유변학적 성질 측정으로 측정한 고분자 계면에서의 반응 kinetics 와 morphology 변화

김황용, 정운용, 김진곤

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Reaction Kinetics and Morphological Changes at Polymer-Polymer Interface measured by Rheological Properties

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Abstract

In this study we investigated the reaction kinetics by a convenient but useful method – rheology to characterize the interface between two immiscible blends with a reactive compatibilizer. Also, we made an attempt to correlate changes of interface roughness with rheological properties.

The blend systems employed in this study was mono-carboxylated polystyrene (PS-mCOOH) and an poly(methyl methacrylate-*ran*-glycidylmethacrylate) (PMMA-GMA). PS-mCOOH was synthesized by an anionic polymerization and PMMA-GMA by a free radical polymerization. We prepared two plates of each polymer using compression molding with a smooth surface molder, then put one upon another. As soon as these two plates welds together inside a rheometer under nitrogen environment, the torque and moduli were obtained with reaction time at different temperatures.

Through the analysis of this modulus change with reaction time, we estimated interfacial reaction and roughening. The increment of modulus in initial state can be correlated to the extent of reaction. We obtained the reaction kinetic constant by fitting appropriate kinetic equation into experimental data. We also showed that increment of modulus in later state was due to by roughened interface.

Introduction

Reactive blending of immiscible polymers is a useful strategy to produce polymeric materials with high performances. In reactive blending system, the reaction kinetics and interfacial roughness are important to analyze the interface between two immiscible blends with a reactive compatibilizer. Nevertheless, only a few methods are available to study reaction kinetics and interfacial roughness. According to recent Bousmina *et al* [1,2], the interdiffusion of polymer chain was calculated by rheological properties. We applied this idea to reactive polymer blend system. Namely, we investigated the reaction kinetics by a convenient but useful method – rheology. And then we made an attempt to correlate changes of interface roughness with rheological properties.

Experimental

We used blend systems consisting of mono-carboxylated polystyrene (PS-mCOOH) synthesized anionically and an poly(methyl methacrylate-*ran*-glycidylmethacrylate) (PMMA-GMA) prepared by a free radical polymerization. For comparison with non reactive blend system, we used poly(methyl methacrylate) (PMMA). Molecular weights of materials used in this study have been summarized in Table 1.

We prepared two plates of each polymer using compression molding with a smooth surface molder and annealed at $130^{0}C$ for 24 hour. As soon as two plates welds together inside a rheometer under nitrogen environment, the torque and moduli were obtained with

reaction time at different temperatures.

We measured the interface thickness by atomic force microscopy (AFM), after removing PS plate by rinsing with selective solvent of cyclohexane at 40^0C.[3] The interface was investigated by Transmission Electron Microscopy (TEM).

Result and Discussion

The complex viscosity ($\eta*$) at 180^0C with time for various blend system is showed in Figure 1. Through the analysis of this complex viscosity change, interfacial reaction and roughening are investigated. At short times of reaction (0 ~ 200 min), the increment of modulus can be correlated with the extent of reaction. We analyzed this reaction by first order reaction and second order reaction rate equation. The conversion was obtained from complex viscosity change as follows:

$$X_A(t) = [\eta^* (t) - \eta^*no(t)]/[\eta^* sat - \eta^*no,sat] \qquad (1)$$

where η $*sat$ is $\eta*(t = t\,sat)$ and η $*no$ is the complex viscosity without coupling reaction

We found that the first order reaction kinetics is slightly better than by the second order reaction kinetics. The reasons might be due to the fact that (1) PS plate is consist of fully reactive species, and (2) the reaction kinetics in reactive blend system is similar to the kinetics of gas/solid in surface science.[4]

It is also found in Figure 1 that complex viscosity (and shear modulus) at longer times (> 200 min) was slowly increased. We considered this increment related the broadening of interface thickness (or the increment of interface undulation). Sharp interface (small interface thickness) may be the barrier to interrupt the transport of momentum. With increasing the interface thickness, more reaction might be expected thus more graft copolymers are formed near the interface. The interface corresponding to higher complex viscosity becomes more roughened.

Summary

The rheological method can be used to investigate reaction kinetics and interface thickness in reactive blending system. From rheological properties changes, our blend system exhibits the first order reaction kinetics. The roughened interface generated by excess reaction induced larger complex viscosity.

References

[1] M. Bousmina, H. Qiu, M Grmela, and J. E. Klemberg-Sapieha, Macromolecules, 31, 8273, (1998)

[2] H. Qiu and M. Bousmina, Macromolecules, 33, 6588, (2000)

[3] J. K. Kim, W.-Y. Jeong, J.-M. Son, and H. K. Jeon, Macromolecules, 33, 9161, (2000)

[4] H. T. Oyama and T. Inoue, Macromolecules, 34, 3331, (2001)

Table 1. Molecular Characteristics of Materials used in this study

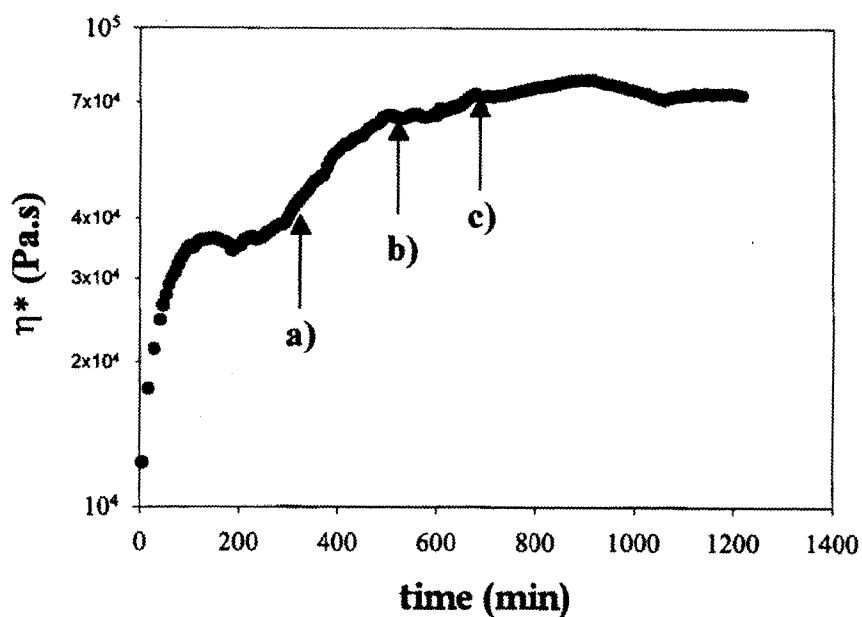| Sample	Mn	Mw	Mw/ Mn
PMMA	80,400	118,100	1.47
PS-mCOOH	119,000	135,000	1.13
PMMA-GMA	68,000	115,500	1.70

Figure 1. Plots of η* at 180°C versus time for PS-COOH/PMMA-GMA blend