338	565	61	37.9	PBT60 GF20 D5 A3-15
Sample 24	338	543	60	39.7	PBT60 GF20 A3-20
Sample 25	346	571	68	30.6	PBT48 PET12 GF20 D15 A3-5
Sample 26	340	556	63	34.7	PBT48 PET12 GF20 D10 A3-10
Sample 27	335	547	63	36.1	PBT48 PET12 GF20 D5 A3-15
Sample 28	355	561	58	40.4	PBT48 PET12 GF20 A3-20

*T_i : Starting Thermal Degradation Temperature
*T_f : Final Thermal Degradation Temperature

4.4 Evaluation of Flame Retardant Properties

4.4.1 UL 94 classification

According to Table 4.7, Figure 4.23 and Figure 4.24, if the samples are examined with different concentrations, all samples, which do not contain phosphorus based flame retardant (diethyl phosphinate), there is no rate in UL 94 classification also horizontal

burning and dripping is occurred. In consequence of these UL 94 classifications, it could be say phosphorus based fire retardant additives have significant influence on fire retardancy properties of PBT. Also, the increment of diethyl phosphinate flame retardant additives in the sample concentration, UL 94 classification is increased. In comparison of Sample 2, which is contained 15% DEPAL/5% Actilox B60, and Sample 17, which is contained 15% DEPAL/5% Actilox B30, there is no significant difference between of using the different type of Actiloxs. Additionally, unreinforced PBT with the same flame retardant additive concentration shows better UL 94 classification than the GF reinforced PBT. As it is excepted, the increment of the sample thicknesses, UL 94 classification is positively increased.

Table 4.7: UL 94 classification of samples.

	Thickness of Samples			
Samples	**0.75 mm**	**1.6 mm**	**3.2 mm**	**Explanations**
Control Sample	NR	NR	V-2	Neat PBT
Sample 1	V-0	V-0	V-0	PBT80 D20
Sample 2	V-0	V-0	V-0	PBT80 D15 A6-5
Sample 3	V-0	V-0	V-0	PBT80 D10 A6-10
Sample 4	V-2	V-2	V-2	PBT80 D5 A6-15
Sample 5	NR	NR	NR	PBT80 A6-20
Sample 6	NR	NR	NR	PBT80 GF20
Sample 7	V-1	V-0	V-0	PBT60 GF20 D20
Sample 8	V-2	V-0	V-0	PBT60 GF20 D15 A6-5
Sample 9	V-1	V-2	V-0	PBT60 GF20 D10 A6-10
Sample 10	V-2	V-2	V-1	PBT60 GF20 D5 A6-15
Sample 11	NR	NR	NR	PBT60 GF20 A6-20
Sample 12	V-2	V-1	V-0	PBT48 PET12 GF20 D20
Sample 13	V-1	V-0	V-0	PBT48 PET12 GF20 D15 A6-5
Sample 14	V-2	V-2	V-0	PBT48 PET12 GF20 D10 A6-10
Sample 15	V-2	V-2	V-2	PBT48 PET12 GF20 D5 A6-15
Sample 16	NR	NR	NR	PBT48 PET12 GF20 A6-20
Sample 17	V-0	V-0	V-0	PBT80 D15 A3-5
Sample 18	V-0	V-0	V-2	PBT80 D10 A3-10
Sample 19	V-2	V-2	V-2	PBT80 D5 A3-15
Sample 20	NR	NR	NR	PBT80 A3-20
Sample 21	V-1	V-0	V-0	PBT60 GF20 D15 A3-5
Sample 22	V-2	V-1	V-1	PBT60 GF20 D10 A3-10
Sample 23	V-2	V-2	V-2	PBT60 GF20 D5 A3-15
Sample 24	NR	NR	NR	PBT60 GF20 A3-20
Sample 25	V-1	V-1	V-0	PBT48 PET12 GF20 D15 A3-5
Sample 26	V-2	V-2	V-0	PBT48 PET12 GF20 D10 A3-10
Sample 27	V-2	V-2	V-2	PBT48 PET12 GF20 D5 A3-15
Sample 28	NR	NR	NR	PBT48 PET12 GF20 A3-20

*** NR**: No Rate

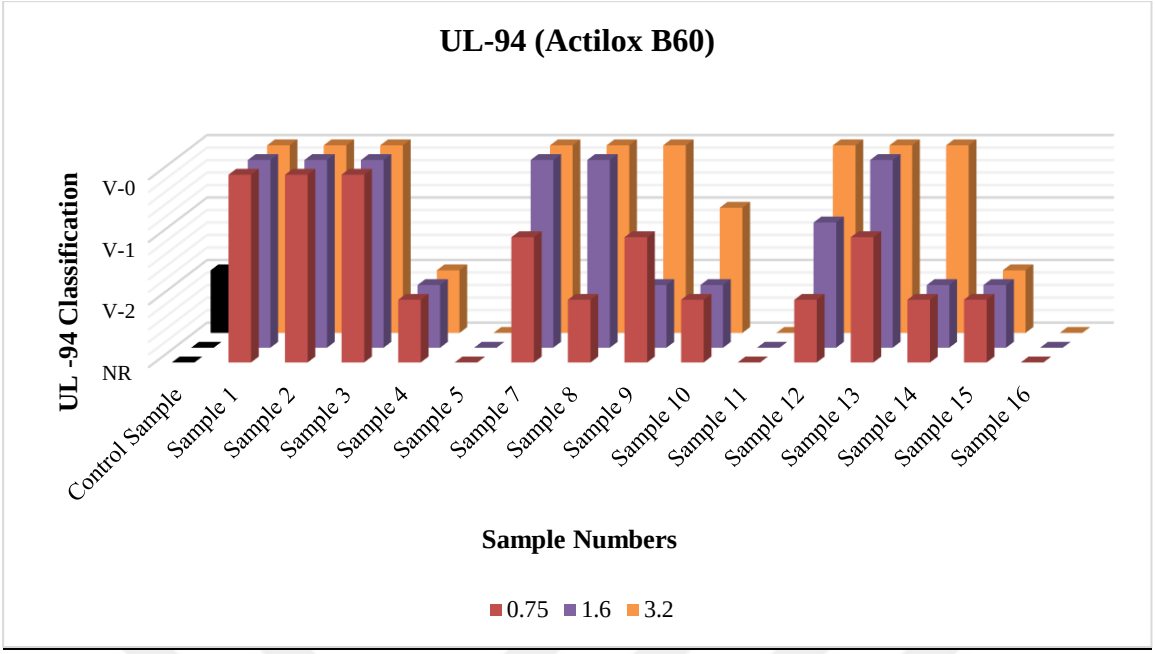

Figure 4.23: UL 94 classification of Actilox B60 samples.

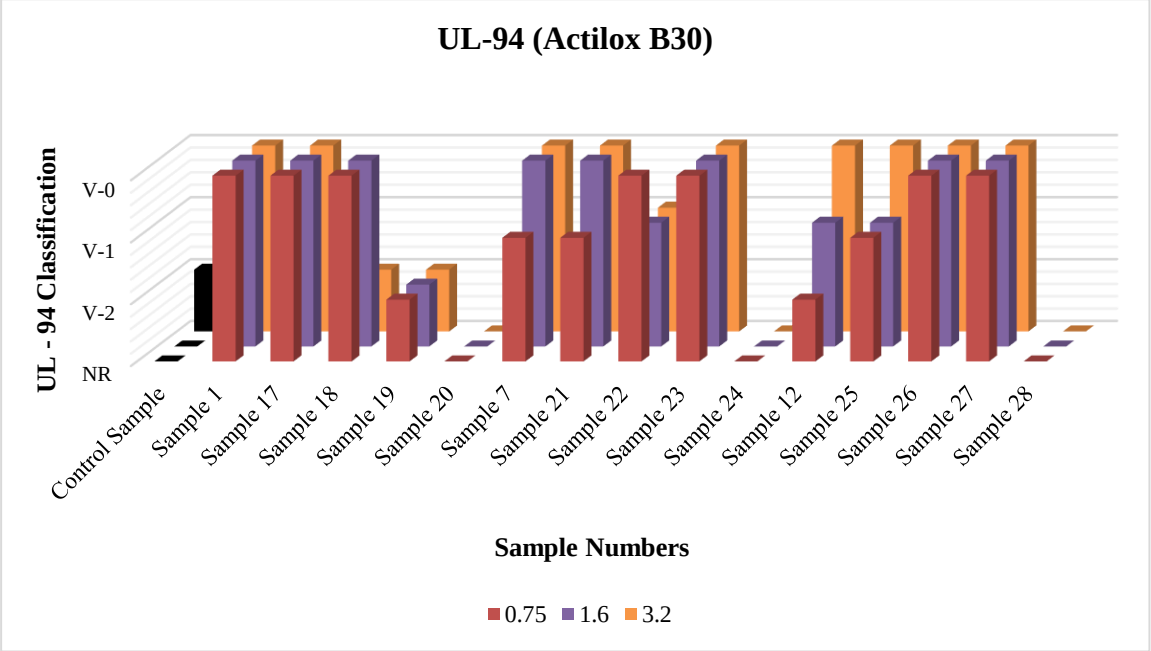

Figure 4.24: UL 94 classification of Actilox B30 samples.

4.4.2 Glow wire ignition temperature

Measurement of glow wire ignition temperature of samples were done as defined as in section 3.4.4.2. The test results are given in Table 4.8 According to test results, measurements of glow wire ignition temperature with 1 mm plaques and 2 mm plaques have the same temperature value except Sample 9. Control Sample, Sample 6, 7, 8 and 9 have the highest glow wire ignition temperature among the all samples. The test

results of other samples are between 725 and 775 °C temperature interval. It is observed that especially glass fiber reinforced samples do not ignite or consumed during the application of glow wire. In comparison of the samples that contain Actilox B60 and Actilox B30, it is seen that the value of the GWIT shows almost same trend but the samples which contains Actilox B60 have slightly higher temperature.

Table 4.8: Glow wire ignition temperature test results.

	Thickness		
Samples	**1 mm plaque**	**2 mm plaque**	**Explanations**
Control Sample	800	800	Neat PBT
Sample 1	750	750	PBT80 D20
Sample 2	775	775	PBT80 D15 A6-5
Sample 3	750	750	PBT80 D10 A6-10
Sample 4	775	775	PBT80 D5 A6-15
Sample 5	750	775	PBT80 A6-20
Sample 6	800	800	PBT80 GF20
Sample 7	800	800	PBT60 GF20 D20
Sample 8	800	800	PBT60 GF20 D15 A6-5
Sample 9	825	800	PBT60 GF20 D10 A6-10
Sample 10	775	775	PBT60 GF20 D5 A6-15
Sample 11	775	775	PBT60 GF20 A6-20
Sample 12	775	775	PBT48 PET12 GF20 D20
Sample 13	775	775	PBT48 PET12 GF20 D15 A6-5
Sample 14	775	775	PBT48 PET12 GF20 D10 A6-10
Sample 15	750	750	PBT48 PET12 GF20 D5 A6-15
Sample 16	775	775	PBT48 PET12 GF20 A6-20
Sample 17	725	725	PBT80 D15 A3-5
Sample 18	725	725	PBT80 D10 A3-10
Sample 19	750	750	PBT80 D5 A3-15
Sample 20	750	750	PBT80 A3-20
Sample 21	750	750	PBT60 GF20 D15 A3-5
Sample 22	775	775	PBT60 GF20 D10 A3-10
Sample 23	775	775	PBT60 GF20 D5 A3-15
Sample 24	750	750	PBT60 GF20 A3-20
Sample 25	775	775	PBT48 PET12 GF20 D15 A3-5
Sample 26	775	775	PBT48 PET12 GF20 D10 A3-10
Sample 27	775	775	PBT48 PET12 GF20 D5 A3-15
Sample 28	750	750	PBT48 PET12 GF20 A3-20

4.4.3 Glow wire flammability index

According to Table 4.9, it is clearly observed that the samples which are not contain phosphorus based flame retardant (diethyl phosphinate), glow wire flammability index test results are failed. In comparison of neat PBT and Sample 6, 20% glass fiber reinforced PBT, glow wire flammability index test results of two of them are failed. Generally, glow wire flammability index test results with different temperature level are the same except Sample 15, which is contain 5% DEPAL/15% Actilox B60 in GF reinforced PBT/PET matrix, and Sample 20, which is contain just 20% Actilox B30 in unreinforced PBT matrix.

Table 4.9: Glow wire flammability index test results.

	960 °C		850 °C		
	1 mm plaque	**2 mm plaque**	**1 mm plaque**	**2 mm plaque**	**Explanations**
Control Sample	FAIL	FAIL	FAIL	FAIL	Neat PBT
Sample 1	PASS	PASS	PASS	PASS	PBT80 D20
Sample 2	PASS	PASS	PASS	PASS	PBT80 D15 A6-5
Sample 3	PASS	PASS	PASS	PASS	PBT80 D10 A6-10
Sample 4	PASS	PASS	PASS	PASS	PBT80 D5 A6-15
Sample 5	FAIL	FAIL	FAIL	FAIL	PBT80 A6-20
Sample 6	FAIL	FAIL	FAIL	FAIL	PBT80 GF20
Sample 7	PASS	PASS	PASS	PASS	PBT60 GF20 D20
Sample 8	PASS	PASS	PASS	PASS	PBT60 GF20 D15 A6-5
Sample 9	PASS	PASS	PASS	PASS	PBT60 GF20 D10 A6-10
Sample 10	PASS	PASS	PASS	PASS	PBT60 GF20 D5 A6-15
Sample 11	FAIL	FAIL	FAIL	FAIL	PBT60 GF20 A6-20
Sample 12	PASS	PASS	PASS	PASS	PBT48 PET12 GF20 D20
Sample 13	PASS	PASS	PASS	PASS	PBT48 PET12 GF20 D15 A6-5
Sample 14	PASS	PASS	PASS	PASS	PBT48 PET12 GF20 D10 A6-10
Sample 15	FAIL	FAIL	PASS	PASS	PBT48 PET12 GF20 D5 A6-15
Sample 16	FAIL	FAIL	FAIL	FAIL	PBT48 PET12 GF20 A6-20
Sample 17	PASS	PASS	PASS	PASS	PBT80 D15 A3-5
Sample 18	PASS	PASS	PASS	PASS	PBT80 D10 A3-10
Sample 19	PASS	PASS	PASS	PASS	PBT80 D5 A3-15
Sample 20	FAIL	FAIL	PASS	PASS	PBT80 A3-20
Sample 21	PASS	PASS	PASS	PASS	PBT60 GF20 D15 A3-5
Sample 22	PASS	PASS	PASS	PASS	PBT60 GF20 D10 A3-10
Sample 23	PASS	PASS	PASS	PASS	PBT60 GF20 D5 A3-15
Sample 24	FAIL	FAIL	FAIL	FAIL	PBT60 GF20 A3-20
Sample 25	PASS	PASS	PASS	PASS	PBT48 PET12 GF20 D15 A3-5
Sample 26	PASS	PASS	PASS	PASS	PBT48 PET12 GF20 D10 A3-10
Sample 27	PASS	PASS	PASS	PASS	PBT48 PET12 GF20 D5 A3-15
Sample 28	FAIL	FAIL	FAIL	FAIL	PBT48 PET12 GF20 A3-20

5. CONCLUSIONS

In this study, PBT, 20 % glass fiber reinforced PBT and 20 % glass fiber reinforced PBT/PET blends were searched for improving the flame retarding properties. For this purpose, the addition of non-halogenated phosphorus based flame retardant (aluminium diethyl phosphinate) and two different kinds of mineral flame retardant (aluminium oxide hydroxide-boehmite) were used with different ratios.

All 29 samples were prepared by extrusion and injection moulding processing methods in order to investigation of mechanical, thermal and fire retardant properties of poly(butylene terephthalate) (PBT) and PBT/PET blends. The samples were extruded with different matrices which are neat PBT, 20% glass fiber reinforced (GF) PBT and 20% GF reinforced PBT/PET blend. These samples contain 1% heat stabilizer, 1% process stabilizer and 3% lubricant however the amount of these additives were ignored in calculations. Two types of aluminium based mineral flame retardant additives, which have different average particle size and specific surface area but they have the same chemical structure, were used as co-flame retardants in preparation of samples. These aluminium based mineral flame retardants are called boehmite in industry and they classified as Actilox B60 and Actilox B30 based on their particle size and specific surface area. The average particle size (D50) and specific surface area of Actilox B60 are 1.2 μm and 5 m2/g respectively. The average particle size (D50) and specific surface area of Actilox B30 are 2.3 μm and 3 m2/g. The main flame retardant was especially selected halogen free phosphorus based aluminium diethylphosphinate (DEPAL) by the reason of legislative restrictions, environmental and health considerations.

This study can be considered as two stages, depending on which aluminium based mineral flame retardant used in preparation. In first stage, Actilox B60 is used as a co-flame retardant with the main flame retardant. In the second stage, Actilox B30 is used as co-flame retardant with the main flame retardant additive. All samples contain totally 20% flame retardant additives except Control Sample that was just prepared

PBT resin. In order to evaluate structural, mechanical, thermal and fire retardant properties of samples with different characterization methods were used.

Structural properties of samples were evaluated by measurements of density and melt flow index (MFI). In order to obtain mechanical properties of samples; stress at break, tensile modulus, strain at break and Izod impact (+23 °C and -30 °C) values are measured. Thermal properties of samples were calculated by heat distortion temperature (HDT), thermal gravimetric analysis (TGA) and differential scanning calorimeter (DSC) analysis. Flame retardant performance of the samples were evaluated by UL 94, glow wire ignition temperature and glow wire flammability index tests.

Density and melt flow index measurements of all samples were done. In density measurement values, there is no significant difference between samples containing Actilox B60 or Actilox B30 mineral based flame retardant as a co-flame retardant. The addition of main flame retardant (DEPAL) to neat PBT, almost no difference is observed. Samples were, in GF reinforced PBT/PET blend matrix, has higher density values than both unreinforced PBT matrix and GF reinforced PBT matrix. According to MFI measurements, Sample 1 which only contain 20% DEPAL has lower viscosity value than other samples which contain only 20% Actilox B60 or Actilox B30. As it is expected, the samples have two times higher viscosity value in GF reinforced PBT matrix. Ascending sort of MFI value of different matrix is GF reinforced PBT, GF reinforced PBT/PET blend and unreinforced PBT matrix. However, there is no important change between samples containing Actilox B60 or Actilox B30. In first stage Sample 10 and 16, in second stage Sample 23 and 27 showed the best results.

The flame retardant addition to the polymers, is really important to the effects on the mechanical properties of blends. In evaluation of mechanical properties; stress at break, tensile modulus, strain at break values and also Izod impact values in two different temperature were measured. Stress at break had decreased 60% with the addition of 20% DEPAL to neat PBT. When 20% Actilox B60 or Actilox B30 flame retardant added to neat PBT, stress at break value remained the same. The stress at break value had increased almost 100% with the addition of 20% glass fiber. The highest stress at break value was obtained from Sample 16 and 28.

Tensile modulus had increased 31% with the addition of 20% DEPAL to neat PBT. The addition of 20% Actilox B60 to neat PBT, tensile modulus had increased almost 50%, on the other hand, tensile modulus almost remained the same with the addition of 20% Actilox B30. As it is expected, GF reinforced PBT samples had a pronounced effect on tensile modulus. Also, samples which GF reinforced PBT/PET blend matrix has slightly higher tensile modulus value than GF reinforced PBT. Sample 15 and 28 have the highest tensile modulus value.

Strain at break values is obviously decreased in case of the addition of flame retardants. Especially the lowest strain at break values are obtained the addition of flame retardants into GF reinforced PBT/PET blend. Actilox B30 flame retardant containing samples have lower strain at break values in comparison of Actilox B60 flame retardant containing samples.

The addition of 20% DEPAL flame retardant additive to neat PBT, the Izod impact value at 23 °C had decreased 150%. While the addition of 20% Actilox B60 or Actilox B30 flame retardant to neat PBT, Izod impact value had decreased 60% and 78% respectively. Izod impact value had slightly increased with the glass fiber reinforcement. The highest Izod impact test results were observed from Sample 12, 16 and 25 at 23 °C.

Izod impact value had decreased 74%, 15% and 20%, when the addition of respectively only 20% DEPAL or only 20% Actilox B60 or only Actilox B30 to neat PBT at -30 °C. In case of 20% GF reinforcement of neat PBT, Izod impact value had increased 31% as it is expected. The highest Izod impact values was obtained from Sample 7, 12 and 24 at -30 °C.

According to mechanical properties, the best samples are Sample 16 and Sample 28. However, if we examined the flame retardant properties of these samples which are Sample 6 and Sample 28 have failed UL 94 flammability test and glow wire flammability index (GWFI).

It was revealed from heat distortion temperature analysis that the addition of only 20% DEPAL or only 20% Actilox B60 had increased the results almost 40%, 10% respectively, while the addition of only 20% Actilox B30 had decreased the result almost 10%. The best results were obtained from Sample 7, 10 and 25 which are in the GF reinforced PBT.

In DSC analysis, the lowest percent crystallinity values are obtained from Sample 12, 16, 25 and 28. In thermal gravimetric analysis, the starting of thermal degradation temperature of neat PBT had decreased by addition of all flame retardant additives. The highest values were evaluated from Sample 11, 24 and 28.

According to thermal properties, the best sample is Sample 28. However, if we examined the flame retardant properties of Sample 28 have failed UL 94 flammability test and glow wire flammability index (GWFI).

The UL 94 test results were showed that non-halogenated phosphorus based flame retardant additive had significant effect on flame properties. All samples, which contain only 20% Actilox B60 or Actilox B30 and no DEPAL, have no UL 94 rate. Even, the addition of small amount of DEPAL flame retardant, UL 94 classification is improved.

The glow wire ignition temperature test results showed that there is no change the addition of Actilox B60 or Actilox B30. GF reinforced samples, which are Sample 6, 7, 8 and 9, reached 800 °C test temperature.

It was evaluated from glow wire flammability index measurement that all samples which contain only 20% Actilox B60 or Actilox B30 and no DEPAL, had failed from the test.

According to fire properties of samples, the best results are obtained from especially Sample 2, 3 and 4 in unreinforced PBT matrix. In comparison of mechanical properties of these samples, were lower than the other samples.

In consequence of these experiments; Sample 27, which contains 5% DEPAL/15% Actilox B30 in 20% GF reinforced PET/PBT blend matrix, is given the best mechanical, thermal and fire retardant performance results.

REFERENCES

[1]**Lu, S. Y., & Hamerton, I.** (2002). Recent developments in the chemistry of halogen-free flame retardant polymers. *Progress in polymer science*, *27*(8), 1661-1712.

[2]**Hull, T. R., Witkowski, A., & Hollingbery, L.** (2011). Fire retardant action of mineral fillers. *Polymer Degradation and Stability*, *96*(8), 1462-1469.

[3]**Bourbigot, S., & Duquesne, S.** (2007). Fire retardant polymers: recent developments and opportunities. *Journal of Materials Chemistry*, *17*(22), 2283-2300.

[4]**Brehme, S., Schartel, B., Goebbels, J., Fischer, O., Pospiech, D., Bykov, Y., & Döring, M.** (2011). Phosphorus polyester versus aluminium phosphinate in poly (butylene terephthalate) (PBT): flame retardancy performance and mechanisms. *Polymer degradation and stability*, *96*(5), 875-884.

[5]**Chiang, W. Y., & Hu, C. H.** (2001). Approaches of interfacial modification for flame retardant polymeric materials. *Composites Part A: Applied Science and Manufacturing*, *32*(3-4), 517-524.

[6]**Laoutid, F., Bonnaud, L., Alexandre, M., Lopez-Cuesta, J. M., & Dubois, P.** (2009). New prospects in flame retardant polymer materials: from fundamentals to nanocomposites. *Materials Science and Engineering: R: Reports*, *63*(3), 100-125.

[7]**Weil, E. D.** Flame Retardancy. Vol.10. *Polymer Research Institute, Polytechnic University.*

[8]**Sullalti, S., Colonna, M., Berti, C., Fiorini, M., & Karanam, S.** (2012). Effect of phosphorus based flame retardants on UL94 and comparative tracking index properties of poly (butylene terephthalate). *Polymer degradation and stability*, *97*(4), 566-572.

[9]**Chen, L., Luo, Y., Hu, Z., Lin, G. P., Zhao, B., & Wang, Y. Z**. (2012). An efficient halogen-free flame retardant for glass-fibre-reinforced poly (butylene terephthalate). *Polymer degradation and stability*, *97*(2), 158-165.

[10]**Hamdani, S., Longuet, C., Lopez-Cuesta, J. M., & Ganachaud, F.** (2010). Calcium and aluminium-based fillers as flame-retardant additives in silicone matrices. I. Blend preparation and thermal properties. *Polymer Degradation and Stability*, *95*(9), 1911-1919.

[11]**Töpfer, O. DR.** (2011). Mineral Based Flame Retardants in Engineering Plastics. *Nabaltech AG.*

[12]**Levchik, S. V., & Weil, E. D. (2005).** Flame retardancy of thermoplastic polyesters-a review of the recent literature. Polymer International, 54(1), 11-35.

[13]**Visakh, P. M., & Liang, M.** (Eds.). (2015). Poly (ethylene terephthalate) based blends, composites and nanocomposites. William Andrew.

[14] **Park, E. S.** (2008). Morphology, mechanical, and dielectric breakdown properties of PBT/PET/TPE, PBT/PET/PA66, PBT/PET/LMPE, and PBT/PET/TiO2 blends. *Polymer Composites*, *29*(10), 1111-1118.

[15] **Scheirs, J., & Long, T. E. (Eds.).** (2005). *Modern polyesters: chemistry and technology of polyesters and copolyesters*. John Wiley & Sons

[16] **Jadhav, J. Y., & Kanter, S. W.** (1988). Polyesters, thermoplastic. *Wiley-Interscience, Encyclopedia of Polymer Science and Engineering. Second Edition.*, *12*, 217-256

[17] **Thomas, S., & Visakh, P. M. (Eds.).** (2011). *Handbook of Engineering and Specialty Thermoplastics, Volume 3: Polyethers and Polyesters* (Vol. 63). John Wiley & Sons.

[18] **Deopura, B. L., Alagirusamy, R., Joshi, M., & Gupta, B. (Eds.).** (2008). *Polyesters and polyamides*. Elsevier.

[19] **Zhang, J., Ji, Q., Zhang, P., Xia, Y., & Kong, Q.** (2010). Thermal stability and flame-retardancy mechanism of poly (ethylene terephthalate)/boehmite nanocomposites. *Polymer Degradation and Stability*, *95*(7), 1211-1218.

[20] **Al-Sabagh, A. M., Yehia, F. Z., Eshaq,G., Rabie, A. M., & ElMetwally, A. E.** (2016). Greener routes for recycling of polyethylene terephthalate. *Egyptian Journal of Petroleum*, *25*(1), 53-64.

[21] **Sinha, V., Patel, M. R., & Patel, J. V.** (2010). PET waste management by chemical recycling: a review. *Journal of Polymers and the Environment*, *18*(1), 8-25.

[22] **Mallick, P. K.** (2007). *Fiber-reinforced composites: materials, manufacturing, and design*. *Third Edition.* CRC press.

[23] **Wallenberger, F. T., Watson, J. C., & Li, H.** (2001). Glass fibers. *Materials Park, OH: ASM International*, *2001*., 27-34.

[24] **Polk, M.** High Performance Fibers. *Wiley-Interscience, Encyclopedia of Polymer Science and Engineering.*

[25] **Lewin, M.** (2006). *Handbook of fiber chemistry*. Crc press.

[26] **Lyon, R. E.** (2005). Flammability. *Wiley-Interscience, Encyclopedia of Polymer Science and Engineering*.

[27] **Macskásy, H., & Palyi, G.** (2012). *Plastics: their behaviour in fires*(Vol. 6). Elsevier.

[28] **Papaspyrides, C. D., & Kiliaris, P. (Eds.).** (2014). *Polymer green flame retardants*. Newnes.

[29] **Horrocks, A. R., & Price, D. (Eds.).** (2008). *Advances in fire retardant materials*. Elsevier.

[30] **Troitzsch, J.** (1983). *International plastics flammability handbook: principles-regulations-testing and approval*. Hanser.

[31] **Visakh, P. M., & Yoshihiko, A.** (2015). *Flame retardants: Polymer blends, composites and nanocomposites*. Springer.

[32] **Innes, J.** (2004). *Plastic flame retardants: technology and current developments current* (Vol. 14). iSmithers Rapra Publishing.

[33] **Weil, E. D., & Levchik, S. V.** (2015). *Flame retardants for plastics and textiles: practical applications.Second Edition.* Carl Hanser Verlag GmbH Co KG.

[34] **Hewitt, F., & Hull, T. R.** (2017). Mineral Filler Fire Retardants. *Fillers for Polymer Applications*, 329-354.

[35] **Dasari, A., Yu, Z. Z., Cai, G. P., & Mai, Y. W.** (2013). Recent developments in the fire retardancy of polymeric materials. *Progress in Polymer Science*, *38*(9), 1357-1387.

[36] **Dufton, P. W.** (2003). *Flame retardants for plastics*. Smart Publications.

[37] **Braun, U., Schartel, B., Fichera, M. A., & Jäger, C**. (2007). Flame retardancy mechanisms of aluminium phosphinate in combination with melamine polyphosphate and zinc borate in glass-fibre reinforced polyamide 6, 6. *Polymer Degradation and Stability*, *92*(8), 1528-1545.

[38] **Braun, U., Bahr, H., & Schartel, B.** (2010). Fire retardancy effect of aluminium phosphinate and melamine polyphosphate in glass fibre reinforced polyamide 6. *e-Polymers*, *10*(1).

[39] **Savaşçı, Ö. T., Uyanık, N., & Akovalı, G.** (2002). *Ana Hatlarıyla Plastikler ve Plastik Teknolojisi*. PAGYAY Yayıncılık.

[40] **Laachachi, A., Ferriol, M., Cochez, M., Cuesta, J. M. L., & Ruch, D.** (2009). A comparison of the role of boehmite (AlO(OH)) and alumina (Al2O3) in the thermal stability and flammability of poly (methyl methacrylate). *Polymer Degradation and Stability*, *94*(9), 1373-1378.

[41] **Friederich, B., Laachachi, A., Sonnier, R., Ferriol, M., Cochez, M., Toniazzo, V., & Ruch, D.** (2012). Comparison of alumina and boehmite in (APP/MPP/metal oxide) ternary systems on the thermal and fire behavior of PMMA. *Polymers for Advanced Technologies*, *23*(10), 1369-1380.

[42] **Köppl, T., Brehme, S., Wolff-Fabris, F., Altstädt, V., Schartel, B., & Döring, M.** (2012). Structure− property relationships of halogen-free flame-retarded poly (butylene terephthalate) and glass fiber reinforced PBT. *Journal of Applied Polymer Science*, *124*(1), 9-18.

[43] **Gallo, E., Braun, U., Schartel, B., Russo, P., & Acierno, D.** (2009). Halogen-free flame retarded poly (butylene terephthalate)(PBT) using metal oxides/PBT nanocomposites in combination with aluminium phosphinate. *Polymer Degradation and Stability*, *94*(8), 1245-1253.

[44] **Braun, U., Bahr, H., Sturm, H., & Schartel, B.** (2008). Flame retardancy mechanisms of metal phosphinates and metal phosphinates in combination with melamine cyanurate in glass-fiber reinforced poly (1, 4-butylene terephthalate): the influence of metal cation. *Polymers for advanced technologies*, *19*(6), 680-692.

[45] **Guido, E., Alongi, J., Colleoni, C., Di Blasio, A., Carosio, F., Verelst, M., ... & Rosace, G.** (2013). Thermal stability and flame retardancy of polyester fabrics sol–gel treated in the presence of boehmite nanoparticles. *Polymer degradation and stability*, *98*(9), 1609-1616.

[46] **ISO 1183** (1999). Methods for Determining Density of Non-Cellular Plastics, *International Standard Organization.*

[47] **ISO 1133** (2005). Determination of the melt mass-flow rate (MFR) and the melt volume-flow rate (MVR) of thermoplastics. *International Standard Organization.*

[48] **ISO 527-1** (2012). Determination of tensile properties- Part1: General Principles. *International Standard Organization.*

[49] **ISO 180** (2000). Plastics, Determination of Izod Impact Strength of Rigid Materials, *International Standard Organization.*

[50] **ISO 3167 Type B** (2002). Plastics, Multipurpose test specimens. Fourth Edition. *International Standard Organization*

[51] **ISO 75-1** (2004). Plastics, Determination of temperature of deflection under load-Part1: General test method. *International Standard Organization*

[52] **ISO 75-2** (2013). Plastics, Determination of temperature of deflection under load-Part1: Plastics and ebonite. *International Standard Organization*

[53] **ISO 3146** (2000). Plastics, Determination of melting behaviour (melting temperature or melting range) of semi-crystalline polymers by capillary tube and polarizing-microscope methods. *International Standard Organization.*

[54] **Sichina, W. J.** (2000). DSC as problem solving tool: measurement of percent crystallinity of thermoplastics. *Perkin Elmer Instruments, and PETech*, *40*.

[55] **ISO 11358** (2014). Plastics, Thermogravimetry (TG) of polymers – Part1: General Principles. *International Standard Organization.*

[56] **UL94** (2013). Standard for Safety, Test for Flammability of Plastic Materials for Parts in Devices and Appliances. Sixth Edition.

[57] **IEC 60695-2-13** (2010). Fire hazard testing – Part2-13: Glowing/hot-wire based test methods – Glow-wire ignition temperature (GWIT) test method for materials.

[58] **IEC 60695-2-12** (2010). Fire hazard testing – Part2-12: Glowing/hot-wire based test methods – Glow-wire flammability index (GWFI) test method for materials.

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