

Effect of Nano Silica on Phase Transformation from Form-II to Form -I of Polybutene-1

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Abstract - Polybutene-1 is an unusual polymer having high environment crack resistance, toughness, creep resistance, low glass transition temperature, flexibility etc. making it attractive for pipe and tubing applications. However, it exists in four polymorphic forms and has most peculiar solid-solid transformation taking place over long period of time (over days) which is the major drawback limiting its applications. There have been several efforts made in the past to accelerate the process of crystal transformation from form-II to form-I which is most stable of all the polymorphs. Techniques such as mechanical stretching, electron beam irradiation, addition of co-monomer, annealing etc. have been tried in the past [1-5] to obtain the stable form-I of polybutene-1 (PB1). In this paper, we describe the effect of addition of nano silica on the rate of transformation of form-II to form-I of PB1.

In this work, Polybutene-1 (Aldrich) was melt compounded with nanosilica (NYACOL NGS-2000) in the Haake PolyLab batch mixer at 150°C with 60rpm speed for 7 minutes to ensure thorough dispersion. Three compositions were prepared containing 3,5,10,15 wt% of nano silica which were compared with the original PB1. The compression moulded films of the composites were prepared with Carver press at 150°C with 100kg/cm² pressure and used for further studies. The crystal-crystal transformation was studied using DSC (model: Perkin Elmer DSC-2) by carrying out the thermal scans repeatedly over 150 hr as well as by isothermal crystallization method at 86°C. These studies clearly indicate the lower melting from-II getting reduced in intensity and higher melting form-I increasing and ultimately becoming single stable component. The crystallization time decreased from 154 s to 84 s with the addition of nano silica. The 3 wt% of nano silica gave the most rapid transformation of form-II to form-I. There was also increase in the final crystallinity (C_i) value going upto 62% in presence of nano silica. Dynamic mechanical properties of the sample were studied using Rheometric model III E dynamic mechanical analyzer in the tensile mode. The data showed an increase in the storage modulus (E') in the presence of nano silica from 1.285 to 1.7158 at around 50°C which could be due to the full transformation to form-I.

KeyWords: Polybutene-1, nanosilica, phase transformation, DSC, Form-I, Form-II.

1. INTRODUCTION:

Crystallization of Poly(1-butene) is of interest because of its spontaneous kinetically favoured (Form-II) to thermodynamically stable (Form-I) phase transformation in solid state. Form-I (hexagonal) shows superior mechanical properties than Form -II (tetragonal). Form -I melts at 125-138 C & Form -II melts at a lower temperature of 110-120 C

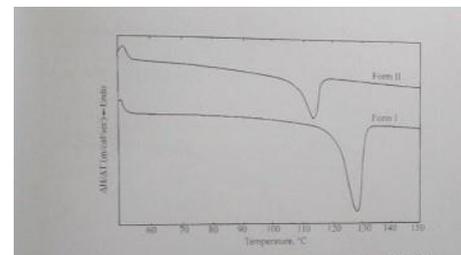


Figure 1: DSC thermogram for Form-I and Form -II of PB-1.

Phase transformation takes about 7 to 10 days to complete and takes place soon after the crystallisation of Form-II. One of the main targets of the studies on PB based materials is to accelerate the transformation to shorten the time needed to obtain crystalline Form -I which has unique property profile.

A revolutionary work first by Usuki et al and later by Iijama initiated a lot of interest in fundamental as well as industrial research in the area of nanocomposites. Subsequent studies in polymer nanocomposites revealed that a very small amount of nanofiller is required for achieving significant improvement in material properties such as modulus, strength, heat resistance and flame retardancy. These nanofillers can act as nucleating agents and help enhance the crystallization rates.

2. RESULTS AND DISCUSSIONS:

2.1 Polybutene used in the study was acquired from Adlrich and has a molecular weight of 570,000g/mol. The nanosilica was manufactured by NYACOL nanotechnologies Inc. with trade name NYACOL, NGS 2000.

2.2 Non-isothermal crystallisation behaviour of PB and PB nanosilica composites was studied to study the effect

of cooling rate and content of nanosilica during crystallization. Also decrease in the cooling rate causes an increase in the crystallization temperatures. This increase in crystallization temperature with nanosilica content reveals a marked interaction between PB and nanosilica.

2.3 The crystallization kinetics of PB and PB nanosilica composites were analyzed using the classic Avrami Equation. (Table.1)

Sample	Φ ($^{\circ}\text{C}/\text{min}$)	Zt	t1/2(min)
PB	5.0	0.17793	0.9937
	10	0.9445	0.8668
	20	4.21483	0.869
PB3NS	2.5	0.2777	1.215
	5.0	1.2373	0.9319
	20	6.9128	0.8576
PB5NS	2.5	0.0604	1.215
	5.0	0.4548	0.9319
	20	5.2481	0.8576
PB10NS	5.0	0.6102	0.9136
	10	4.7611	0.8850
	20	19.371	0.8789
PB15NS	2.5	0.06503	1.1739
	10	4.9712	0.8870
	20	18.7685	0.8655

The values of crystallization rate constant Zt are found to increase with increase in the cooling rates for both PB and PB nanosilica composites while the values of t 1/2 decreased as the rate of cooling increased. The higher values of Zt and lower values of t 1/2 for the PB nanosilica as compared to PB indicates that there is an enhancement in the crystallization rate by addition of nanosilica.

2.4 Isothermal Crystallization studies for PB and PB nanosilica composites was done in the temperature range of 76 $^{\circ}\text{C}$ to 86 $^{\circ}\text{C}$ for PB and 82 $^{\circ}\text{C}$ to 95 $^{\circ}\text{C}$ for PB nanosilica composites. In the isothermal crystallization the sample is heated at 40 $^{\circ}\text{C}/\text{min}$ upto 150 $^{\circ}\text{C}$ and held for 2 minutes, then quenched at a cooling rate of 160 $^{\circ}\text{C}/\text{min}$ to the desired crystallization temperature (72 $^{\circ}\text{C}$ to 96 $^{\circ}\text{C}$).

From this study the effect of incorporation of silica on crystallization behaviour was studied. It is seen from the graph that the total crystallization time was lowered for nanocomposites of PB and nanosilica than PB alone (Fig.1)

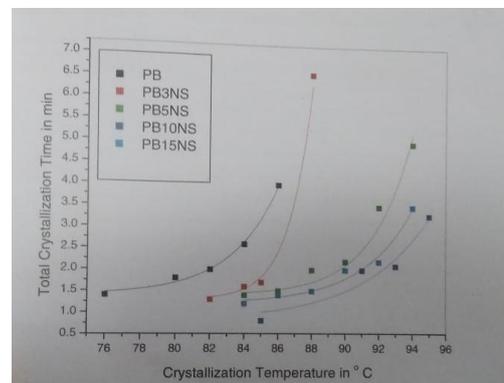
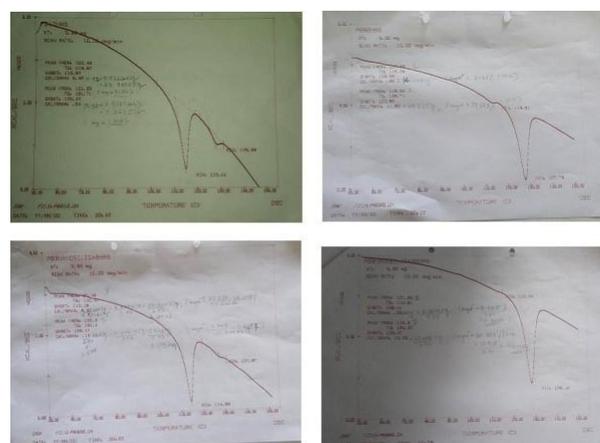


Fig.1: Total crystallization time in minutes vs crystallization temperature in degree centigrade.

Phase transformation studies using DSC was studied for PB and PB nanocomposites at room temperature by measuring the heat of fusion for the two forms at various time intervals. For 100 % PB Form I the heat of fusion = 125.4J/g and for Form -II the heat of fusion = 75.2 J/g

.The heating scans for melt crystallized PB and PB 3NS samples both exhibit 2 peaks corresponding to Form -I and Form -II.



Optical micrographs revealed smaller spherulites for nanocomposites with no change in spherulitic morphology.

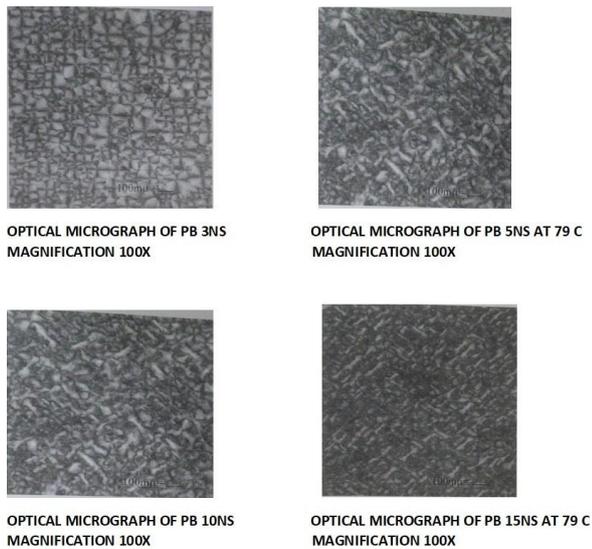
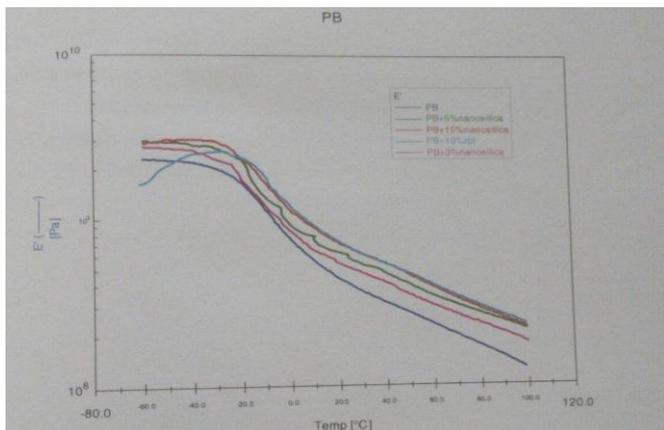


Figure 4: Showing the spherulites using Optical microscope

Dynamic Mechanical Analysis study the reinforcing effect of nanosilica was clearly observed as the storage modulus in the rubbery regime was significantly higher than for PB nanocomposites.



3. CONCLUSIONS

1. Poly(1-butene) nanocomposites were successfully prepared by melt processing technique using nanosilica.
2. We have investigated the surface morphology, crystallization behaviour, phase transformation kinetics and dynamic mechanical behaviour of these nanocomposites.
3. The introduction of nanofillers in PB affects the overall crystallization behaviour. The nanocomposites exhibited higher crystallization temperature than pristine PB. The higher values of Zt derived from Avrami theory for nanocomposites compared to pristine PB suggests heterogeneous nucleation.

4. Isothermal crystallization studies exhibited enhanced crystallization rate of PB in presence of nanofillers than that of PB.
5. The fractional conversion of Form -I with time increased in phase transformation study.
6. Optical micrographs revealed smaller spherulites for the nanocomposites with no change in spherulitic morphology
7. In Dynamic Mechanical Analysis study the reinforcing effect of nanosilica was clearly observed as the storage modulus in the rubbery regime was significantly higher than for PB nanocomposites.

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BIOGRAPHIES



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