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PHASE BEHAVIOR OF WATER/FORMIC ACID/POLYAMIDE 6 IN PRESENCE OF TWO KINDS OF NANOCLAYS

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SUMMARY: The effect of two kinds of modified nanoclays, Cloisite 15A (C15A) and Cloisite 30B (C30B), on the thermodynamics instability of formic acid/ polyamide 6 solution immersed into water, has been investigated. Several solutions, filled and unfilled samples, with different polymer content were prepared to study how phase separation takes place. The amount of filler was 2% by mass with respect to PA6 mass. The cloud points of solutions were measured to assess the phase demixing behavior. This is done by titration of water into solutions. It is found that the amount of water needed for appearance of cloud point (the onset of phase separation) is affected by nature filler modifiers as well as polymer content. It follows that C30B>unfilled>C15A. In the case of C15A, an earlier nucleation was observed in which it was probed by microscopy. The optical photomicrographs show that there is a dense phase surrounding nanoparticles in which it could be distinct through the phase contrast technique. It seems that the polymer chains move from solution onto the particles which behave as nuclei. It can be happened when the solution become unstable. It would then follow that an earlier demixing takes place prior to the separation of polymer solution. In contrast with C15A, in case of C30B the solution was separated into two phases without earlier nucleation. Furthermore the binodal curve shifted toward polyamide 6/water side. Consequently, the stability of solutions filled by C30B increases thermodynamically while which of filled by C15A decreases. In this work we are presenting a detailed observation with strong argument for assessing the equilibrium and non-equilibrium stability of polymer solution filled with silica nanolayers.

KEYWORDS: phase behavior, silica nanolayers, non solvent induced phase separation

INTRODUCTION

Most of polymeric products have been produced by polymer blends or polymeric solutions. These polymeric systems maybe undergo phase separation during manufacturing procedure. The associated mechanical, chemical, thermal, and various other properties of products are largely determined by the resulting phase behavior. In some studies it was shown that the introduction of solid filler into a binary polymer mixture could affect thermodynamic and kinetic of phase separation [1-5]. These effects are especially important because they can have a significant impact on the processing and properties of the materials.

It is worth saying that introduction of nanofillers may lead to an increase or a decrease of the miscibility between the two polymers [3-4]. Theoretical and experimental studies show that when polymer radius of gyration is smaller than nanoparticle radius, addition of nanoparticles depresses the stability of homogenous phase in polymer blends and vice versa [2-3]. Lipatov and coworkers [4] have investigated the effect of filler concentration on the phase separation in polymer blends. For the first time, they observed that thermodynamic stability of the filled blend may increase or decrease depending on the amount of the filler introduced.

By the addition of nanoparticles into polymeric blends miscibility of blend may increase. Increase in miscibility can be considered from two viewpoints: (1) equilibrium compatibilization- after the filler introduction, thermodynamic stability of the system increases due to decrease of the free energy of the system. That is because of favorable exothermic interactions between polymer chains and functional groups on surface of filler. (2) Non-equilibrium comatibilization while due to interaction of polymer chains with nanoparticles, the mobility of the macromolecules diminishes and therefore, kinetic of phase separation decrease dramatically [5]. From this point of view though the system is in a thermodynamically unstable state, it is not able to phase separates due to restrictions in molecular mobility of polymer chains imposed by the filler surface in the border layer.

All of the previous researches have investigated thermal induced phase separation (TIPS) processes. In the present work the effect of two types of organically modified montemorillonites on the phase separation behavior of water/formic acid/polyamide6 (PA6) system will be investigated in a nonsolvent induced phase separation (NIPS) process.

EXPERIMENTAL

PA6 pellets were obtained from Alyaf Company with viscosity-average molecular weight of 50 kDa. Formic Acid and Distilled water were used as solvent and nonsolvent respectively. Two types of silica nanolayers with trade mark Cloisite 15A (C15A) and Cloisite 30B (C30B) were used. C15A and C30B are natural montemorillonites that modified with a dimethyl, dehydrogenated tallow, quaternary ammonium ion, and a methyl, tallow, bis-z-hydroxyethyl ammonium ion respectively.

In order to blend PA6 pellets and nanoparticles melt blending technique was used. First of all, PA6 pellets, C15A, and C30B were dried in an oven for 16h at 80°C to prevent polymer degradation in extruder. A certain amount of C15A was mixed with PA6 pellets in a twin screw extruder to perform pellets containing 2%wt of C15A. Similar procedure was done for PA6 pellets containing 2% wt of C30B. A certain amount of these chips were dissolved in formic acid (FA) to perform solutions with 3%, 5%, 8%, and 10% wt/wt. Phase separation behavior of these solutions was studied by titration a certain amount of water into them. Cloud points were measured 24 h after titration.

RESULTS AND DISCUSSION

By considering phase separation in filled and unfilled solutions, for the first time it was observed experimentally that two steps of phase separation may take place in filled polymeric solutions. The distance between silica nanolayers after intercalation of polymer chains can be calculated through $\delta = V / S$ [4]. V and S are the volume of solution and silica nanolayers specific area respectively. Only when $\delta \leq R_g$ **,** all of polymer chains can transit into the filler surface (in the border layer). The amount of silica nanolayers that were used in this study were very low inasmuch as even by assumption that they were exfoliated totally, only a low fraction of polymer chains were able to transit in the border layer. So, a lot of polymer chains have not been able to interact with functional groups on silica nanolayers or with the surface of them because in our experiments δ is about 60 times more than R_g. Then these polymer chains stay in the bulk. In this case it is reasonable to assume that silica nanolayers divide the system to two subsystems-a border layer system and a bulk one, which have different Gibbs free energies.

As expected two steps of phase separation for C15A filled solutions were observed. However for C30B filled solutions only one step of phase separation was seen. By comparison the organic modifiers of these two fillers, two outstanding differences can be considered. The more important one is that C30B modifier has two hydroxyl groups which is able to form hydrogen bonds with PA6 chains and with water and formic acid molecules; however C15A modifier not only is not able to form any favorable interactions with PA6 chains, it has also endothermic interactions with them. The second difference is that C30B modifier has only one aliphatic tail while C15A modifier has two aliphatic tails. So PA6 chains are able to interact with C30B surface easier than C15A surface. By considering cation exchange capacity (CEC), specific surface, and organic modifier of these silica nanolayers it is demonstrated that PA6 chains are not able to reach to the surface of C15A in order to form favorable interactions with C15A surface. Besides PA6 chains which exist in border layer must pay entropic penalty as a result of stretching. Then in C15A filled solutions Gibbs free energy of border layer system is highest in comparison with bulk system or unfilled solutions. Therefore phase separation in border layer system of C15A filled solutions takes place by lower values of nonsolvent in comparison with unfilled solutions or the bulk system. Then in C15A filled solutions the first step of phase separation takes place in the border layer system and the second one takes place in the bulk system. These claims were demonstrated by experiments. Fig. 1 shows two steps of phase separation in a typical C15A filled solution. Fig. 1a shows the solution before addition nonsolvent. It is not a transparent solution because of presence of silica nanolayers. By the addition a certain amount of water to this solution, phase separation in border layer system takes place and after 24 h PA6 chains in the border layer and silica nanolayers precipitate in the shape of a white clod (Fig. 1b). The solution above the white clod is completely transparent and then it is reasonable to conclude that there are not any silica nanolayers in the solution. By addition more water, phase separation in the solution above the white clod takes place too (Fig. 1c).

Fig. 2 represents cloud point curves of unfilled solutions and first step of phase separation in C15A filled solutions. It seems that presence of C15A decreases thermodynamic stability of PA6/FA solutions. By precipitation of some PA6 chains in the first step of phase separation, the solution above the white clod become more dilute than unfilled solutions then it can endure more values of water at second step of phase separation in comparison to unfilled solutions.

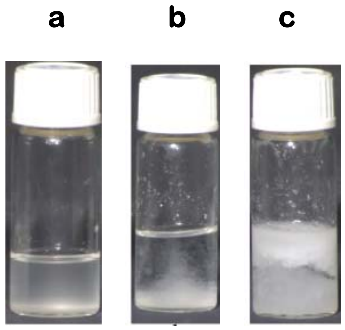

Fig. 1 C15A filled solution: (a) before addition of nonsolvent; (b) first step of phase separation; (c) second step of phase separation.

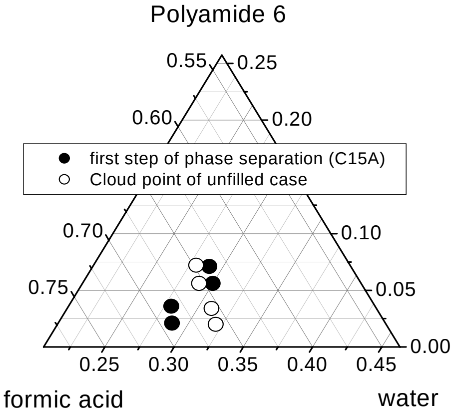

Fig. 2 Cloud point curves of unfilled solutions (°) and first step of phase separation in C15A filled solutions (•).

As mentioned earlier for C30B filled solutions, only one step of phase separation was observed. In C30B filled solutions due to formation of hydrogen bonding between PA6 chains and hydroxyl groups of C30B modifier and possibility of favorable interactions between PA6 chains and C30B surface, Gibbs free energy of border layer system is less than Gibbs free energy of bulk system. Therefore, phase separation in bulk system of C30B filled solutions takes place by lower values of water in comparison to border layer system. In our experiments bulk systems form high fraction of filled solutions. So in C30B filled solutions, by occurrence of phase separation in bulk system, all the solutions undergo turbidity. Therefore, it seems to be impossible to detect the second step of phase separation experimentally. This is related to border layer system by addition of more water to the solutions. Fig. 3 compares cloud point curves of unfilled and C30B filled solutions. It seems that the presence of C30B increases the thermodynamic stability of PA6/FA solutions.

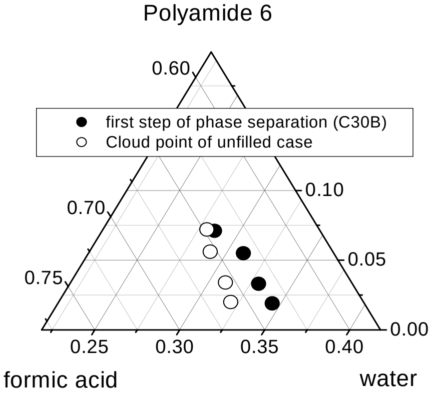

Fig. 3 Clod point curves of unfilled solutions (°) and first step of C30B filled solutions (•).

CONCLUSION

Ginzburg [3] and Mackay et al. [2] have demonstrated that the addition of nanoparticles, depending on particle radii, may increase or decrease the compatibility of polymer blends. Lipatov and coworkers have shown that compatibility of polymer blends may decrease or increase by introduction of nanofillers depending on concentration of nanofillers. In the present work we have demonstrated that addition of silica nanolayers-depending on the type of their surfactant may increase or decrease thermodynamic stability of polymeric solutions.

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