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ORIGINAL PAPER

Controlling the rheological behavior of nucleated polypropylene via incorporating dimethylbenzylidene sorbitol (DMDBS) masterbatch

Maryam Shokrollahi[1], Bahareh T. Marouf[2], Reza Bagheri[1*]

[1]Polymeric Materials Research Group (PMRG), Department of Materials Science & Engineering, Sharif University of Technology, Azadi Ave., P.O. Box 11155-9466, Tehran, Iran
[2]Department of Materials Science & Engineering, Faculty of Engineering, Urmia University, Urmia, Iran

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ABSTRACT

Dimethylbenzylidene sorbitol (DMDBS) is a common nucleating/clarifier agent used in polypropylene (PP). So many researchers have looked at different aspects of incorporating this additive on the crystallization behavior of PP. The current study is focused on a rather new topic and that is the role of the carrier resin of DMDBS masterbatch on the rheological behaviour of polypropylene. This objective has been achieved through studying the role of the carrier resin on the phase separation behavior of DMDBS upon cooling. It has been shown that a permanent bond is formed between the molecules of carrier resin and DMDBS in the masterbatch and this bond slows down the crystallization kinetics of DMDBS in the final blend which in turn, influences its rheological behavior. Frequency sweep experiments conducted on a block copolypropylene showed that lower values of storage shear modulus (G′), loss shear modulus (G″), and complex shear viscosity (η*) are observed if DMDBS is incorporated as a masterbatch. Interestingly, a different effect was observed when the masterbatch constituents were employed directly into polypropylene, illustrating the importance of the mentioned bond between DMDBS and the carrier resin in the masterbatch. **Polyolefins J (2023) 10: 21-26**

Keywords: Polypropylene; nucleating agent; masterbatch; rheology; phase separation.

INTRODUCTION

Nucleating agents are usually added to polypropylene to enhance its physical and mechanical properties [1]. Dibenzylidene sorbitol (DBS) derivatives such as the third generation product, 1,2,3,4-bis(3,4-dimethylbenzylidene sorbitol) abbreviated as DMDBS have been extensively used in the last decades as highly efficient clarifiers for isotactic polypropylene (iPP) [2, 3]. DMDBS dissolves in polypropylene melt in a certain temperature and concentration range, and crystallizes out into a network of about 5-10 nm diameter fibrils during the cooling. The finely dispersed DMDBS nano-scale network nucleates iPP crystallization on subsequent cooling below the polypropylene crystallization temperature [4-6]. The way these additives self-assemble

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[*] Corresponding Author - E-mail: rezabagh@sharif.edu

may have a significant impact on the nucleating agent efficiency as well as the properties of the final products [7]. DMDBS phase separation creates an abrupt increase in the melt viscosity during the cooling. The temperature at which this sudden increase in the viscosity happens is considered as the phase separation temperature [8]. In the existing literature, the effects of several factors such as imposing shear flow on the melt [9], matrix molecular weight and isotacticity [4], matrix polarity [10], chain architecture [11], solubility between the polymeric matrix and the DBS [12] and cooling rate conditions [13] have been investigated so far.

Nucleating agents and clarifiers such as DMDBS are added at a rather low level to polymers, and some investigators have attempted this by incorporating nucleating agent masterbatches to facilitate processing, develop a formulation, and eliminate dispersion difficulties [14]. Despite several investigations on the effects of different factors on DMDBS phase separation from the melt, the possible effect of using masterbatch on this phenomenon has not been investigated yet. Therefore, following to an interesting useful outcome resulted from very recent research on the role of nucleating agent masterbatch carrier resin in the nonisothermal crystallization kinetics of polypropylene [15], the aim of this study is to investigate the effects of carrier resin of DMDBS nucleating agent masterbatch on the rheological behaviour of polymer melt and phase separation of DMDBS from a pipe-grade PP block copolymer.

EXPERIMENTAL

In this research, a pipe-grade polypropylene block copolymer known as EPD60R from Shazand Petrochemical Co. (Iran) and a fiber-grade isotactic polypropylene under the trade name HP552R from Jam Polypropylene Co. (Iran) were used as the parent matrix and masterbatch carrier resin, respectively. The nucleating agent DMDBS with the commercial name UCLEAR 183 was obtained in powder form from USTAB (China) and used as received.

Four samples were made according to Table 1. The control sample designated as B was free of nucleating agent and the other three samples contained 0.3 wt% DMDBS. In BNH, first DMDBS nucleating agent 5 wt% in masterbatch with the carrier of polypropylene homopolymer was prepared by a twin-screw extruder (Nanjing Giant) with L/D = 20 and then diluted in the parent matrix using the same extruder in the second step. B+N+H sample had the same composition as BNH, but all the constituents were added in one step, i.e. the masterbatch was not made before to the final compounding. BN sample containing 0.3 wt% of nucleating agent was also made in one step. The extruder temperature changed from the feeder to the nozzle in the range of 180-210°C. The screw rate was kept constant at 300 rpm.

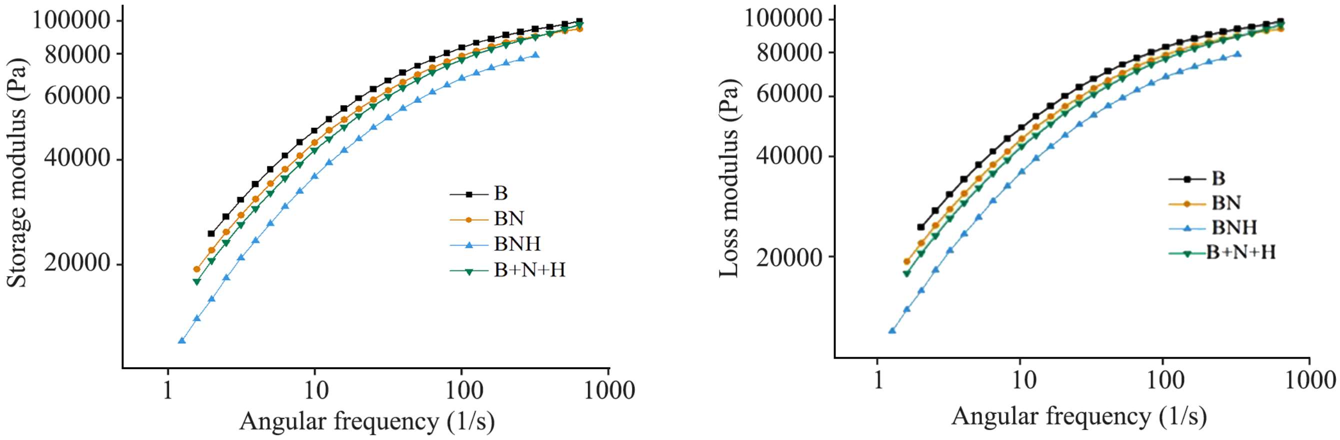
Table 1. Nomenclature terms of the samples used in this study.

Sample	Parent matrix (%)	Masterbatch with the carrier of homo-PP (%)	DMDBS (%)	homo-PP
B	100	-	-	-
BN	99.7	-	0.3	-
BNH	97	3	-	-
B+N+H	97	-	0.3	2.7

A frequency sweep experiment was performed for all samples using a rheometric mechanical spectrometer (RMS, Model MCR 301, Anton Paar, Austria) at 210°C. In all cases, plate-plate geometry with a gap distance of 8 mm was used. Rheological measurements in temperature sweep were conducted using an Anton Paar MCR-501 rheometer with cone and plate geometry with a diameter of 25 mm, a cone angle of about 1 and a gap distance of 59 μm at the rim. All measurements were made in oscillatory shear at 1 Hz and 2% strain amplitude, and the temperature was scanned at heating and cooling rates of 5°C/min.

RESULTS AND DISCUSSION

Figure 1 shows the variation of storage shear modulus (G') and loss shear modulus (G") as a function of frequency at a constant shear stress within the linear viscoelastic regime. The shear storage and loss moduli decreased with the addition of DMDBS at low frequencies, while the values of G' and G" were not affected at higher frequencies. These results agree with the observations of other investigators reported in the literature [16-18]. This is because the high frequency



(a)
(b)

Figure 1. Variation of modulus as a function of test frequency: (a) storage modulus and (b) loss modulus. The test temperature was kept constant.

dynamic response reflects small segment molecular dynamics. It is also evident that the DMDBS incorporation by means of masterbatch further decreased G' and G''. It may be argued that the positive effect of using masterbatch on the properties affected by the good dispersion of additives in the matrix is well-known. This is true that masterbatch helps achieving better dispersion of the additive in the matrix. However, it seems that DMDBS dispersion in PP is good enough that using the masterbatch does not improve its performance with better dispersion. This was shown in our previous study [15]. By conducting DSC analysis on samples containing DMDBS with and without masterbatch, it was observed that the crystallization temperature increased by about 16°C in both cases (which is significantly high) [15]. However, it has been shown in the literature that for other nucleating agents such as clay [19] or CNT [20], the changes in properties are much more significant when the additive is added using a masterbatch due to better dispersion. In fact, according to the literature, the formation of the nanofibril network is responsible for the desirable dispersion of DMDBS, which is independent of the addition method. According to Ref. [21], the introduction of DMDBS below 1 wt% into the polymer results in a perfectly uniform dispersion of the nucleating agent in the polymer because DMDBS at the aforementioned concentration completely dissolves in the molten polymer. Figure 2 shows a similar trend for the complex viscosity (η^*). In other words, the nucleating agent incorporation method also influenced the rheo-method on complex viscosity behavior.

DMDBS does not dissolve in the carrier resin during masterbatch production because its concentration is higher than 1wt% [17]. However, the different viscosity values for BNH and B+N+H samples suggest that the carrier resin chains and DMDBS particles are bonded together during masterbatch production. Bonds are likely to be preserved during subsequent heating and cooling. Therefore, short homo-PP chains, acting as plasticizers, are bonded to the nanofibril network in the BNH sample, while the network is connected to the long random-coil co-PP chains in B+N+H. As a result, chains movements are more facilitated in BNH melt than B+N+H sample, leading to a lower viscosity. To demonstrate the possible bonding formed between PP and DMDBS, the Fourier-transform infrared

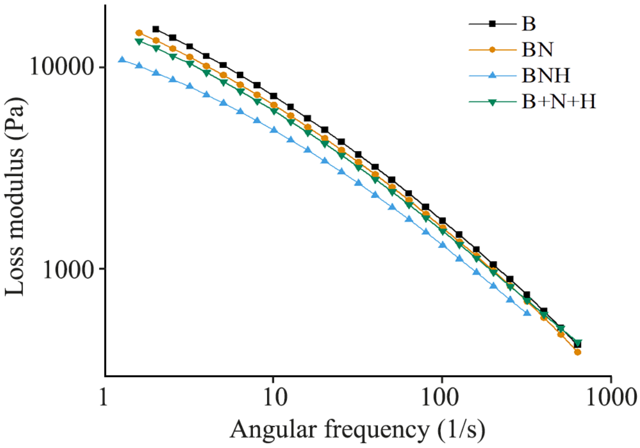


Figure 2. Variation of complex viscosity as a function of test frequency when temperature was kept constant.

(FTIR) technique is helpful, which its results will be explained in our complementary studies.

Figure 3 shows the complex viscosity as a function of temperature at a constant shear rate. All nucleated samples show an abrupt increase in complex viscosity at specific temperature. Such an abrupt increase in viscosity on cooling polypropylene containing sorbitols has been demonstrated to be due to self-assembling DMDBS into nanofibrils that form a network-like structure in the polypropylene matrix [22-24]. It should be noted that the second abrupt increase in complex viscosity is related to the polymer matrix crystallization. The addition of 0.3 wt% DMDBS, regardless of the incorporation method, leads to increased crystalline temperature at about 16°C. DMDBS phase separation occurs at about 156, 169 and 164 K for BN, BNH, and B+N+H, respectively. This shows a significant decrease in when DMDBS is added using masterbatch. Thus, it can be concluded that DMDBS incorporation using masterbatch hinders network formation. Differential scanning calorimetry (DSC) findings, reported in our previous study [15], support these observations. In this experiment, DSC results from the cooling cycle would only show the crystallization temperature. This would confirm that the second increase in the viscosity is indeed due to the crystallization. Although, the DSC was not performed exactly at the same cooling rate of the rheology test done in this study. The DSC result from our previous study [15] and similar works in the literature [23] show that the temperature at which the second viscosity increase happens agrees with the crystallization temperature range reported for PP+DMDBS.

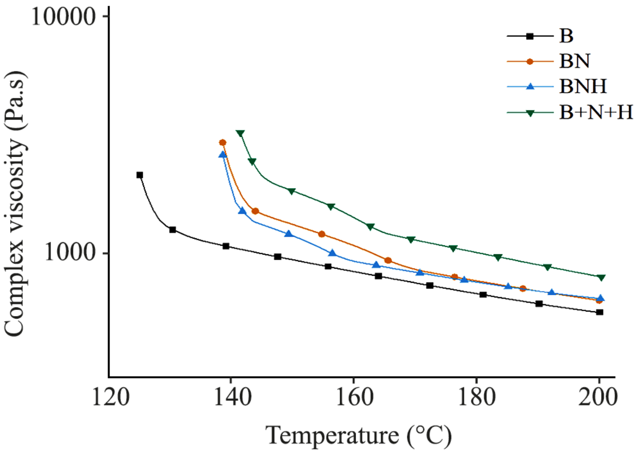


Figure 3. Variation of complex viscosity as a function of temperature when the nucleating agent was incorporated into PP via different methods. The test was performed at a constant frequency.

Comparing Figures 2 and 3, it can be concluded that the nanofibril network forms at a lower temperature for samples with lower complex viscosity at a certain frequency sweep. Although the crystallization temperature is almost the same for BN and BNH samples, different might affect the size and structure of the crystals as well as the crystallization kinetics. This is probably because of higher chain movements in BNH at a certain temperature, which impedes network formation at higher temperatures. Another possible explanation of this phenomenon is that there may be more interactions between DMDBS and the matrix in BNH.

In brief, this work demonstrated that incorporation method can influence the DMDBS phase separation temperature and the rheological behaviour of the polypropylene matrix, which might provide a useful tool for studying self-assembling organic materials.

CONCLUSIONS

This study shows that the phase separation temperature of DMDBS from polypropylene copolymer is influenced by the DMDBS incorporating method. The phase separation temperature of DMDBS decreased by about 13°C, when it was incorporated with masterbatch. Storage modulus, loss modulus, and complex viscosity at a certain frequency sweep were also influenced by the incorporation method. The different rheological behaviour and phase separation temperature are probably due to the formation of permanent bonds between DMDBS particles and polymer chains. Supplemental studies are needed to confirm this hypothesis. The mechanism by which the carrier resin affects the DMDBS phase separation is still not fully understood.

CONFLICTS OF INTEREST

The authors declare that they have no conflicts of interest.

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