

Producing Interpenetrating Networks from Waste Tires Rubber with Commercial Unsaturated Polyester

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Abstract:

Waste tires constitute environmental problems because of their three-dimensional complicated structure. The presence of different additives within their composition makes them difficult to degrade. In this research, the waste tire rubber is used as raw material after inserting effective groups, like carboxylic group within the rubber to be used directly without the need to separate additives or recover the rubber individually. Ground tire rubber (GTR) was modified by functionalizing with different ratios of maleic anhydride. Network polyester was prepared from modified GDR and diethylene glycol. Interpenetrating networks IPNs were prepared from polyester of GTR with trade unsaturated polyester. The characterization of the IPNs was studied via infrared spectroscopy, thermal analysis, X-ray diffraction analysis and AFM pictures. The results indicate that there is a complete interaction between the two types of the networks and the IPNs are of one phase. Also increasing the MAn ratio in the GTR gives more homogeneity to the produced IPNs, whereby the number of crosslinking increases.

Keywords: waste tire rubber; maleic anhydride; unsaturated polyester; interpenetrating network.

انتاج شبكات متداخلة من نفايات مطاط الاطارات مع البولي استر غير المشبع التجاري

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قسم الكيمياء، كلية العلوم، جامعة الموصل، الموصل، العراق

الخلاصة:

بسبب البنية المعقدة ثلاثية الابعاد ووجود عدد كبير من المواد المضافة داخل تركيبة الاطارات سيؤدي إلى صعوبة تحللها طبيعياً وبذلك يزداد تراكم الاطارات المستهلكة بصورة متزايدة يوماً بعد اخر مما ستشكل مشكلة بيئية خطيرة. في بحثنا هذا سوف تستعمل الاطارات المستهلكة كمادة أولية بعد إدخال مجاميع كاربوكسيلية فعالة إلى المطاط المكون لها وتحويله إلى مطاط كاربوكسيلي مباشرة من دون اللجوء إلى فصل المواد المضافة أو إسترداد المطاط لوحده. تم تطوير مطاط مسحوق الاطارات عن طريق ادخال مجموعة وظيفية (انهريد المالنك) وبتراكيز مختلفة الى تركيبة المطاط. حضوت شبكة بولي استر من المسحوق المطور بتفاعله مع ثنائي اثيلين الكلايكول. تم تحضير الشبكات المتداخلة IPNs من هذا البولي استر مع البولي استر غير المشبع التجاري. درست صفات الشبكات بواسطة طيف الاشعة تحت الحمراء والتحليل الحراري وحيود الاشعة السينية وتصوير مجهر القوة الذرية. اظهرت النتائج ان هناك تداخل تام بين شبكات البولي استر وان ال IPNs كانت بطور واحد. كما اثبتت الدراسة بان مع زيادة نسبة انهريد المالنك في مسحوق امطاط يزداد. تجانس الشبكة حيث تزداد عدد التشابكات.

1. Introduction

It is well known that the tires are a complexity of rubber composite and they are non-biodegradable materials [1,2]. The three dimensional structure of the tires make a big challenge of recycling for the researchers and the industrialists [3,4]. The waste tires are growing and growing dramatically and formed environmental problem [5]. Many methods are employed for recycling the waste tires to be reused in another useful field or to recover the rubber [6]. The recovered waste tires can be considered as a source of valuable raw materials which can be used for producing new goods with utilitarian significance [7]. The waste tires must be shredded and granulated before any recycling process, as for using by incorporation into other polymeric products [8]. This process is regards as downsizing cycling [9]. The incorporation of the ground tire rubber (GTR) into commercial polymers for producing new useful products is another way to overcome the problem of environmental pollution with the waste tire [10]. It was noticed that when the GTR was used in a polymeric materials, the formed matrices are deteriorate, whereby the vulcanized structure of GTR renders the polymeric blends and fail to enhance the properties [11]. The compatibilization of GTR with HDPE by using peroxide as a catalyst was studied [12]. It was proved that the formed system is interpenetrating network [13]. Another system of GTR with poly (ethylene-co- vinyl acetate) (EVA) was prepared [14]. The new matrices have poor mechanical properties. To explain the fail in the properties of the matrices, many factors are suggested. The main factors of failing are belong to the failing of adhesion between the GTR and EVA [15]. In order to overcome the failing, a reclaimed rubber was used instead of GTR.

Another method was followed for using GTR in blending is by retreatment of GTR before applying [16]. The treatment is functionalized the GTR with some active moieties (maleic anhydride and maleimic acid) [17]. The functionalized GTR was blended with waste of paper and with poly (ethylene terephthalate) [18]. The produced matrices are homogenous and have good mechanical properties. It was shown that active functional moieties give good adhesion properties between the GTR and the incorporated polymers. Within the frame of this work, the GTR was functionalized with different percent of maleic anhydride. Polyester was formed from the functionalized GTR with diethylene glycol. Interpenetrating network was prepared between the new polyester with commercial polyester.

2. Experimental

Materials:

Table (1) shows the chemicals which were used as received

Table (1): The chemicals

sources	material
Labtech	Maleic anhydride MAn
Fluka	Di-ethylene glycol (DIGOL)
BDH	Sodium hydroxide
Eskim	ES-1060 polyester .batch No:036
Fluka	Ethanol Absolute
Fluka	Benzoyl peroxide
AKPA	KXC ₆ – Cobalt bis (2-thylhexanoate), toluene, potassium 2-ethylhexanoate (catalyst)
AKPA	(A1 Base) Butane2, 2 diyldihydroperoxid and dioxydibutane-2, 2-diyldihydroperoxide Hardener)
Diwaniyah tire factory	Ground tire rubber (GTR)

Equipment:

F.T.IR spectra were accomplished by using (BRUKER F.T.IR Infrared. The spectra are obtained using KBr pellets. Thermal analyses were measured by **Metler**, the heating speed of measuring TGA and DTA of the prepared samples was 20°C \ min. X- ray diffraction was carried out by using XRD-6000 Shimadzu. AFM was done by using TESCAN Vega 3 (Tehran University).

Methodology:

Treatment of ground tire rubber (GTR) with maleic anhydride:

Freshly maleic anhydride MAn was recrystallized from dried chloroform. Mixtures of 10gm of powder GTR with different amount of MAn (1-4gm) and the initiator benzoyl peroxide (BPO) (0.1%) was mixed thoroughly in closed stainless steel mixer at 120°C for 3hrs. The product was refluxed with water for a period of 0.5 hr., filtered and dried under vacuum. The filtrate was titrated with standard solution of sodium hydroxide to calculate the amount of unreacted MAn.

Table (2) shows the experimental amount of treatment

Table (2): GTR modification with Man

No.	Rubber/g	MAn/g added	Benzoyl peroxide/g	Temp./C°	Time/hr.	MAn/g reacted
1	10	1	0.2	120	3	0.9
2	10	2	0.2	120	3	1.8
3	10	3	0.2	120	3	2.7
4	10	4	0.2	120	3	3.4

Preparation of polyester from modified GTR and diethylene glycol:

1g of diethylene glycol was mixed with 1g of the modified GTR (samples 1-4 in table 2). The mixture was heated at (130°C) for a period of 2hrs. A dark brown viscous mixture was formed. Absolute ethanol was used to precipitate the polymer.

Preparation of IPNs from polyester of GTR with tread polyester:

In a beaker 40g of functionalized GTR was mixed with 4g of diethylene glycol for 15min. at room temperature, calculated amount of the tread polyester (5%.10% and 15% according to ratio of the MAn presented in GTR) was added. The reaction was completed in the closed stainless steel mixer at 130°C for a period of 1hr. Two samples of modified GTR [1and 4] was used in this preparation, the amount of the reactants are shown in tables 4 and 5.

Table (4): Reactants in preparation of IPN from GTR [1]

Tread Polyester %	Diethylene glycol/g	Modified rubber\g	No.
5 %	4.24	40	R1a
10 %	4.24	40	R1b
15 %	4.24	40	R1c

Table (5): Reactants in preparation of IPN from GTR [4]

Trade Poly ester %	Diethylene glycol /g	Modified rubber\ g	No.
5 %	14.4	40	R4a
10 %	14.4	40	R4b
15 %	14.4	40	R4c

X-ray diffraction analysis:

The X-ray diffraction was carried out for measuring the angle (2θ) at range (10° - 90°) and scan speed 3° / min using filter of type (Cu- K beta). The used current is of $30 \mu\text{A}$ and the voltage is 40Kv. The wave length can be calculated by using Bragg law:

$$\lambda = 2 \cdot d \cdot \sin \theta$$

where; n = number of waves , λ = wavelength , d = the distance between the surfaces of the crystal lattice, θ = the value of the half-angle at the top of the wave, and the volume of the crystal (V) was calculated according to the equation:

$$V = 0.9 \lambda / B \cdot \cos \theta$$

Where is the width of mid-top?

3. Results and discussions:

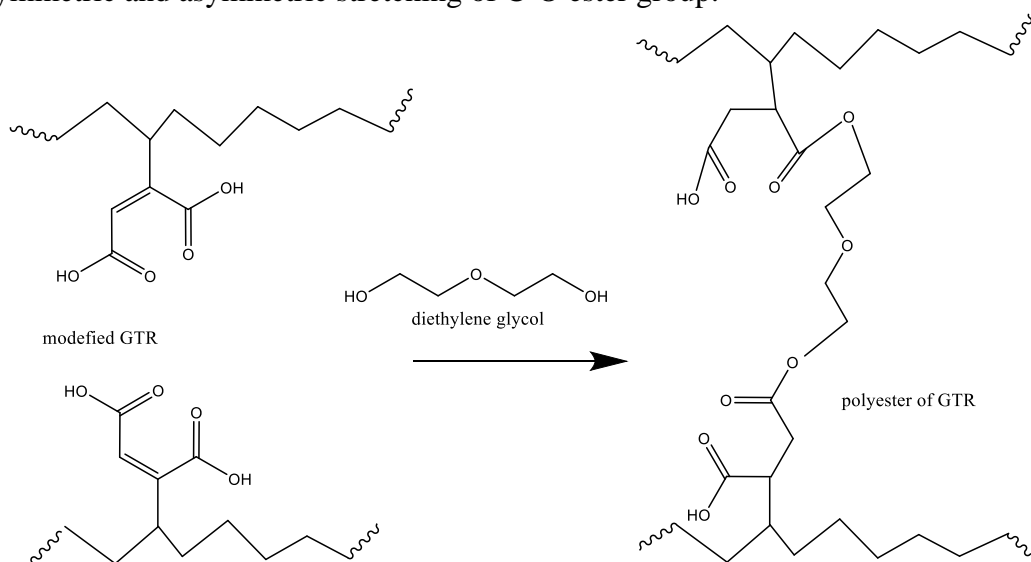
Modification of GTR with MAN:

As styrene butadiene rubber make up ratio of about 60-65% in the waste rubber of tiers [19], it can be react with MAN via free radical reaction in the presence of the benzoyl peroxide as initiator. The product of this reaction can be considered as a carboxylated rubber. Four ratios of MAN were used in the reaction processes (1- 10%). The analysis of titration show that about 95% of all the added MAN have been react with the rubber in all the samples of the experiments (table 2).

The functionalized GTR was characterized by infrared spectrum. In comparison with the spectrum of GTR (figure 1), the spectrum (figure 2) shows peaks at 1707 cm^{-1} and at 1645 cm^{-1} which are related to the carbonyl group of the anhydride moiety, whereby the peaks at 1165 cm^{-1} and at 1066 cm^{-1} are belong to the stretching vibration of C-O group. In contrast, the absorbance of C=C of the rubber of GTR (figure 1) which appeared at 1741 cm^{-1} was disappeared in the modified GTR (17).

Reaction the modified GTR with di-ethylene glycol:

The presences of carboxylic acid moieties within the frame of GTR come on place for the reaction with diols (diethylene glycol) to form polyester. FTIR spectrum of the esterified GTR was shown in figure (3). The spectrum revealed the absorbance peaks at (1369 cm^{-1}) and at (1435 cm^{-1}) which are related to symmetric and asymmetric stretching of C-O ester group.



Preparation of IPN of unsaturated polyester with modified GTR:

The trade unsaturated polyester is cured by styrene monomer to form solid network polymer. IR spectrum of the cured trade unsaturated polyester was shown in figure (4). The spectrum indicates the absorbance of stretching vibration of aromatic C-H at 3066 cm^{-1} , while the stretching vibration of aliphatic C-H group appears at 2956 cm^{-1} . On the other hand the vibration of C-O ester was appeared at 1126 cm^{-1} and at 1043 cm^{-1} . The mixing of this polyester with the polyester of modified GDR will produced an interpenetrating network (IPN) of the two types of the networks polyester, as will

proved latter with X-ray diffraction analysis. Figure (5) is the FTIR spectrum of the prepared IPN. The spectrum shows the absorbance of the featured moieties of both networks with little shifts from the original one. The absorbance appeared at 1112 cm^{-1} and at 1074 cm^{-1} are belong to the stretching vibration of C-O of esters of the GDR and trade polyester respectively.

Thermal analysis:

The TGA analysis of the GTR and its derivatives with MAn and their IPNs are accomplished at a heating rate of $20^\circ\text{C}/\text{min}$. The crude GTR shows thermal stability until 110°C , where it started loss 1% of its weight. The pyrolysis of weight loss of about 10%, at $250\text{-}300^\circ\text{C}$ (figure 6). The DTA curve (figure7) shows that the rate of pyrolysis increased at 300°C to reach $0.0125/\text{min}$. This results confirm with previous studies that show the pyrolysis of the synthetic rubber ranged between $300\text{-}500^\circ\text{C}$ (20). Figures 8 and 9 show the TGA and DTA of the GTR functionalized with 10% MAn. The thermal behaviors show some differences from the crude GTR. The sample started endothermic reaction and loss about 2% of its weight at $100\text{-}150^\circ\text{C}$ in rate of $0.008/\text{min}$. This belongs to the liberation of water molecules as a result of cyclization of the maleic acid. At $150\text{-}220^\circ\text{C}$ the sample lose 9% of its weight with rate of about $0.0150/\text{min}$ exothermically. Whereby the maleic anhydride molecules started disintegrate. At $220\text{-}300^\circ\text{C}$ the sample started decomposed completely.

In the other hand, the polyester of GTR with diethylene glycol gives other thermal characteristics. TGA and DTA (figures 10&11) indicate that the sample loss about 44% of its weight between $150\text{-}225^\circ\text{C}$, whereby the ester linkage start dissociates.

In contrast, the IPN between the networks of cured trade polyester and ester of GTR have thermal stability in comparison with every network alone. TGA and DTA (figures 12&13) reveal that the IPN loss only 15% of its weight between $150\text{-}300^\circ\text{C}$. These results emphasize the complete interaction between the two types of networks.

X-ray diffraction analysis:

It is well known that the rubber is an amorphous material; its degree of crystallinity was increase when the temperature decreases below 0°C . The rubber give a wide band and low diffraction intensity in X ray [21]. In comparison between sample R1a and R4a, where the ratio of MAn are 0.9 and 3.4% respectively (figures 14&15), it was noticed that sample R4a have two crystalline region while sample R1a is completely amorphous. The results can be explained by that when MAn moiety increased, more network formed and giving more chance to form crystalline regions. The values of parameters estimated from figure 15 for IPN R4a are shown in table 5.

Table (5): X-ray diffraction parameters estimated for sample R4a

ν	λ	B at (deg)	Height	d at(Å)	Peaks at 2θ
0.4480	1.5415	3.1488	67.37	4.18208	21.2457
8.9367	1.5403	0.1800	402.33	1.51904	60.9413

Atomic force microscopy analysis:

Figure (16 and 17) shows the AFM pictures of IPNs of R1a and R4a respectively. The pictures indicate the homogeneity of the sample with the appearance of black regions in the cavities which is related to the carbon black.

The statistical analyses of the two IPNs are shown in figures (18 &19). The results indicate that dimensions of the particles are between (73 – 150 nm) and (90-230nm), whereby the effect of the MAn content is clearly observed. As increasing MAn ratio in GDR, more networks is formed and the homogeneity increase.

4. Conclusions:

- 1-The GTR was developed to be used as a reactive chemical.
- 2-The modified GTR can be reacted with ethylene glycol to form network polyester.
- 3-The network polyester has thermal stability more the modified GTR.
- 4-The polyester of modified GTR can form IPN smoothly with network of trade polyester.
- 5-The prepared IPNs have structural and thermal stability and have one phase.

5. Acknowledgements: The authors wish to thank the collage of material engineering/Babylon university for help in measuring the electrical, thermal properties and IR spectroscopy. Special thanks to Prof. Mohammed H. Al Maamori for his technical information.

6. References:

- [1] M. Arabiourrutia, G. Lopez, M. Artetxe, J. Alvarez, J. Bilbao, M. Olazar, Waste tire valorization by catalytic pyrolysis—A review, *Renewable and Sustainable Energy Reviews* 129, 109932(2020).
- [2] A. Mohajerani, L. Burnett, J.V. Smith, S. Markovski, G. Rodwell, M.T. Rahman, H. Kurmus, M. Mirzababaei, A. Arulrajah, S. Horpibulsuk, Recycling waste rubber tyres in construction materials and associated environmental considerations: A review, *Resources, Conservation and Recycling* 155,104679 (2020).
- [3] B. S Thomas, and R. C Gupta, A comprehensive review on the applications of waste tire rubber in cement concrete. *Renewable and Sustainable Energy Reviews*, 54, 1323-1333 (2016).
- [4] G. Etefa, and A. Mosisa, Waste Rubber Tires: A Partial Replacement for Coarse Aggregate in Concrete Floor Tile Production. *American Journal of Civil Engineering*, 8(3), 57-63 (2020).
- [5] Y, Nakao and K. Yamamoto, Waste tire recycle and its collection system, *JIS*, 500, 4202 (2002).
- [6] P. Song, X. Wu, and S. Wang,. Effect of styrene butadiene rubber on the light pyrolysis of the natural rubber. *Polymer Degradation and Stability*, 147, 168-176 (2018).
- [7] A. Sultan and F. H. Jabrail. Treatment of scrap tire for rubber and carbon black recovery, *Recycling*,7, 27 (2022).
- [8] T. Amari, N. J. Themelis, and I. K. Wernick, Resource recovery from used rubber tires. *Resources Policy*, 25, 179-188 (1999)
- [9] J. Karger-Kocsis, L. Mesaros, and T. Barant, Ground tyre rubber (GTR) in thermoplastics, thermosets, and rubbers. *Journal of Materials Science*, 48, 1-38 (2013).
- [10] S. Ramarad, , M. Khalid, C. T RatanaA, L.A. Chuah, and W., RashmiI, Waste tire rubber in polymer blends: A review on the evolution, properties and future. *Progress in Material Science*, 72, 100 – 140 (2015).
- [11] S. Ramarda, C.T. Ratnam, M. Khalid, L.A.Chuah, Improving the properties of reclaimed waste tire rubber by blending with poly(ethylene-co vinyl acetate) and electron beam irradiation. *Journal of Applied Polymer Science* 132, doi: 10.1002/app.41649 (2015).
- [12] J. I. Kim, S.H. Ryu and Y.W. Chang, Mechanical and dynamic mechanical properties of waste rubber powder/HDPE composite. *Journal of Applied Polymer Science*, 77, 2595-2602 (2000).
- [13] M. Awang, H. Ismail. and M.A. Hazizn, Processing and properties of polypropylene-latex modified waste tyre dust blends (PP/WTDML). *Polymer Testing*, 27, 93-99(2008)
- [14] R. Suganti, Improving the properties of reclaimed waste tire rubber by blending with poly(ethylene-co-vinyl acetate) and electron beam irradiation. Ph.D. thesis, University of Nottingham (2016).
- [15] Y. Li, Y. Zhang, and Y. Zhang, Mechanical properties of high-density polyethylene/scrap rubber powder composites modified with ethylene propylene–diene terpolymer, dicumyl peroxide, and silicone oil. *Journal of Applied Polymer Science*, 88, 2020-2027 (2003).
- [16] H. I. Kim, S. H. Ryu, and Y.W. Cange, Mechanical and dynamic mechanical properties of waste rubber powder/HDPE composite. *Journal of Applied Polymer Science*, 77, 2595-2602 (2000).
- [17] S.K. Saeed and A.F. Khattab, Functionalizing of Waste Tire Rubber with Active Functional Groups, *Egyptian Journal of Chemistry*, vol. 64, no. 11, pp. 6399-6405 (2021).
- [18] A. F. Khattab and S.K. Saeed, Industrialization of thermal insulators from expended tires rubber with Scraps papers and poly (ethylene terephthalate), Iraqi patent, 406, (2022).
- [19] X. Tang, Z. Chen, J. Liu, Z. Chen, W. Xie, F. Evrendilek, M. Buyukada, Dynamic pyrolysis behaviors, products, and mechanisms of waste rubber and polyurethane bicycle tires, *Journal of Hazardous Materials* 402, 123516 (2021).

- [20] T. Menares, J. Herrera, R. Romero, and P. Osorio, Arteaga-Perez, L.E., Waste tires pyrolysis kinetics and reaction mechanisms explained by TGA and Py-GC/MS under kinetically-controlled regime. *Waste Manag.*, 102, 21–29 (2020).
- [21] D.S. Deshpande, A.K. Bajapi and K. Banhipai, Synthesis and characterization of acrylonitrile incorporated PVA based semi interpenetrating polymeric network, *Int. J.*, 3, (3), 74-82 (2011).

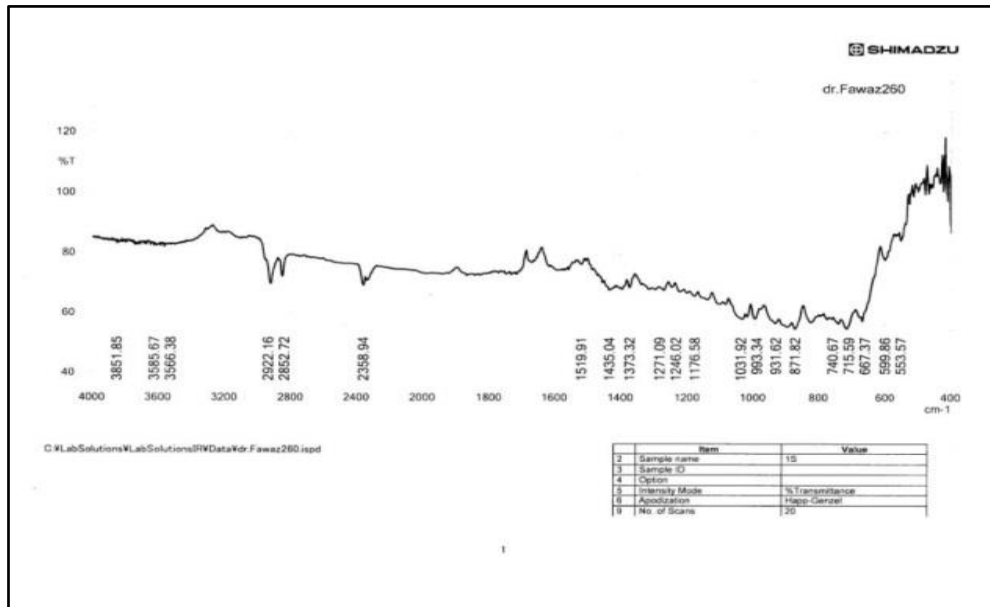


Figure 1: IR spectrum of wasted rubber

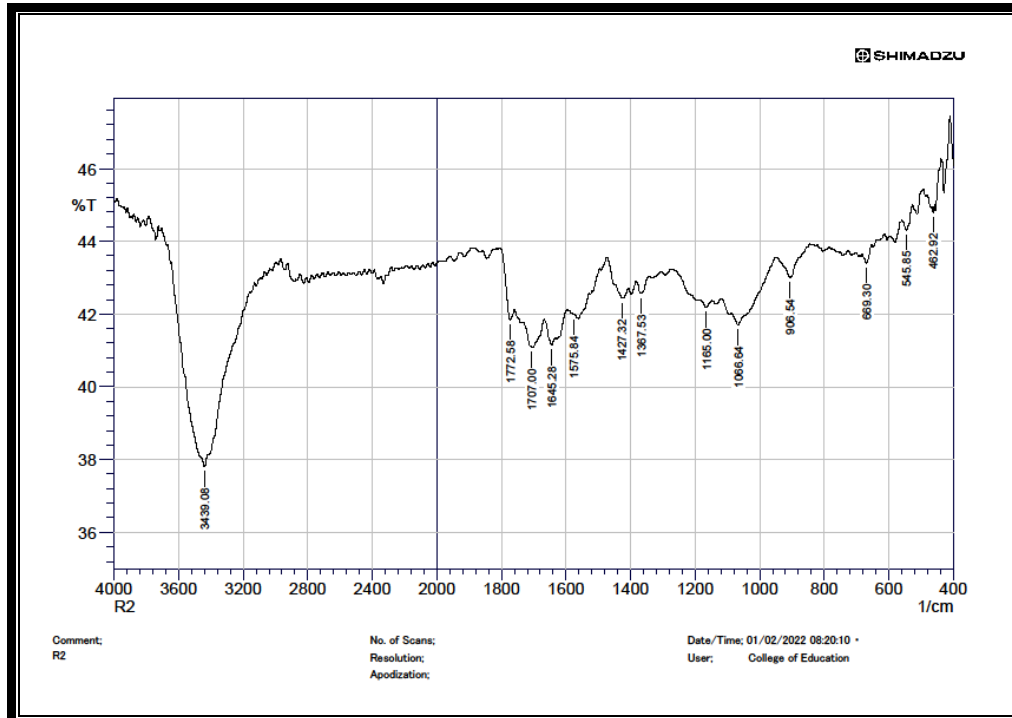


Figure 2: IR spectrum of modified GTR with MAN

Figure 2: IR

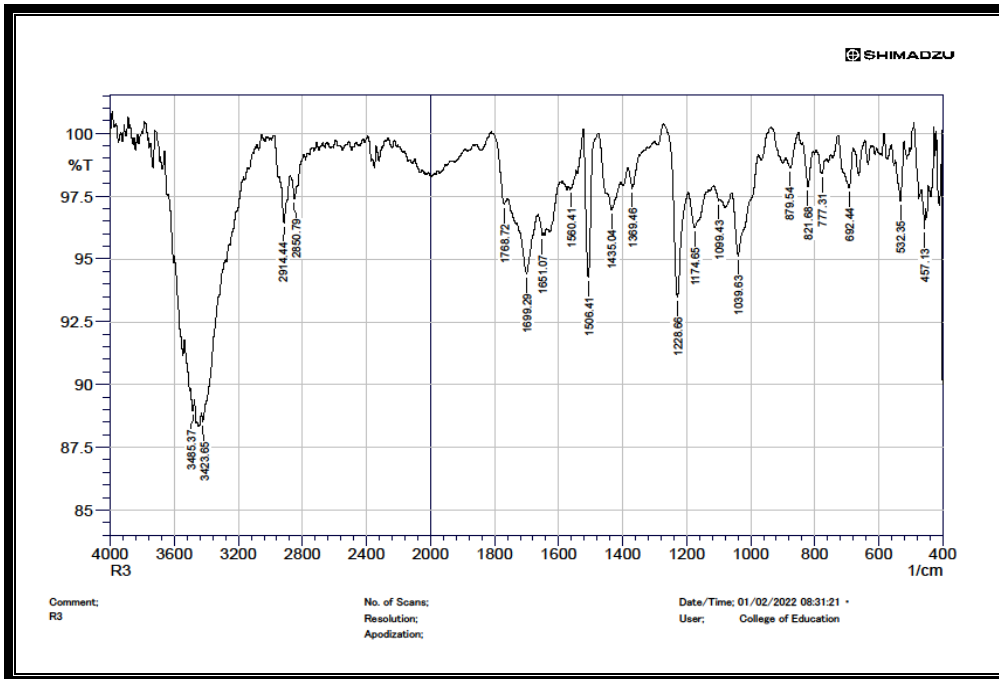


Figure 3: IR spectrum of esterified GTR with diethylene glycol.

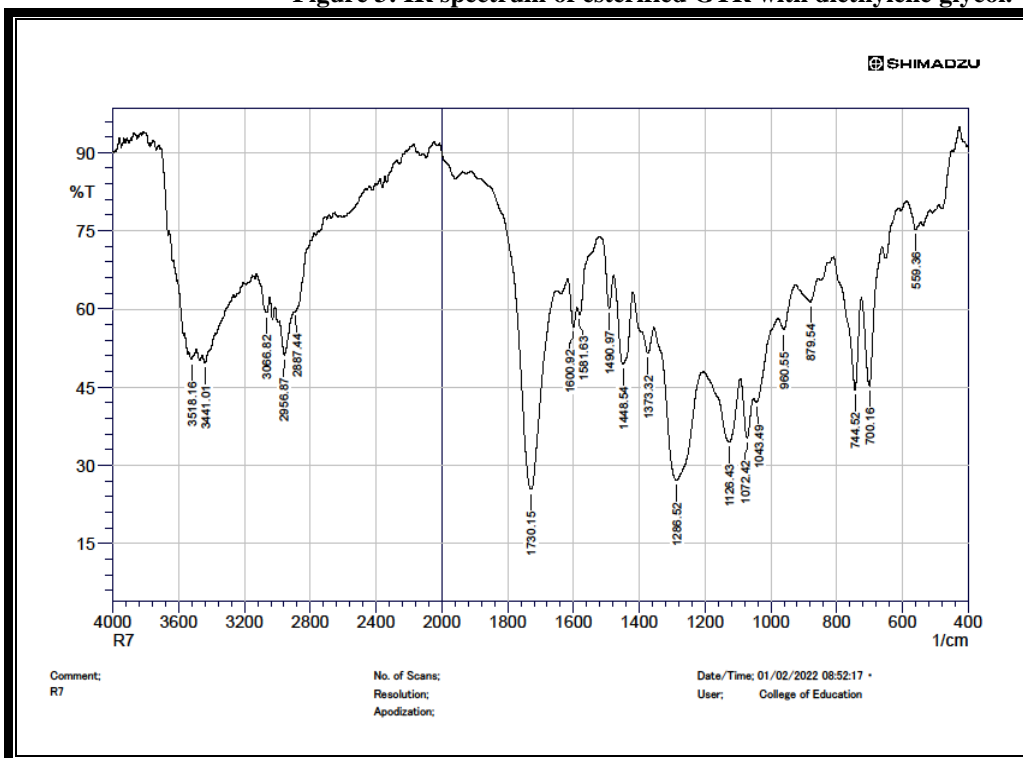


Figure 4: IR spectrum of the cured trade unsaturated polyester.

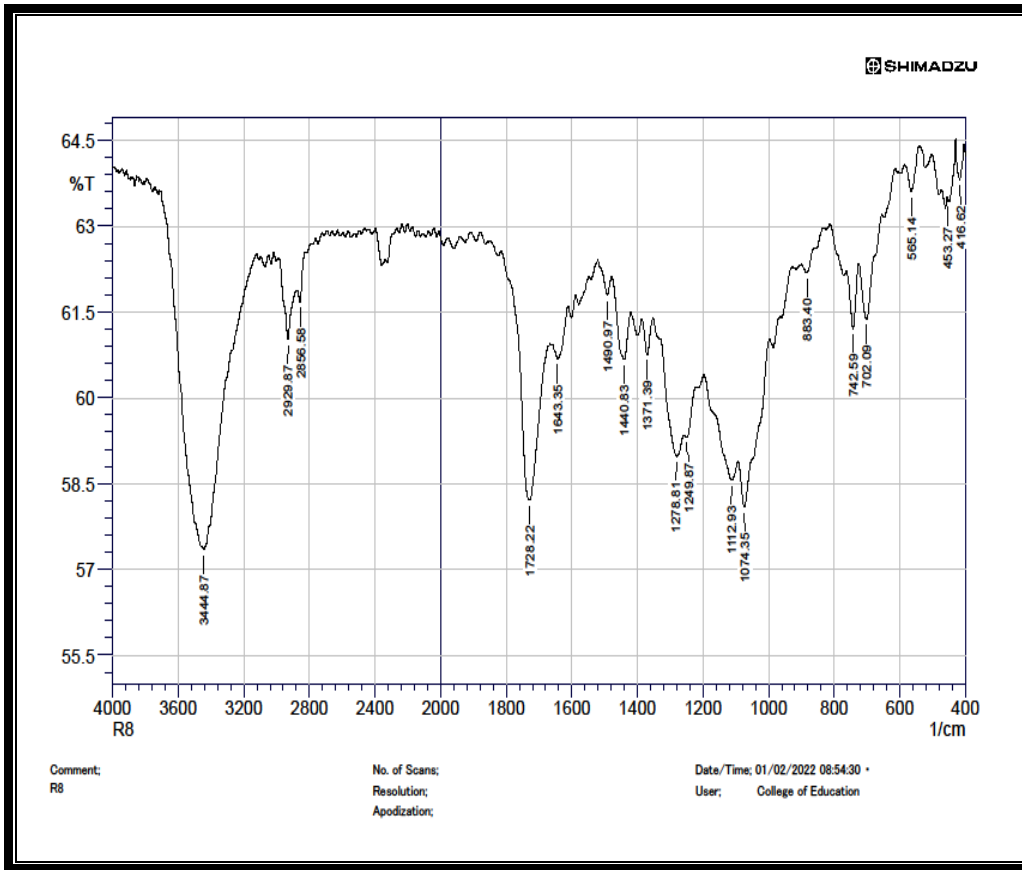


Figure 5: IR spectrum of the IPN of trade unsaturated polyester with polyester of GTR.

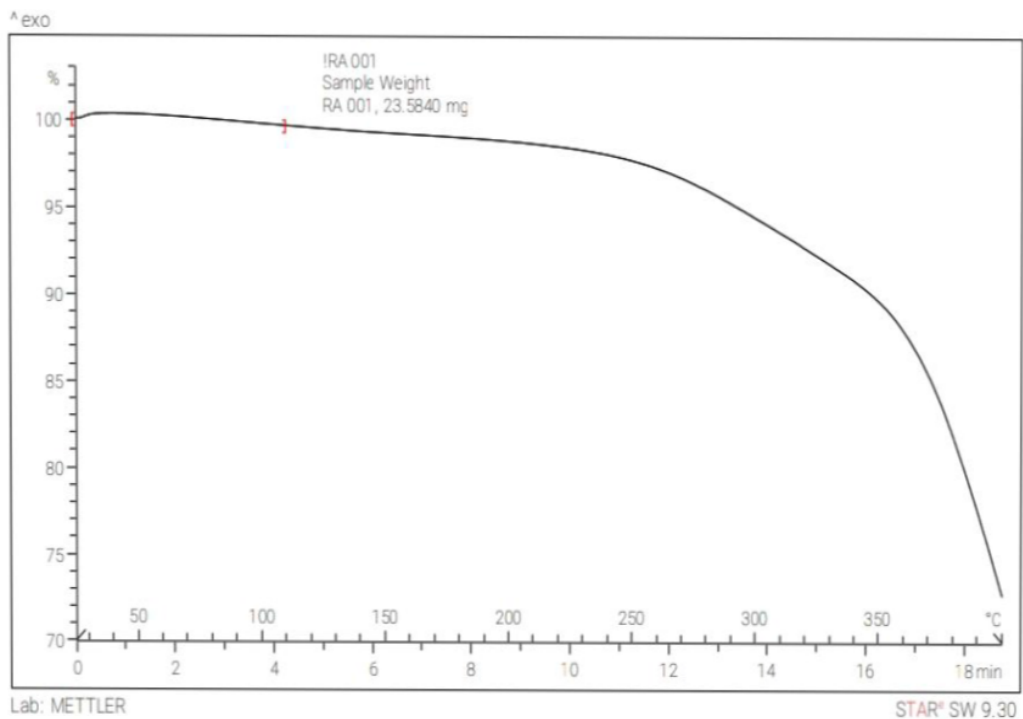


Figure 6: TGA of crude GTR

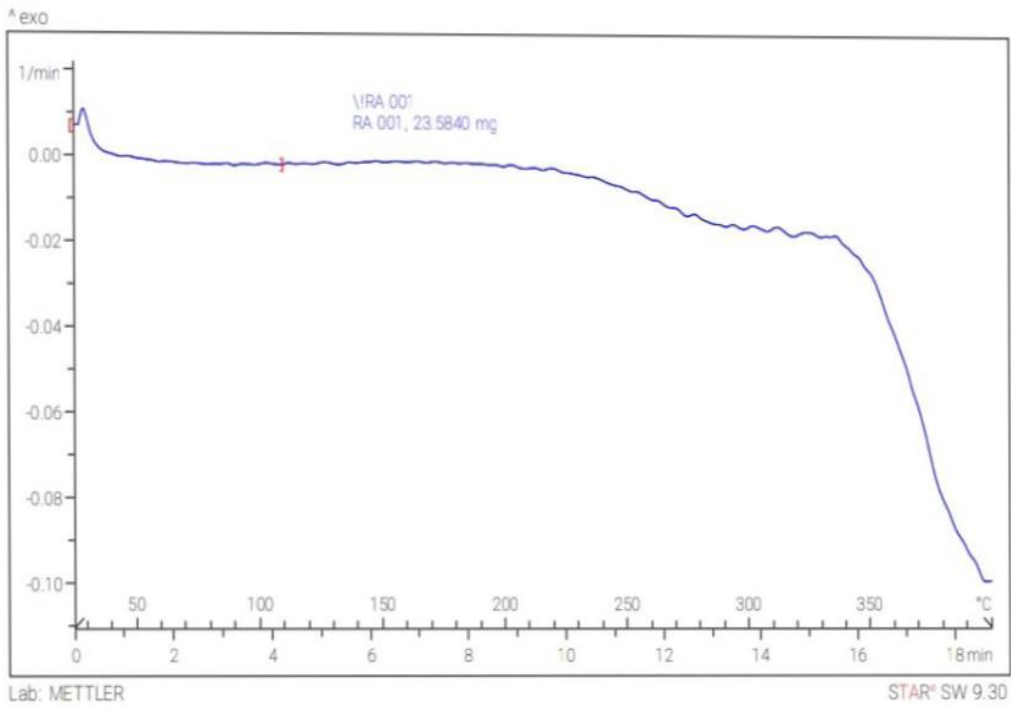


Figure 7: DTA of crude GTR

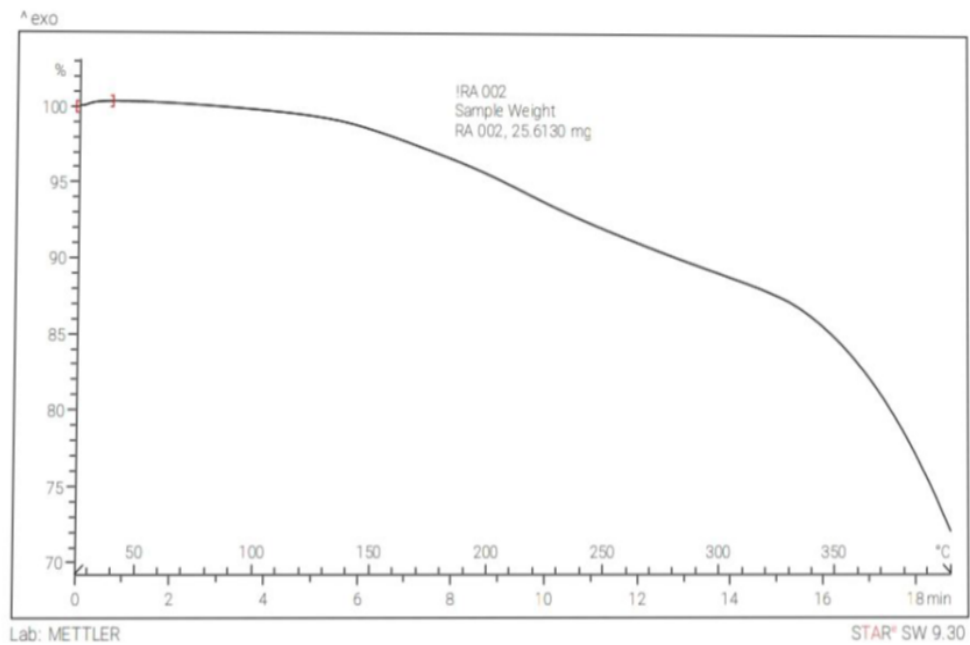


Figure 8: TGA of GTR functionalized with 10% MAn.

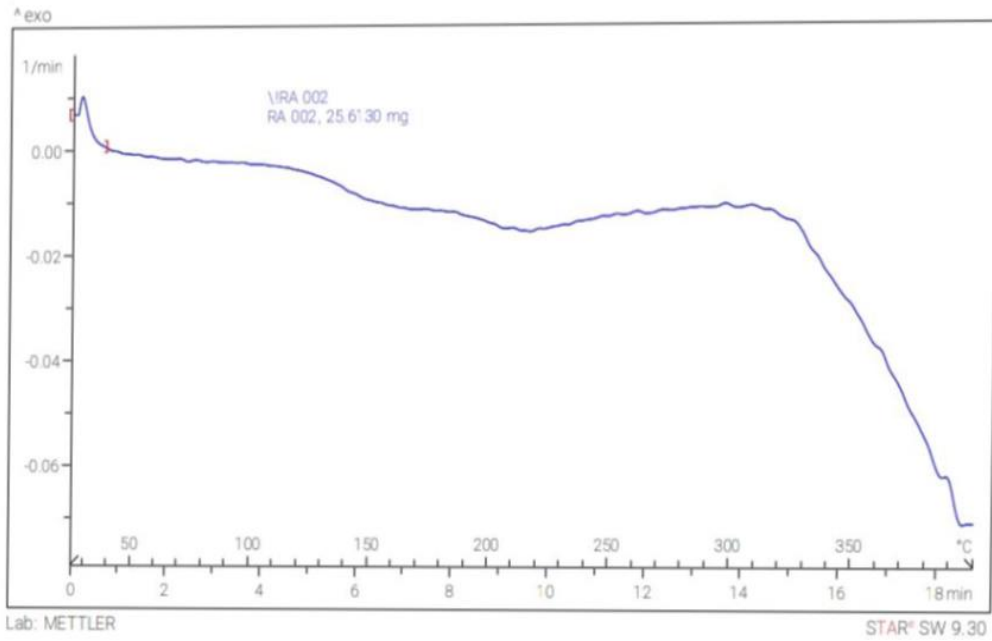


Figure 9: TDA of GTR functionalized with 10% MAN

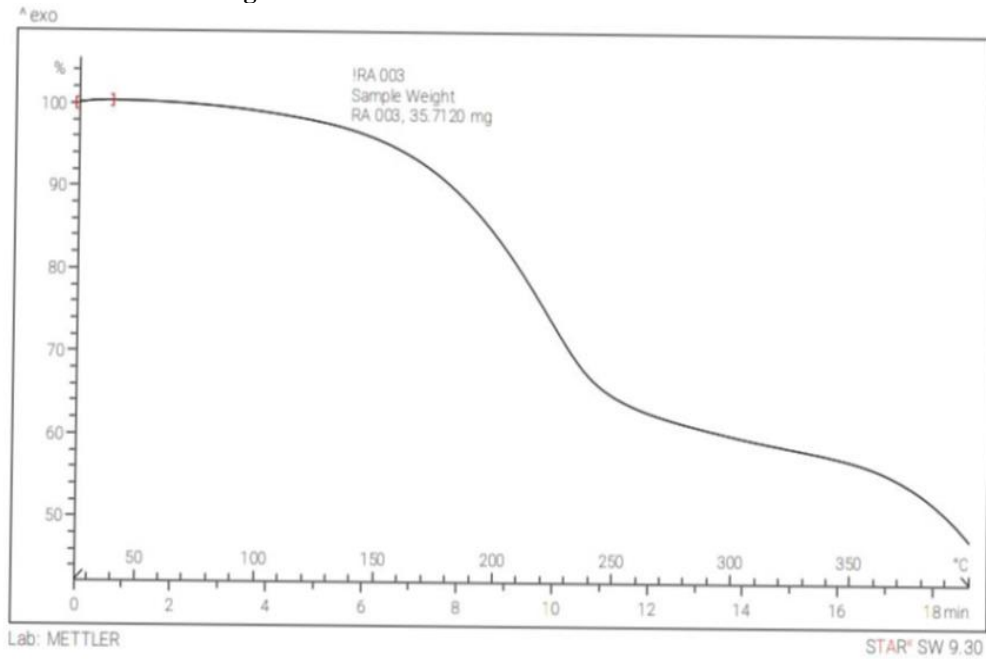


Figure 10: TGA of polyester of modified GTR and diethylene glycol

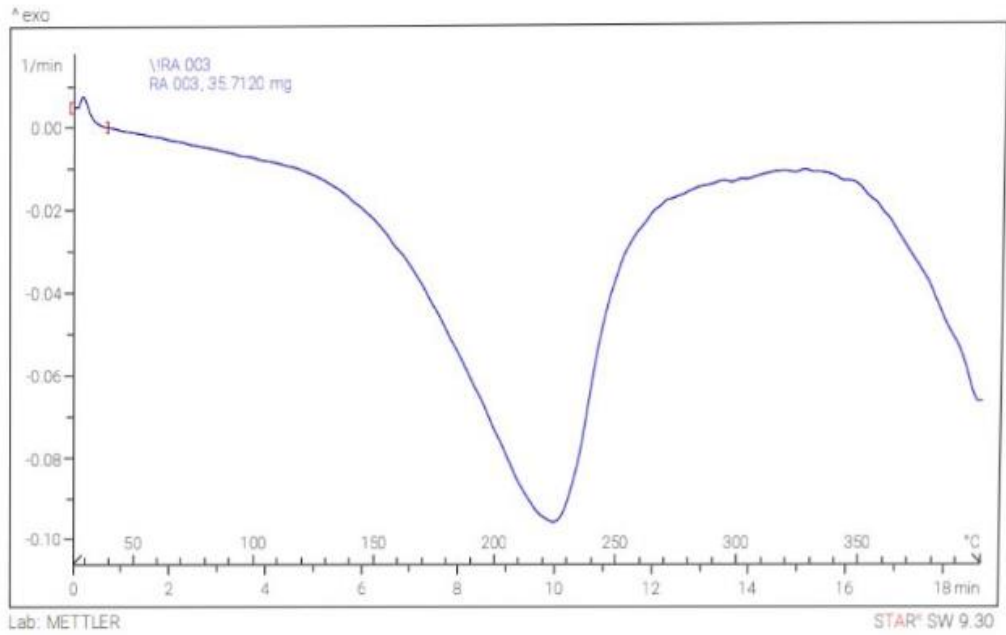


Figure 11: DTA of polyester of modified GTR and diethylene glycol

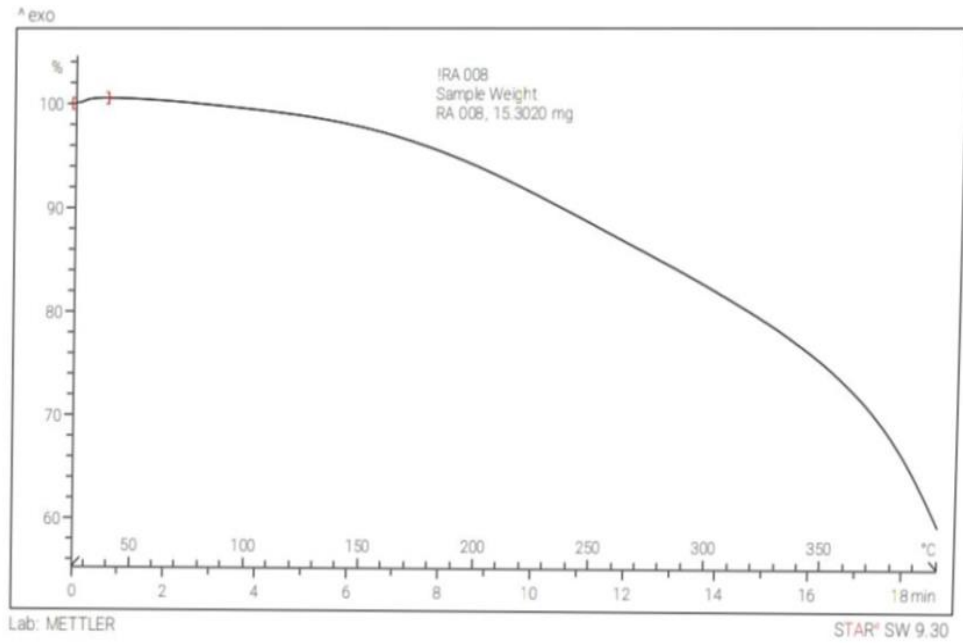


Figure 12: TGA of IPN

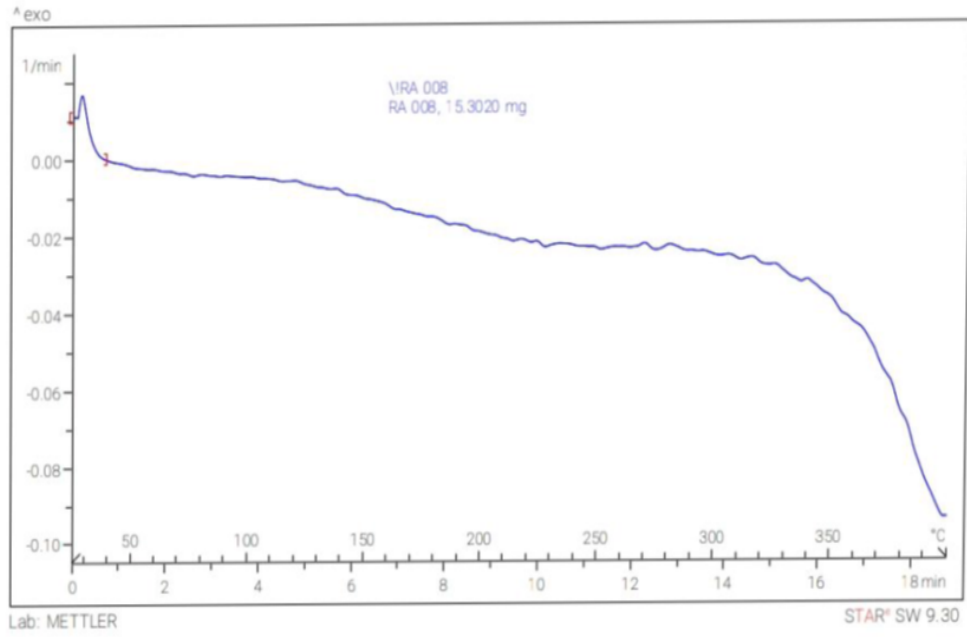


Figure 13: DTA of IPN

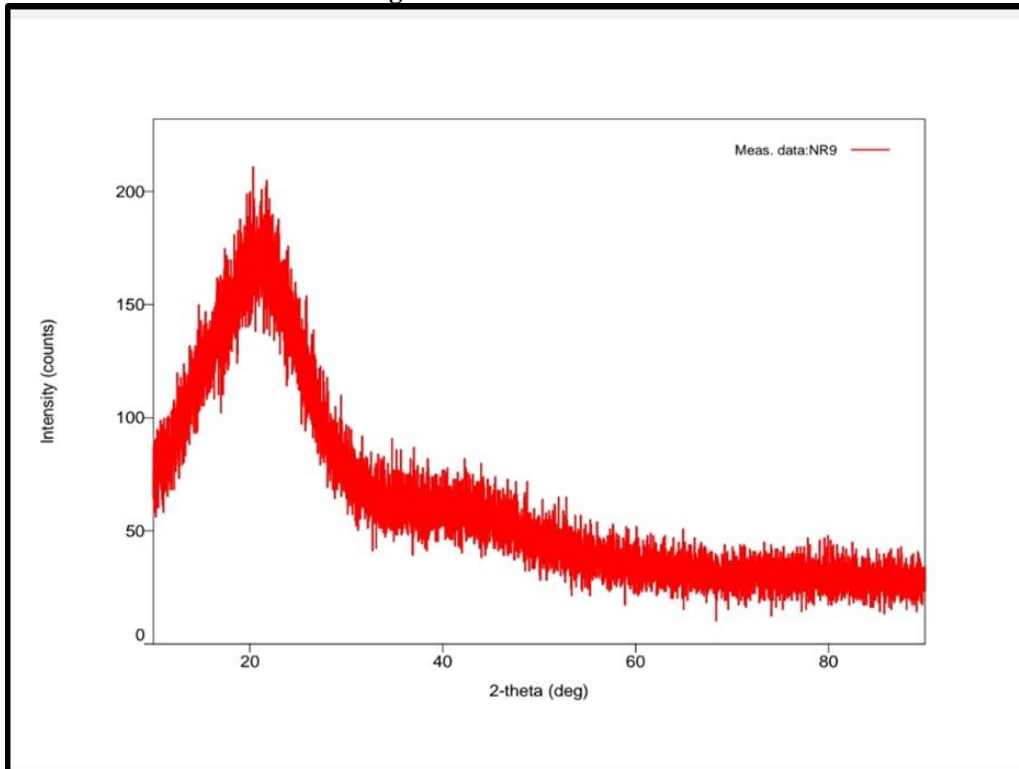


Figure 14: X-ray diffraction of IPN R1a

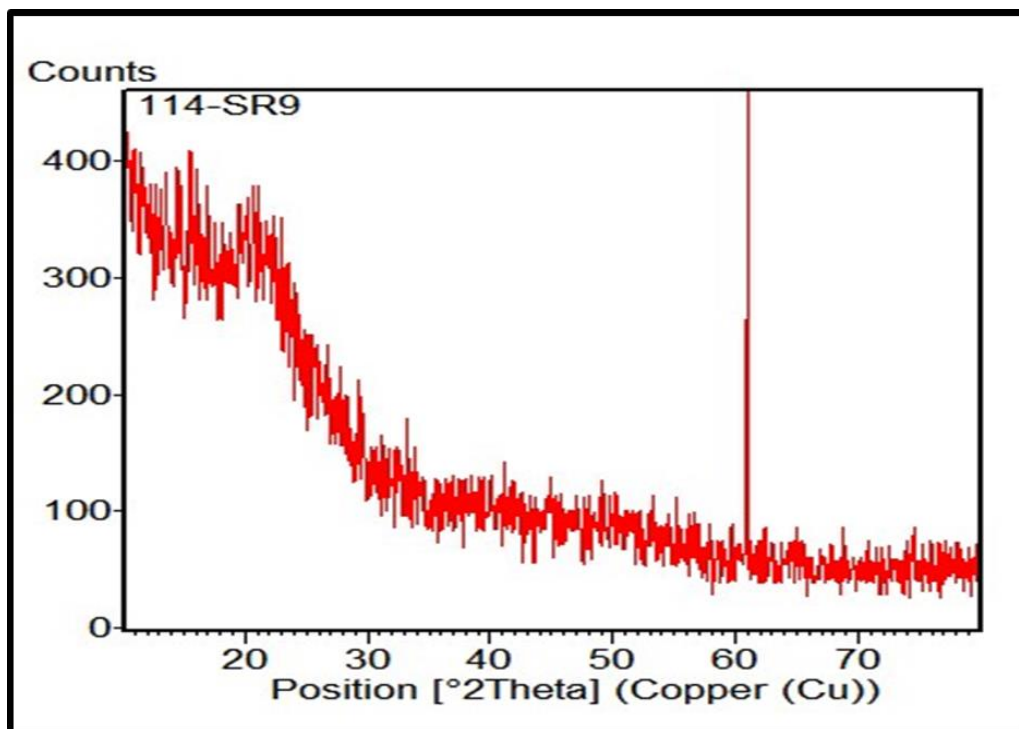


Figure 15: X-ray diffraction of IPN R4a

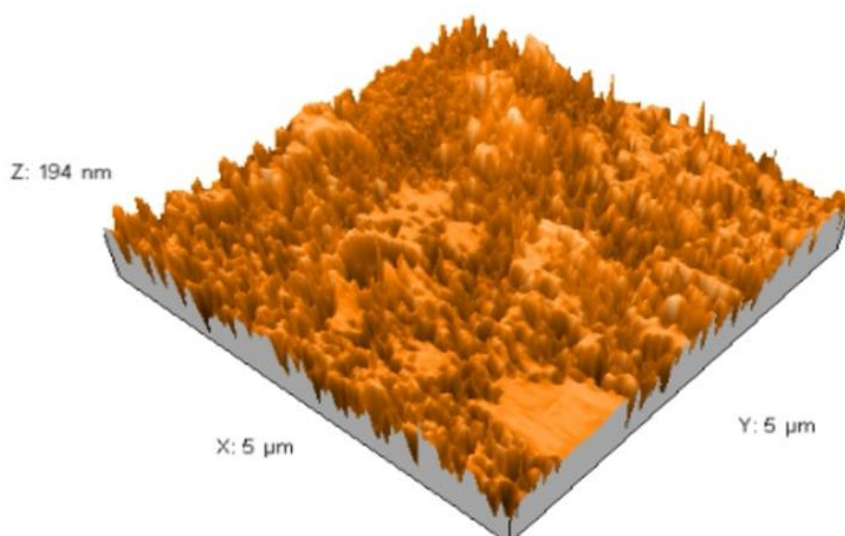


Figure 16: AFM picture of sample R1a

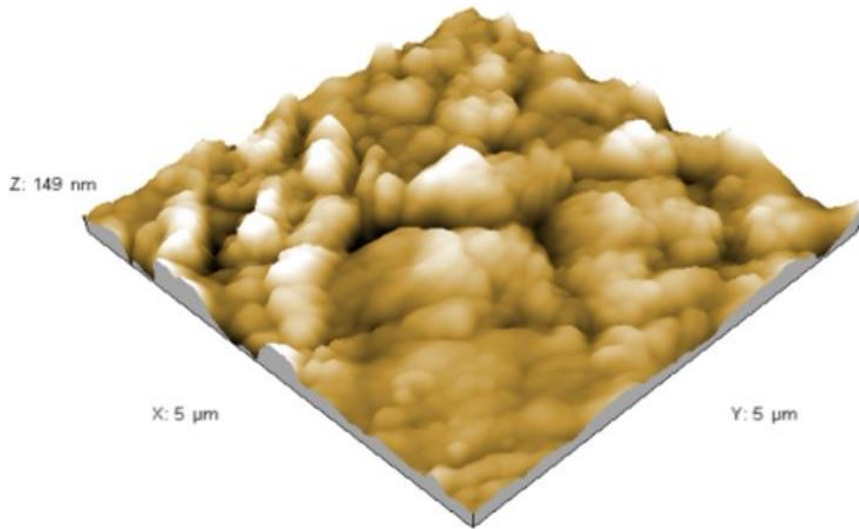


Figure 17: AFM picture of sample R4a

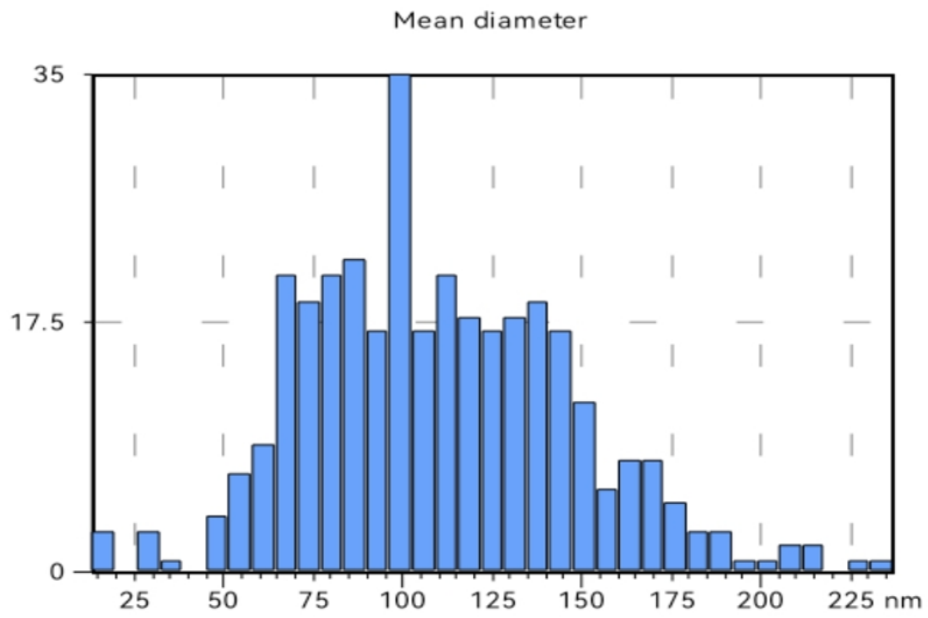


Figure 18: statistical analysis of AFM of R1a

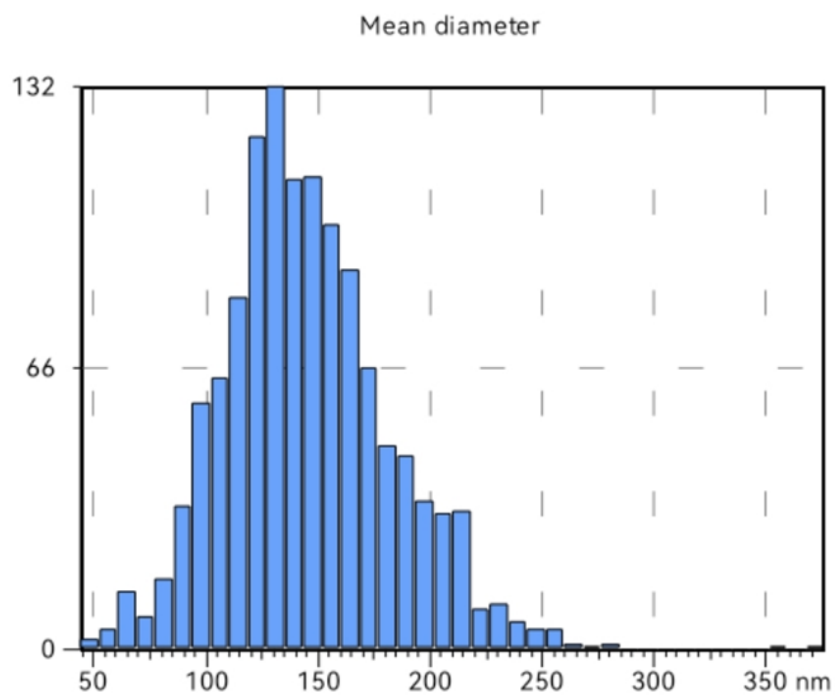


Figure 19: statistical analysis of AFM of R4a