

Study of mechanical and physical properties of Nano composite based on PBT/Epoxy/Nanoclay

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Abstract

PBT is conventional semi-crystalline engineering polymer with a high degree and rate of crystallization, good chemical resistance, thermal stability and excellent flow properties. PBT is used in various high volume automotive, electrical modulus and other engineering applications because it possesses good tensile strength, flexural modulus and dimensional stability, especially in water and high resistance to hydrocarbons. However PBT suffers from having low-heat distortion temperature the properties of PBT can be modified in three ways to meet the requirements of specific applications. Copolymerization, blending with other polymer such as epoxy to modify properties of PBT that this way. The results of PBT/Epoxy blend sample exhibits two separate peaks, indicating two phases for this samples. The low molecular weight epoxy is soluble with many of polar thermoplastics such as PBT and presents an upper critical separation type phase diagram.(UCST) The Tensile test points that in PBT/Epoxy blend sample by addition curing agent increases tensile modulus.

Key words: Curing agent, Nanoclay, Epoxy, Blend, PBT

1.Introduction

Need for polymers with complex micro structure is progressively increasing as the kind of application of polymer materials in different fields such as, nanotechnology, biotechnology, packaging transportation, aerospace, electronics and, has become complicated^[1]. Since synthesis and production of new polymers with relevant properties is a complex, time consuming and costly process, techniques such as, modification with reinforcing materials (including micro particles or Nano) or alloying present polymers as more flexible and more economic methods for producing polymers with desired physical and mechanical properties have been noted by many

researchers in recent years. Formation of strong interfacial layer between these two polymers is one of the advantages of epoxy alloying with PBT thermoplastic which has led to excess use of this thermoset in PBT alloying with other polymers and fillers as a compatibilizer^[2]. Studies on this field have been mostly on improving the physical and mechanical properties of alloy and the compatibilizing role epoxy has there, while because of complexity of reaction and the limitation of methods of evaluation and direct observation of reaction little studies have been done on synthesis of reaction between PBT and epoxy. The relational process between PBT and epoxy can be divided into three separate stages. Stage I: Fast

increase of viscosity rate of alloy complex (η^*) in the early reaction; Stage II: Stability of η^* rate in the middle of reaction; Stage III: relatively slow increase of η^* in the rest of reaction. Wu et al. have also done the experiment with PBT alloy and paraffine and observed that because paraffine lacks active groups for reaction with PBT therefore η^* rate stays stable over time and it is possible to attribute the increase of η^* in PBT alloy and epoxy to these two polymers. The goal of this paper is study and the analysis of mechanical – physical properties of poly butylene terephthalate / epoxy / Nano composites Materials and tools^[3].

2. Materials

poly butylene terephthalate (PBT) made by Bayer co. of type Pocan® B 1505 with the melt flow rate of about 23.4 g/10 min (260°C and 2.16 kg wt) and melt temperature 225°C was used. The resin epoxy used was of kind DGEBA made by Nan Ya Plastic Cor. Of type HPES-629 which is of high heat strength as well. Curing agent of resin epoxy MDEA, which is a product of Aldrich, acts at high temperature and does the cure process. Modified clay cloister 30B, which is produced by southern clay company of the U.S and is modified by quaternary ammonium salt. In preparing the initial samples, the internal mixing apparatus (Bra bender W50) with the compartment volume of 60cc and rollers made by Bra bender Co. of Germany; scanning electron micro scope of model: Seron AIS-2100 located at the central laboratory of Amir kabir University, transition electron micro scope of model: Philips EM 208 located at the research house of science and technics of Iran Atomic Energy organization, spectrometer of X ray diffraction (XRD) which diffract meter model: Philips X pert located at Najafabad Azad University was applied for that, Dynamic remoter (RMS) of model: UDS200 made by Paar Physical present at the plastic workstation of Industrial University of Amir kabir, DSC of model: Perkin Elmer DSC-7 present at the polymer engineering faculty of Amir kabir University, stretch test machine of model: SMTS made by SANTAM company at Isfahan University, hit test machine (GTECH) made in Taiwan of model: GT.7045-MD 1 coated at Shahreza Azad University, hit hammer of model: Izod were used.

3. Results and discussion

In fig.1, temprometer DSC for PBT, cured alloy and uncured alloy is presented to analyse the extent of compatibility or discompatibility of BPT with epoxy. The data related to thermo analysis is also presented in fig.1. As shown in the figure, PBT / epoxy alloy

has two separate peaks at temperatures 540° and 77°C which is related to glass transition temperature (T_g) of each of the components (glass transition) temperature of PBT and epoxy is 56 and 75°C respectively) and indicates the biphasic being of this alloy in melt state. Generally epoxy with low molecular weight is compatible with many polar thermoplastics and shows UCST phase behavior^[4]. As the molecular weight of epoxy increases, compatibility is reduced, due to a reduction in the mixing entropy of conformation, and the obtained alloys are usually biphasic. Considering the high molecular weight of resin epoxy in this paper (2400-3000g/eq) and observing two T_g s for alloy, it can be concluded that PBT / epoxy alloy is biphasic. Results also show that as PBT / epoxy alloy is cured the characteristic peak of T_g epoxy (at 77°C) is disappeared while the peak of PBT is still present. This result shows that the operation of epoxy curing has no effect on PBT phase and occurs only selectively in epoxy phase and leads to the cure of dispersed phase (epoxy). Although PBT crystalizing extent in cured alloy (BE) is the same as the pure PBT (in spite of the fall of melting point which is about 5°C and indicates a strong interaction between dispersed phase of epoxy and PBT bed), crystalizing extent of PBT goes through as 25 percent fall in cured alloy (cure BE) which might be due to the prohibitions caused by the cured grains of epoxy for PBT chains to move and the slowness of movement to the crystalized layers. Fig.2, shows the micrograph (SEM) for this alloy. This alloy shows the bed-disperse microstructure in which the mean size of particles of dispersed phase is about 2 μ m is well dispersed over the bed.

3.1. Rheologic properties of poly butyl enter phthalate / epoxy alloy

Fig3. Shows the curve of variations of complex viscosity (η^*) interims of angular frequency for PBT, epoxy, and uncured alloy (BE). PBT shows a plastic like behavior while epoxy has a Newtonian behavior in all the frequencies. The complex viscosity of alloy BE of the low of compounds has a positive variance which indicates a strong interaction between PBT bed and the dispersed phase of epoxy. This strong interaction between PBT and epoxy is because of side reactions between groups of carboxyl PBT and the groups of epoxy resin epoxy and the copolymer formation in the intersection which acts as a compatibilizer or interfacial factor and leads to the reinforcement of intersection and the increase of viscosity^[5-6]. Curves of linear viscoelastic properties for PBT / cured and uncured epoxy alloys are shown

in fig4. As shown in the figure, the behavior of cured alloy (cure BE) is similar to filled dense composites and dynamic cured thermoplastic elastomers and complex viscosity (η^*) and storage modulus (G') shows a high increase in low angular frequencies. As it is observed, the behavior of cured alloy is similar to suspensional bases^[7-9]. Fig5. Shows the values of complex viscosity, in terms of angular frequencies, for poly butyl enter phthalate (PBT), and cure agent contained PBT over which the complementary cure operation was conducted. This test is only done to analyse the influence of cure agent upon PBT chain and the results show that the cure agent has no effect upon PBT chains and has exclusively and selectively moved to the epoxy phase of the alloy of this agent and causes the cure of resin epoxy. The curves of the variations of complex viscosity in terms of the time of PBT / epoxy alloy and BE alloy which contains cure agent (ratio of estocuemetry) at 260°C are shown in the figure. As is shown in fig6, complex viscosity stags stable with the passage of time and begins to increase at a certain time (gelling point). Gelling point occurs very faster in alloy containing cure agent (about 1200 sec. compared with 2000 sec. for alloy wanting cure agent). Viscosity increase rate in alloy containing cure agent is more than the rate in BE alloy which shows the increase of the velocity of the process of curing in the presence of cure agent. The interesting point is the viscosity increase with time in the BE simple alloy which indicates the occurrence of structural variations (of the kind of viscosity increase) in the alloy. This increase can be a result of side reactions between groups of PBT carboxyl and the groups epoxy resin epoxy and copolymer formation in the intersection and reinforcing it. Another reason for the increase of viscosity in this base is probably because of partial cure of resin and its self curing nature. This relative increase of linear viscoelastic properties as a result of complementary cure in BE alloy without cure agent in comparison to the BE simple alloy is shown in fig7. By summation of the obtained results in this section, we can say that the linear viscoelastic behavior of cure Be alloy is severely controlled by the cure of epoxy dispersed phase and the formation of a strong intersection.

3.2. Results of XRD curve of PBT / epoxy alloy

We can sider the range $2\theta = 10-40$ to nanlyse the crystalizing of PBT / epoxy alloy. As it is show from the XRD curves of samples of PBT and poly butyl enter phthalate / epoxy alloy, it is observed that rate of crystalizing in both samples is similar which is in

accordance with the DSC thermo analysis test and the results in table 1, fig8, fig9.

A good conformity between the results obtained form the XRD test and DSC test is achieved.

3-3- Effect of Nano clay on the process of epoxy cure

The curve of complex viscosity variations in terms of time for epoxy containing cure agent and epoxy / Nano clay containing cure agent at 240°C is shown in fig.10. As is shown in the figure, Nano clay increases both the time of the reaction of cure and velocity of reaction in epoxy. Dean et al^[10],also reported similarly and pronounced the catalytic role of ciliate layers of Nano clay in the reaction of epoxy cure as the cause. In other words, proton cation amines in Nano clay layers shows more activity as a acid catalyzer compared to cure agent and causes epoxy to cure faster^[11].

3.4. Results of Rheology

Fig 11 shows the curve of complex viscosity variation (η^*) and storage modulus (G') in terms of angular frequency for PBT, PBT / Nano clay, Nano clay (BN), epoxy, and epoxy / Nano clay (EN). It is evident that the samples BN and EN show non-ultimate behavior in storage modulus and upward roll of viscosity in low frequencies. It seems that the PBT and epoxy has an equal capability in creating calibrating structure in Nano composite and this result is well accorded with the results observed in XRD test. The following three kinds are repaired to analyse the influence of feeding order parameter on the properties of Nano composite: 1) simultaneous feeding of three components of PBT, epoxy and Nano clay (BEN), 2) preparing sample based on master batch Nano clay in PBT (BN-E), 3) preparing sample based on master batch Nano clay in epoxy (B-EN). Properties of linear viscoelastic of the sample of compound Nano composites are shown in fig12. As is shown in the figure, the order of feeding has much influence upon the rheological behavior of Nano composite. These results are in contrast with the results observed in X ray diffraction test where it was observed that the order of feeding has no influence upon the rate of opening of the Nano clay layers and is almost equal for the three samples. Both samples of BEN and BN-E have a higher viscosity and elasticity that the sample of B-EN and show solid like behavior in angular frequencies which is because of the presence of Nano clay in the bed and its better distribution in Nano composite compared with the sample of B-EN. In the sample of B-EN, grains of Nano clay are blocked in epoxy drops and can not move from the drop into the bed of PBT because of

high aspect ratio and high viscosity and dispersed phase. Therefore, no non-ultimate behavior is observed for B-EN in storage modulus and upward roll of viscosity in low frequencies^[12]. This theory is well proved by the micrographs of TEM which is presented in fig 13. As is seen in the above figure, both samples of BEN and BN-E show calibrated and stratified microstructure and the plates and the layers of Nano clay are well dispersed in the bed of PBT, while the grains of Nano clay in the sample of B-EN are blocked in the drops of epoxy dispersed phased. By summation of the results of the test of rheology and XRD of the sample of complex Nano composites it can be stated that the order of feeding has a high influence on Nano clay distribution and its part in each phase, although it has no influence on the rate of calibration and Nano clay dispersion. Because the time of emigration and movement of Nano clay from epoxy drops to the bed of PBT is higher than the time of mixing process and in spite of equal thermodynamic trend of PBT and epoxy with Nano clay, Nano clay can not move from epoxy drop to the bed in the sample of B-EN. Obtained results from similar rheological tests on the sample of cured compound Nano composites show a similar process which was described for the uncured samples (fig.14). From the obtained results, we can conclude that the curing process caused partial changes in the extent of distribution and the distribution of Nano clay which is in accordance with the results observed in XRD test. Increase of complex viscosity and storage modulus of cured samples compared with the uncured samples is majorly because of curing the epoxy drops and the increase of interfacial adhesiveness of dispersed phase and bed^[13-14].

4. Summation and conclusion

- Results from thermal analysis and rheology speak of biphasic being of PBT / epoxy alloy which can be resulted from high molecular weight of the applied epoxy. It is also shown that the curing process in alloy has selectively turned the epoxy phase into lattice and has influence on PBT.
- In the analysis of X ray diffraction, cure agent has no influence on PBT crystallization as cure has no influence on PBT but resin epoxy itself influences the PBT crystallization.
- From the result of tensile test, we understood that adding epoxy to PBT cause the increase of modulus and the increase of chain strength and this increase of modulus is because of strong interaction between OH groups of epoxy resin and the groups of carboxylic poly butylinterphthalate.
- Results from tensile test of PBT / epoxy alloy show that adding cure agent causes the increase of tensile modulus since curing causes the rigidity and strength of chain.

REFERENCES

- [1] .C.M. Gómez, I. Porcar, I.S. Monzo, C. Abad, A.N. Campos, *Eur. Polym. J.*, 43, 360, (2007).
- [2]. F. Xie, C.X. Zhou, W. Yu, D.F. Wu, *Eur. Polym. J.*, 41, 2171, (2005).
- [3]. F. Xie, C.X. Zhou, W. Yu, *Polym. Composites*, 72, (2008).
- [4]. H. Zhang, SH. Sun, M. Ren, Q. Chen., J. Song, H. Zhang, Z. Mo, *J. Appl. Polym. Sci*, 109, 4082, (2008).
- [5]. A. Saadat, H. Nazockdast, F. Sepehr, M. Mehranpour, *Polym. Eng. Sci.*, 50, 2340, (2010).
- [6]. T. E. Sandhya, C. Ramesh, S. Sivaram, *Macromolecules*, 40, 6906, (2007).
- [7]. Y. W. Mai, Z. Zh. Yu, *Polymer Nanocomposites*, Woodhead Publishing Limited, CRC Press, (2006).
- [8]. K. Jayanarayanan, T. Jose, S. Thomas, K. Joseph, *Eur. Polym. J.*, 45, 1738, (2009).
- [9]. M.M. Salehi, H. Nazockdast, Gh R Pircheraghi *Journal of Macromolecular Science, Part B*(2012)
- [10]. X. Yi, L. Xu, Y.L. Wang, G.J. Zhong, X. Ji, Zh.M. Li, *Eur. Polym. J.*, 46, 719, (2010).
- [11]. E. Nazockdast, H. Nazockdast, F. Goharpey, *Polym Eng. Sci.*, 48, 1240, (2008).
- [12]. Y. W. Mai, Z. Zh. Yu, *Polymer Nanocomposites*, Woodhead Publishing Limited, CRC Press, (2006).
- [13]. D. Dean, R. Walker, M. Theodore, E. Hampton, E. Nyairo, *Polymer*, 46, 3014, (2005).
- [14]. R. Foudazi, H. Nazockdast, *Appl. Rheol.*, 20, 12218, (2010).

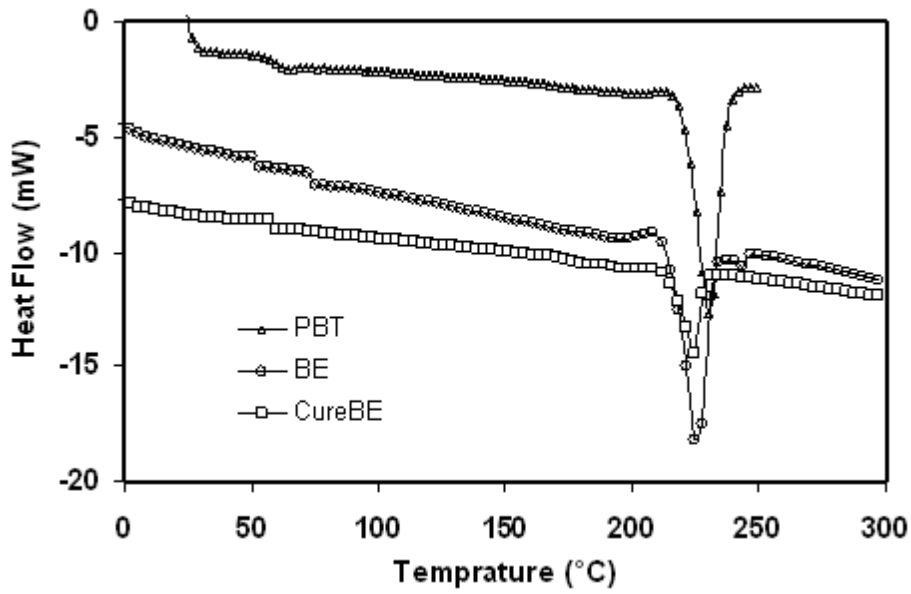


Fig.1. Thermograph for poly butelinterphetelate (PBT), cured alloy (cure BE) and uncured alloy (BE).

Tabel.1. Thermo analytical results of first materials and related alloys.

	PBT	Epoxy	BE	CureBE
T_g (°C)	56	75	54/77 two T_g s	57
ΔC_p ($J g^{-1} K^{-1}$)	0.20	0.31	0.25	0.19
ΔH_f ($J g^{-1}$)	42.8	-	42.4	30.1
T_m (°C)	229.95	-	224.80	223.82

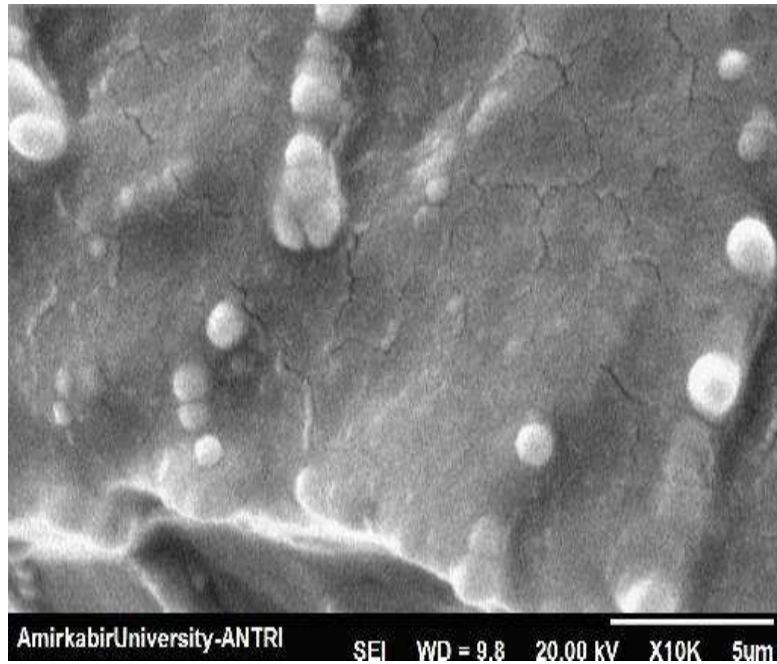


Fig.2. Micrograph (SEM) for PBT / epoxy alloy

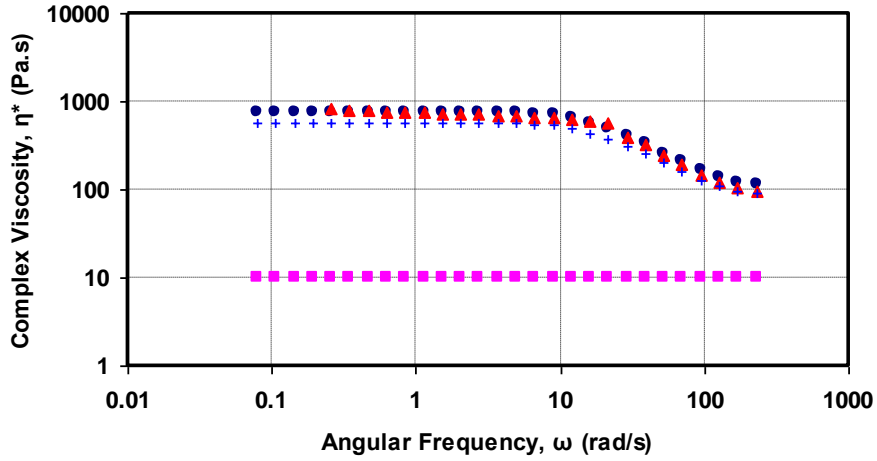


Fig.3. Values of complex viscosity (η^*) in terms of angular frequencies for samples PBT (●), epoxy (■), uncured alloy (BE) (▲) and the law of compounds (○).

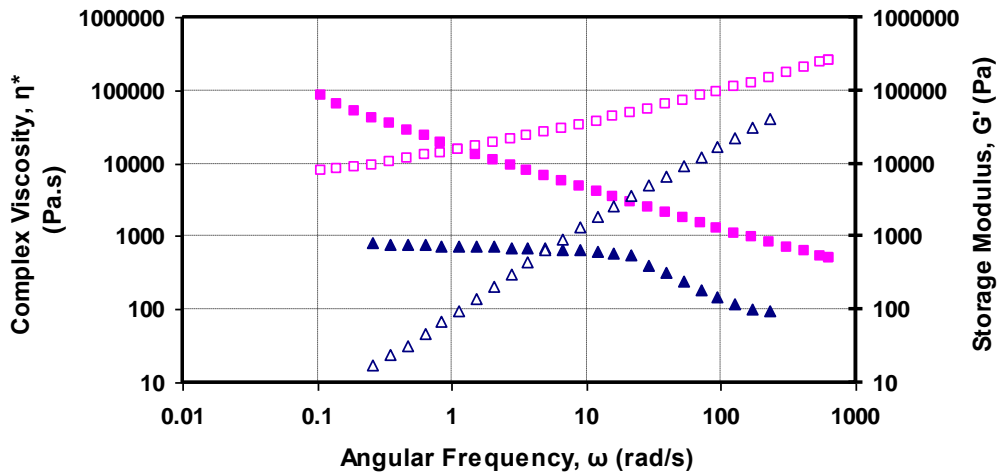


Fig.4. Values of complex viscosity (η^*) and storage modulus (G') in terms of angular frequencies for uncured alloys (BE) (Δ, \blacktriangle) and cured alloys (cure BE) (\square, \blacksquare). Blank symbols relate to storage modulus and filled symbols relate to complex viscosity.

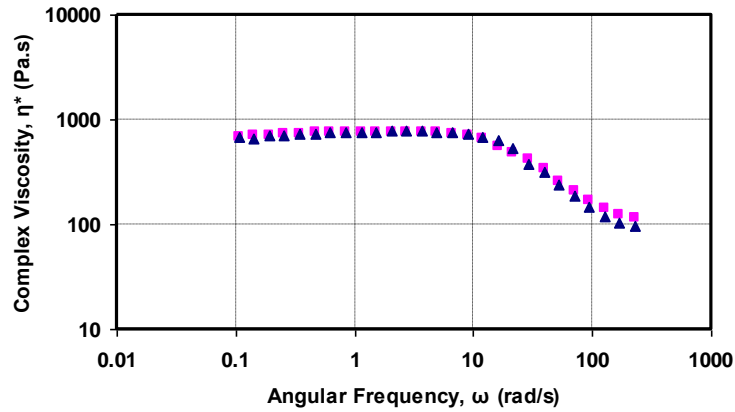


Fig.5. Values of complex viscosity (η^*) in terms of angular frequencies for PBT (■) and PBT containing cure agent (cure PBT) (▲).

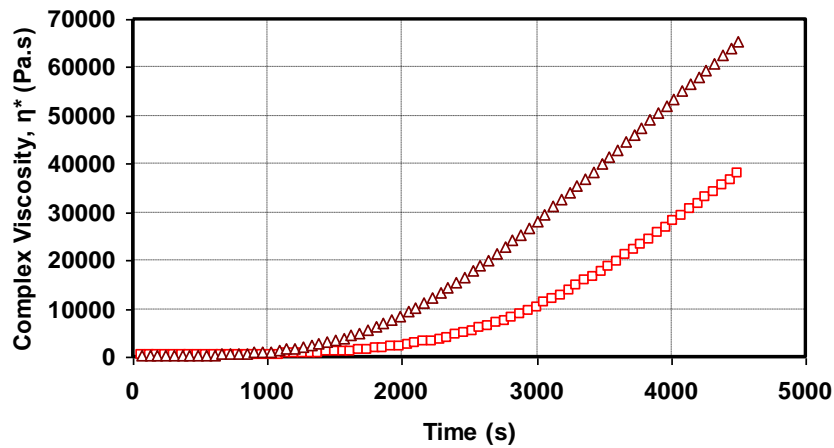


Fig.6. Complex viscosity variation (η^*) in terms of BE alloy time (□) and BE alloy containing cure agent (Δ) at 260°C.

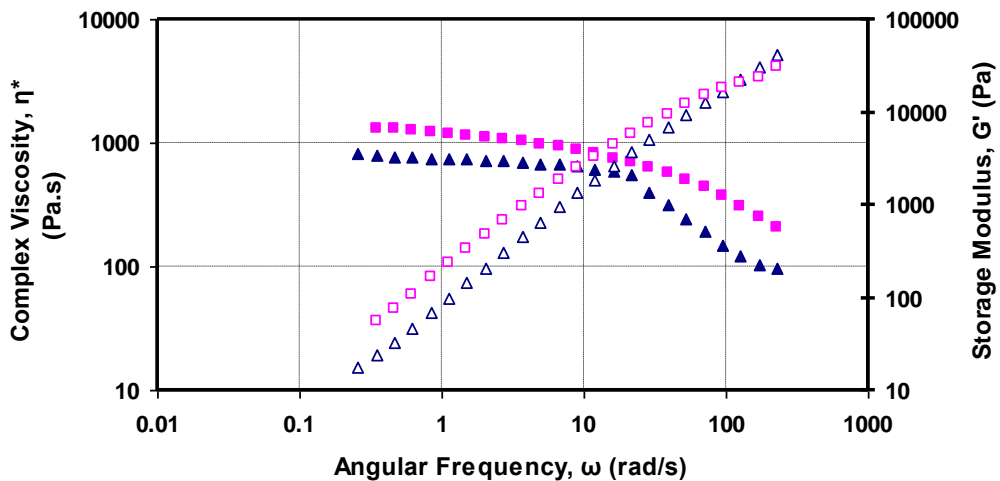


Fig.7. Values of complex viscosity (η^*) and storage modulus (G') in terms of angular frequency for uncured alloy (BE) (Δ , \blacktriangle), and BE alloy of completed cure (\square , \blacksquare). Blank symbols relate to storage modulus and filled symbols relate to complex viscosity.

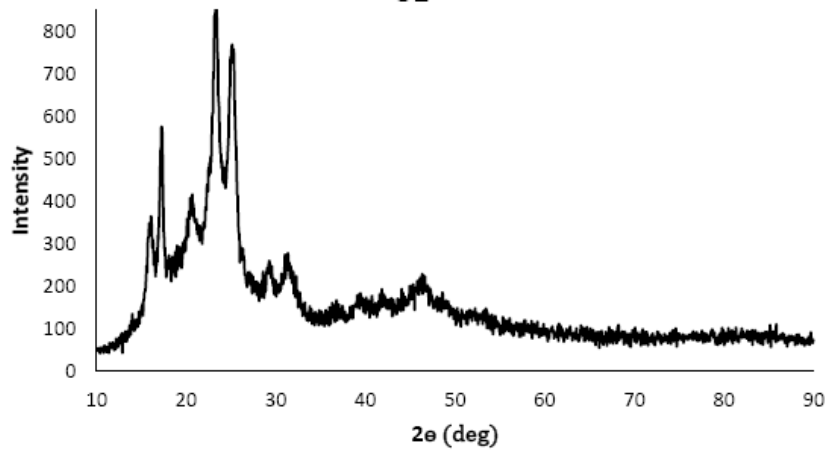


Fig.8. XRD curve of sample PBT.

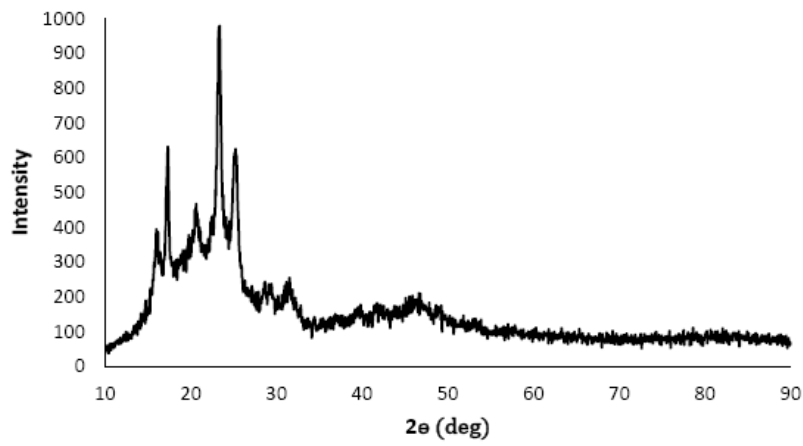


Fig.9. XRD curve of sample BE.

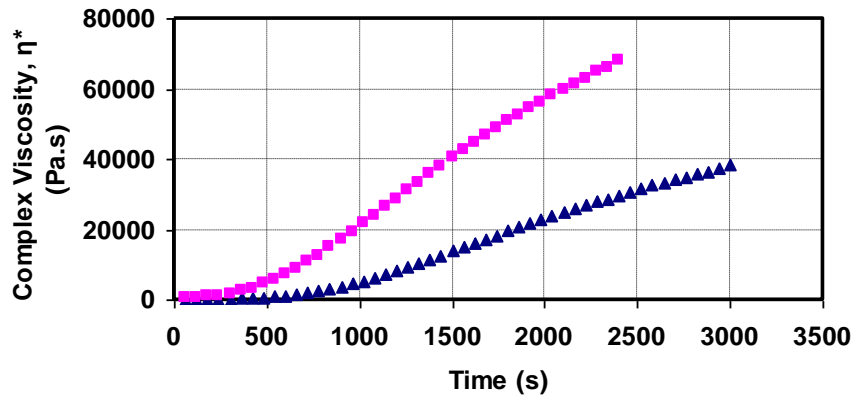


Fig.10. Complex viscosity variation (η^*) in terms of epoxy time containing cure agent (\blacktriangle) and epoxy / Nano clay (EN) containing cure agent (\blacksquare) at 240°C.

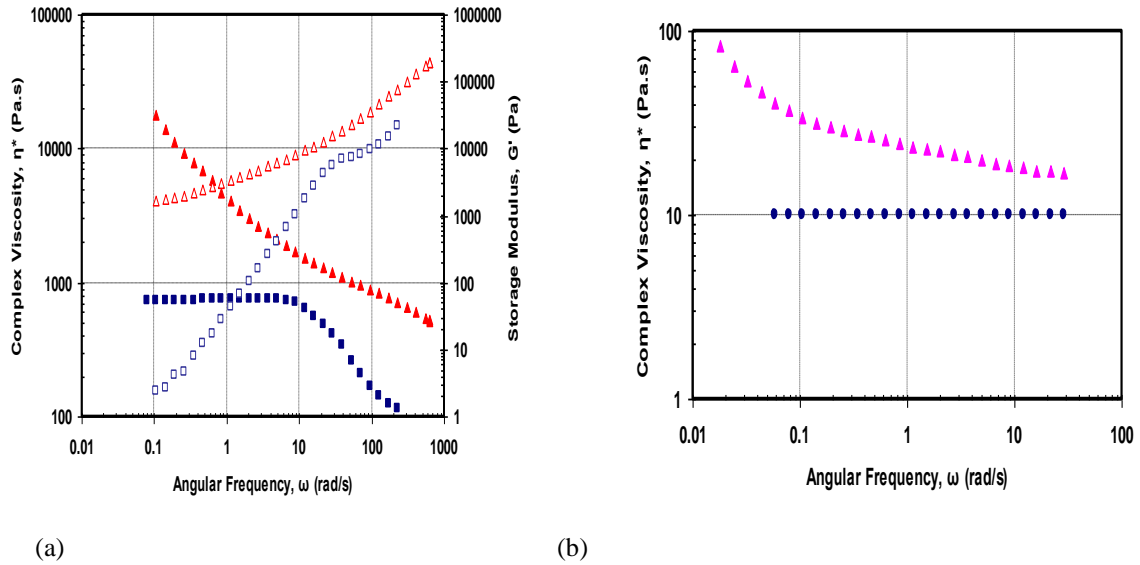


Fig.11. values of complex viscosity (η^*) and storage modulus (G') in terms of angular frequency for a) PBT (\square , \blacksquare) and PBT / Nano clay (BN) (Δ , \blacktriangle) and b) epoxy (\bullet) and epoxy / Nano clay (BN) (Δ). Blank symbols relate storage modulus and filled symbols relate to complex viscosity.

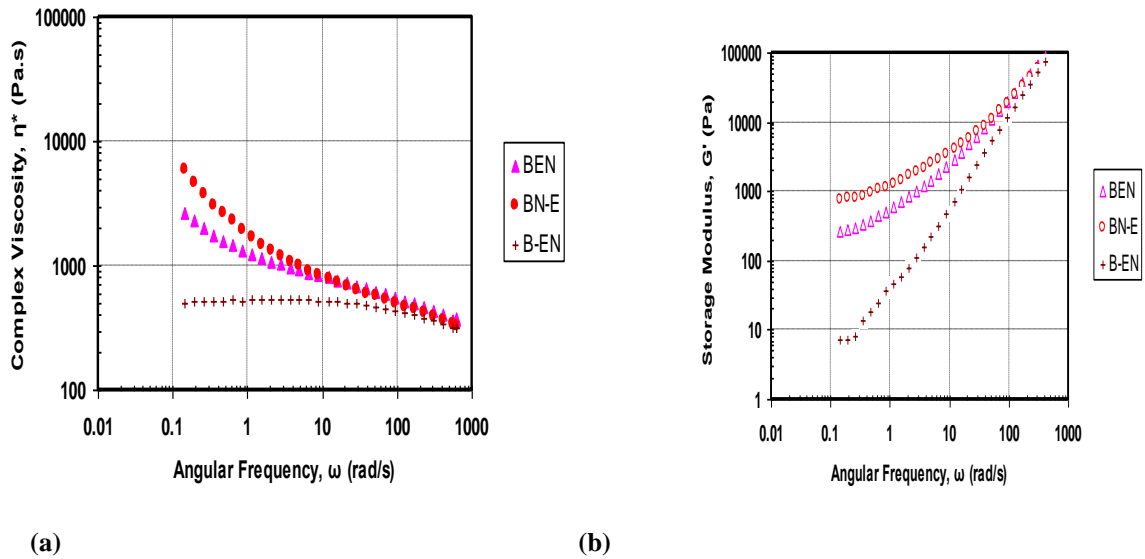


Fig.12. Curve a) complex viscosity (η^*) and b) storage modulus (G') in terms of angular frequency for compound Nano composites BEN, BN-E and B-EN.

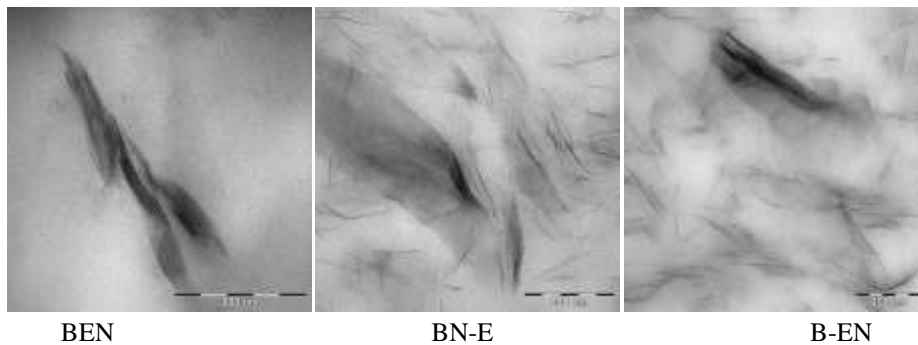


Fig.13. Micrograph TEM concerning to Nano composites samples of BEN, BN-E and B-EN.

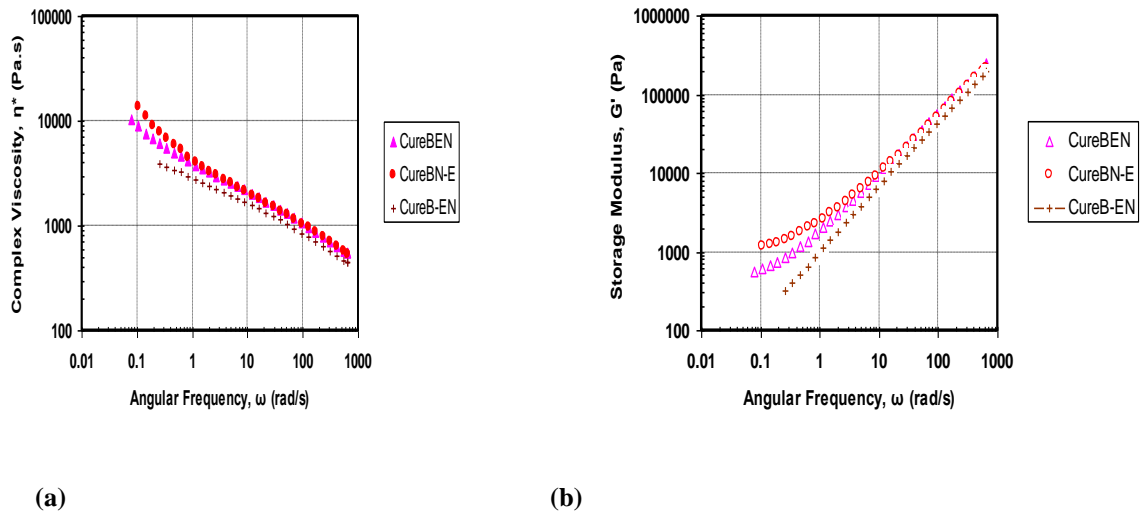


Fig.14. Curve a) complex viscosity (η^*) and b) storage modulus (G') in terms of angular frequency for cured complex Nano composites cure B-EN, cure BN-E and BEN.