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Shear Influence on the Phase Behavior of Systems Containing a Homopolymer A and a Block Copolymer AB

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Summary: Cloud point temperatures (T_{cp}) and crystallization temperatures ($T_{l/s}$) of the ternary system tetrahydronaphthalene/poly(ethylene oxide)/poly(dimethyl siloxane-*b*-ethylene oxide) have been measured at different constant shear rates using a rheo-optical device and an advanced rheometer. The cloud points temperatures (UCST-type phase diagram) are reduced by several degrees as the system flows; i.e. the shear can suppress the phase separation and enlarge the homogenous region. The crystallization kinetics of PEO in the ternary mixtures has been investigated isothermally and non-isothermally at quiescent state and under shear. The shear could strongly enhance the crystallization i.e. the $T_{l/s}$ shifts to higher temperatures and the induction time, t_0 (the time needs for the onset of crystallization) substantially decreases with increasing shear rate during the non-isothermal and isothermal crystallization processes, respectively. The isothermal crystallization kinetics at quiescent state and at different shear rates was analyzed on the bases of Avrami approach. The Avrami exponent which provides qualitative information about the nature of the nucleation and growth process, was found to be shear rate and temperature dependent. The Avrami exponent increased from ~3 at the quiescent state to as large as 9 at $\dot{\gamma} = 100\ \mathrm{s}^{-1}$.

Keywords: Avrami exponent, cloud point, crystallization kinetics, shear rate, ternary mixture

Introduction

The influence of flow on the phase behavior of polymer blends and polymer solutions has been recognized for several decades.[1-3] Knowledge of such behavior would aid in the process design and control the final products. Shear-induced mixing and demixing have been observed, as opposed to the case of small molecular mixtures where only shear-induced mixing reported. In the early study, Silberberg and Kuhn[1] have investigated a ternary polymer mixture of polystyrene/ethyl cellulose in benzene under steady shear flow. They found that the polymer droplets were elongated at moderate shear rates. At higher shear rates the droplets break-up into small sizes leading to homogenization. An increase in the cloud point temperature as large as 28K for solutions of polystyrene in dioctyl phthalate at shear rate

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up to 1360 s^{-1} has been observed by Rangel-Nafaile et al.[2] The effects produced by shear have been different perpendicular and parallel to the flow direction for the polystyrene/ polybutadiene/dioctylphthalate (PS/PB/DOP) mixture.[3] Previously we have also initiated systematic experimental and theoretical investigations of shear-induced phase changes in polymer blends and solutions.[4-9] One of the central observation of that work concerns the dominant role the rheological properties of polymers play for shear effects.

A great deal of effort has been devoted to elucidate the structure formation of crystalline polymers under shear flow.[10-15] The earliest work was reported by Trelour and Gent who observed a decrease in the onset of crystallization for cross-linked natural rubber with increasing extension ratio.[10,11] Fritzsche et al. investigated the crystallization kinetics of poly(ethylene oxide), PEO, under varying condition of shear rate and temperature.[12,13] They found that the kinetics of crystallization process was altered by shear, which was seen as a decrease in the induction time and elevation of the Avrami exponent. Eder et al.summarized some of the efforts made in the past to cast more light on the mechanisms of flow-induced crystallization in polymer melts.[15] Similar investigations for other systems, which led to the same conclusion, have recently been reported.[16-18]

In this work we shall investigate the simultaneous effect of shear on the phase separation and crystallization transitions of a ternary mixture of two immiscible polymers in a common solvent which is thermodynamically good for both components. The isothermal and non-isothermal crystallization kinetics will be investigated at quiescent state and at different constant shear rates. The isothermal crystallization kinetics will be also analyzed on the bases of Avrami approach.

Experimental Part

Materials and methods

Poly(ethylene oxide), PEO, and poly(dimethyl siloxane-*b*-ethylene oxide), P(DMS-*b*-EO), COP were obtained from Fluka Chemical Co., Germany. The weight average molecular weight, M_w, and the polydispersity, M_w/M_n, of PEO were 27 kg/mol and 1.3, respectively. The COP contains 75 wt% EO and is relatively low molecular weight (M_w = 0.6 kg/mol), its M_w/M_n = 1.3. PEO was dried for 7 days at 50 °C under vacuum before use. COP was employed without treatment. The solvent 1,2,3,4-tetrahydronaphtalene, THN, was also obtained from Fluka Chemical Co., Germany with 99.8 wt% purity and used as supplied. The boiling point was 205 °C and the density 0.969 g/cm.^{3}

Details of rheo-optical apparatus have been described elsewhere[9]. The apparatus was designed to measure the transmitted light intensity, I/I_0, where I is the twice of light intensity having passed through the solution and I_0 is the intensity of primary laser beam. The measurements were carried out at different constant shear rates ranged from 0 to 500 s^{-1} at 0.25 °C/min cooling rate.

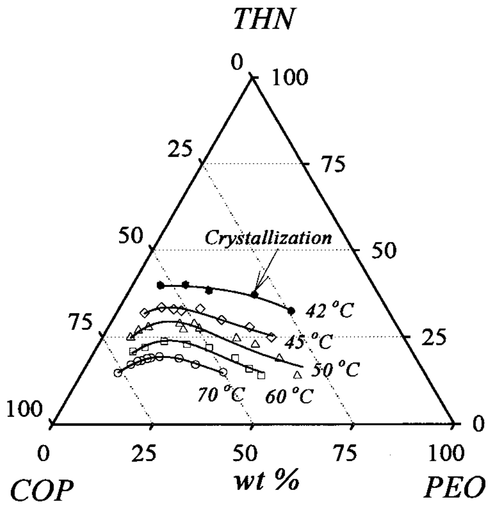

Figure 1. Equilibrium phase diagram of the system THN/COP/PEO at the indicated temperatures as obtained from turbidmetric titration.

The equilibrium cloud point temperatures, T_{cp}, and crystallization temperatures $T_{l/s}$ were estimated in the course of turbidimetric titration. Different solutions of PEO in THN (ca. 5 ml) of typical PEO content were titrated with the block copolymer at constant temperature. Figure 1 demonstrates the equilibrium phase diagram, obviously a typical UCST-type phase diagram was determined at different temperature, however, at 42 °C only $T_{l/s}$ was observed. The existing of only $T_{l/s}$ was conformed by polarized light microscope, which shows only the spherulitic structure of PEO in the mixtures without any indication for the phase separation morphology. The block copolymer may incorporate small amounts of PEO and form mixed crystals, this effect is not considered in the present paper.

The rheological measurements during the crystallization process were carried out using an advanced rheometer, AR 1000 with two 40 mm cone-and-plate geometry with cone angle = 1°. The measurements were carried at different constant shear rates up to 100 $s.^{-1}$

Results and Discussion

Crystallization kinetics at quiescent state

In order to understand the effect of shear on the crystallization kinetics, the crystallization process at quiescent state must be investigated. A typical isothermal crystallization process for THN/COP/PEO = 40/43/17 mixture after melting at T_m = 80 °C for 10 min and rapid quenching to different crystallization temperatures is demonstrated in Figure 2. The figure shows the crystallization time dependence of transmitted light at different crystallization temperatures. The crystallization occurs isothermally at the onset of decreasing the transmitted light of a completely transparent sample (melt sample). The induction time of

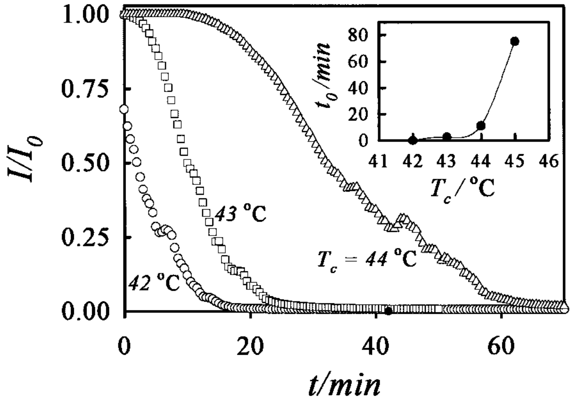

Figure 2. Crystallization time dependence of the transmitted light for THN/COP/PEO = 40/43/17 mixture after melting at 80 °C for 10 min and quenched to different T_c. The inset shows the crystallization temperature, T_c, dependence of the induction time, t_0.

crystallization, t_0, is defined as the time at which the transmitted light starts to decrease. With the present system the changes in the transmittance of light upon the crystallization time are very sharp and repeated measurements reproduce t_0 within an interval of 30 sec. The crystallization kinetics is substantially affected by the crystallization temperature i.e. t_0 greatly increases with increasing the crystallization temperature; t_0 at 44 °C is approximately four times greater than the corresponding value at 43 °C under the same experimental conditions. Obviously, the crystallization at a temperature lower than 43 °C is very fast and could produce a considerable amount of crystals already during cooling from the melt to the crystallization temperature. However the crystallization process at temperatures higher than 44 °C is very slow and the time needs for complete crystallization is very long.

A general treatment of the crystallization kinetics was developed by Avrami[19] and first applied to polymeric systems by Mandelkern et al.[20] According to this theory the overall crystallization process of PEO can be described by

$$X_t = 1 - \exp(-kt^n) \qquad (1)$$

where X_t is the weight fraction crystallized at a time t, k is the rate constant which is a function of crystallization temperature, and n is the Avrami exponent. The rate constant, k includes the combined effects of nucleation and growth; however, the Avrami exponent provides qualitative information about the nature of the nucleation and growth processes. Linearity between the light transmittance and the degree of crystallinity is assumed (arbitrary hypothesis) for this analysis. The change of the transmitted light during the crystallization process can be converted to the normalized light transmittance, $I_n(t)$:

$$I_n(t) = \frac{I/I_0(t) - I/I_0(0)}{I/I_0(\infty) - I/I_0(0)} \qquad (2)$$

where $I/I_0(t)$ is the light trnsmittance at time t, $I/I_0(0)$ is the melt value, and $I/I_0(\infty)$ is the value at the end of crystallization process. Using this value of the normalized light transmittance, the Avrami-type equation can be rewritten as follows

$$I_n(t) = 1 - \exp(-kt^n) \qquad (3)$$

The kinetics parameters of this equation (the exponent n and the rate constant k) can be obtained by taking the double logarithm of equation 3 and expressing it as

$$\log(-\ln(1-I_n(t))) = \log k + n\log t \qquad (4)$$

The plot of $\log(-\ln(1-I_n(t)))$ *vs.* $\log t$, yields straight line with a slope equal to n and an intercept equal to $\log k$. A typical Avrami-type plots for the THN/COP/PEO = 40/43/17 mixture at different crystallization temperatures are shown in Figure 3. The values of Avrami exponent determined for this mixture was in the range of 1.7 - 3.5 at the temperature range 42 - 44 °C. The rate constant, log *k*, was also found to be temperature dependent and changed from –0.87 at 42 °C to be –5.8 at 44 °C. The sharp decrease in the *k* value with increasing temperature is attributed to the fact that the crystallization rate at 42 °C is several times faster than that at 44 °C (see Figure 2).

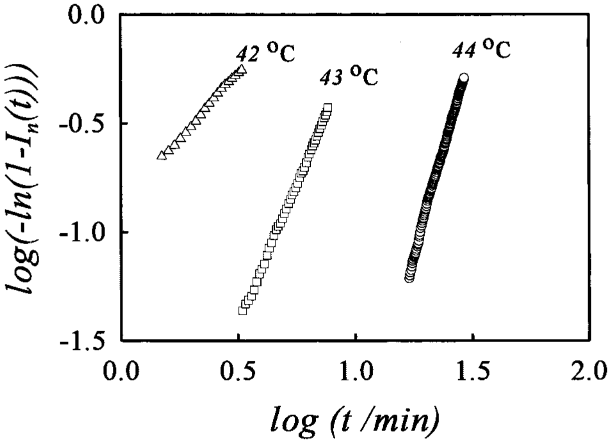

Figure 3. Avrami-type plot for the normalized light transmittance at different crystallization temperatures for THN/COP/PEO = 40/43/17 mixture.

Effect of Shear on the Crystallization Kinetics

The non-isothermal crystallization process of THN/COP/PEO = 40/43/17 mixture under different constant shear rates is shown in Figure 4. The sample is melted at 80 °C for 10 min and then cooled (0.25 °C/min) under different constant shear rates. Obviously as T falls below the crystallization temperature at constant shear rate, the shear stress σ increases dramatically. This substantial increase in the σ during the crystallization process is attributed to the continuos increase of the volume fraction of the crystalline part which may act like crosslinks. The onset of crystallization shifts to higher temperature with increasing shear rate. This behavior is attributed to the fact that the shear increases the orientation in the molecular chains and consequently lowers the conformational entropy. This reduction in the total entropy of fusion allows the crystallization to occur at higher temperatures than in the quiescent state.[21,22]

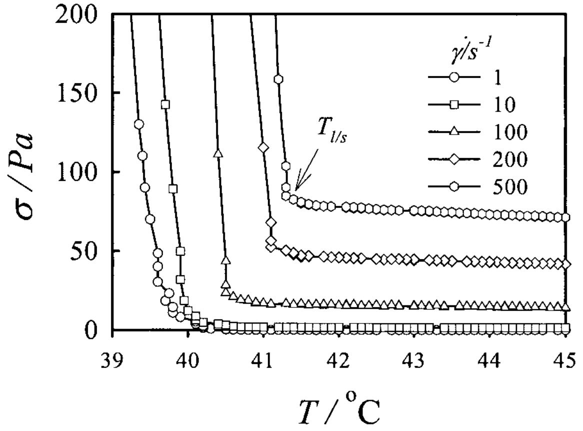

Figure 4. Temperature dependence of the shear stress σ for THN/COP/PEO = 40/43/17 mixture at different shear rates. The crystallization temperature $T_{l/s}$ is marked by a rapid increase in the σ.

Similar behavior (shear-induced crystallization) can be also obtained from the isothermal rheological measurement of the same mixture as shown in Figure 5 which represents the crystallization time dependence of the steady shear viscosity η at different constant shear rates. Once the crystallization process takes place a rapid increase in the sample viscosity was observed. A decrease in the viscosity with crystallization time at high shear rates was also detected as clearly seen in the Figure. This experimental fact is due to the disruption of the crystalline aggregate during shear. The disruption of the crystalline aggregate increases with shear rate. Several authors including us have successfully investigated the kinetics of crystallization for semi-crystalline polymers using rheological measurements.[23-29] The rheological technique for studying the crystallization kinetics was considered to be more sensitive than conventional techniques like DSC.[23,24] Linearity between viscosity and the degree of crystallization is also assumed. Based on this hypothesis one can convert the

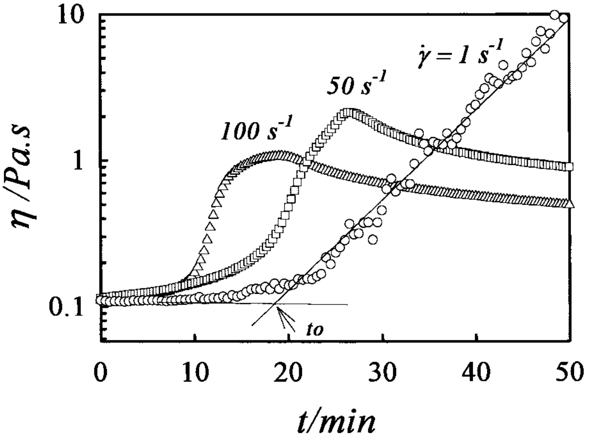

Figure 5. Crystallization time dependence of the steady shear viscosity for THN/COP/PEO = 40/43/17 mixture at 43 °C and different shear rates, the tangent drawn to determine t_0.

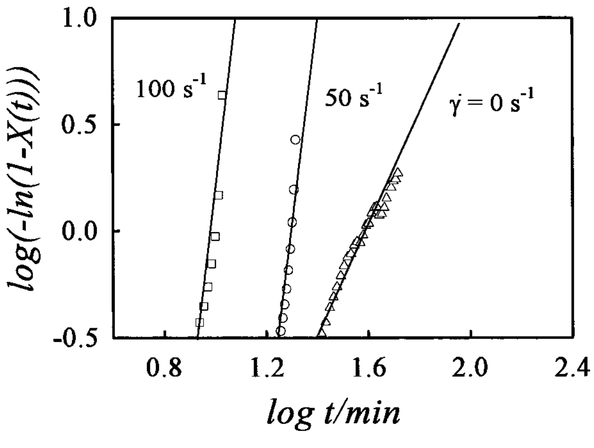

Figure 6. Avrami-type plot for the normalized shear viscosity at different shear rates and for the normalized light transmittance at quiescent state.

steady shear viscosity during the crystallization (Figure 5) to its normalized form as applied for the light transmittance (see equation 2). The Avrami-type plots at 43 °C at different shear rates (the figure includes also the sample at quiescent state obtained from figure 2) are shown in Figure 6. It is apparent that the value of the Avrami exponent increases dramatically with shear rate i.e. the exponent n increases from about 3 at quiescent state to 9 at $\dot{\gamma} = 100 s.^{-1}$ This behavior was attributed to the fact that, when a crystalline aggregate is growing in a melt under shear, it is subjected to stress. This stress not only causes orientation in the melt but also could cause disruption of the crystalline aggregate. This disruption results in the introduction of more nuclei into the melt as the crystallization proceeds and consequently accelerates the nucleation process. Similar behavior has been observed recently for the crystallization kinetics of some semi-crystalline polymers under shear flow using rheological technique.[28,29]

Simultaneous Shear effect on the T_{cp} and $T_{l/s}$

A typical example for the temperature dependence of the light transmittance for the THN/COP/PEO = 25/58/17 mixture is demonstrated in Figure 7. This composition contains both the T_{cp} (liquid-liquid) and $T_{l/s}$ (liquid-solid or crystallization), so it would be interested to

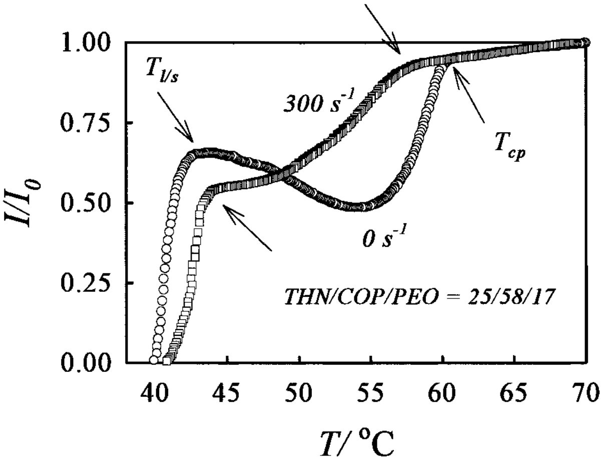

Figure 7. Light transmittance, I/I_0, of THN/COP/PEOP = 25/58/17 mixture as a function of temperature at quiescent state and at $\dot{\gamma} = 300 s.^{-1}$

check the effect of shear on these two transitions. The sample is phase separated upon cooling (0.25 °C/min) from one-phase regime and then crystallized at a temperature close to the crystallization temperature of PEO. Obviously the shear can significantly influence on both T_{cp} and $T_{l/s}$ transitions. The T_{cp} shifts several degrees to lower temperature, however on the other hand, the $T_{l/s}$ shifts to higher temperature with shear. Based on this experimental fact one can say that the shear can simultaneously induced mixing and crystallization within a single mixture. The data in Figure 7 can be quantitatively represented as shear dependence of the T_{cp} and $T_{l/s}$ transitions (see Figure 8).

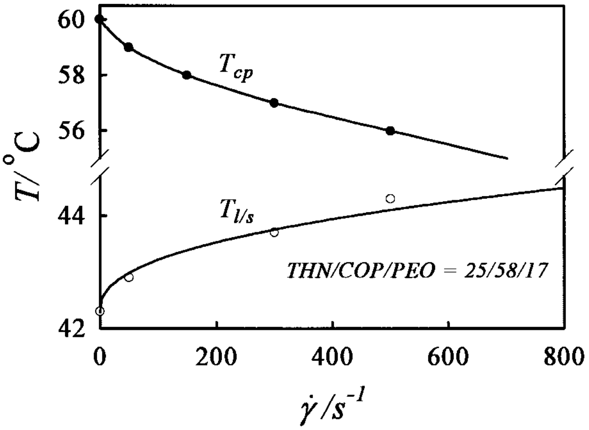

Figure 8. Shear rate dependence of T_{cp} and of $T_{l/s}$ for THN/COP/PEO = 25/58/17 mixture.

Conclusion

Shear effect on the phase behavior of a homopolymer A and a block copolymer A-B in a common solvent has been investigated. The liquid-liquid and liquid-solid transitions were found to be strongly influenced by shear flow. Shear-induced mixing and shear-induced crystallization have been observed in a single mixture. The crystallization kinetics was also changed by shear flow. The induction time, t_0, of the crystallization process decreases dramatically with increasing shear rate. An elevation in the Avrami exponent was also detected under shear, indicating that the shear accelerated the nucleation of crystallization process. These results are interpreted in the terms of the orientation of the molecular chains induced by the shear and consequently an enhancement of the crystallization process.

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