Reaction Kinetics Studies on Plasma-Treated Polypropylene–Polystyrene Interfaces

Da Yan, Chu Guo, Xinhua Xu, Guiqiu Ma, Jing Sheng

School of Materials Science and Engineering, Tianjin Key Laboratory of Composite and Functional Materials, Tianjin University, Tianjin 300072, China

ABSTRACT: In this article, the effects of low temperature Ar glow discharge plasma modification on the surface of polypropylene (PP) and polystyrene (PS) plates were characterized by X-ray photoelectron spectroscopy, and the temporal change of the complex viscosity (η^*) of PP/PS plates with a sandwich structure were measured by a rotational rheometer. The results showed that the formation of reactive groups on the surface of PP and PS plates was due to the reaction of O_2 with some free radicals when exposed to air. In the rheology study, because of the increase of interfacial adhesion strength due to the coupling reaction between the reactive groups at the interface, η^* increased with welding time. There were two distinct stages for the changes of η^* with welding time. In Stage I, η^* increased rapidly and indicated a reaction-controlled kinetics, the apparent reaction kinetics was a first-order reaction; in Stage II, η^* increased slowly and indicated a diffusion-controlled reaction. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: surface modification; polymer rheology; interfaces, kinetics

INTRODUCTION

Since most of polymers are thermodynamically immiscible, their interfacial adhesion is quite poor due to poor mutual diffusion of molecules at the interface.[1] To obtain useful polymer blends and alloys, researchers focus on the interfacial adhesion, because the final physical or chemical properties of polymer blends and alloys depend mostly on the interfacial properties as well as the properties of both component polymers.[2] *In situ* reactive blend is an approach that can be used to improve the interfacial properties without compatibilizer.[1–7] One method of reactive blends is the formation of an *in situ* graft or a block copolymer by chemical reactions between reactive groups on component polymers.[5–8] Though such interfacial agents have been used for a long time, the diffusion of functional groups to the interface is still quite difficult,[2] especially in the blends of chemically inert polymers, such as polypropylene (PP) and polystyrene (PS). Therefore, grafting functional groups, which can interact with other polymers, on the polymer backbone has become an important research area in the reactive blends. Lots of methods have been used in the surface modification.[2,9–11] Among them, plasma is a clean and green method to modify the surface properties of polymers.[12–20] Pascu[13] found that Ar plasma treatment led to the incorporation of polar groups on the exposed polymer films.

Reactive blends are usually prepared by using a bachelor mixer or two-screw extruder, where there is a complex flow combined by shear and elongational flows. Thus, some research groups use a planar geometry of two polymers in the study of reactive kinetic to exclude the effect of complex flows. Kim et al.[21] developed a rheological technique to evaluate the reaction kinetics by employing the assumption that the rheological properties were related to the amount of the *in situ* formed graft (or block) copolymers for a reactive blend. In this case, viscosity is simpler than more sophisticated methods such as forward recoil spectrometry and X-ray photoelectron spectroscopy (XPS) to determine the compatible and reaction at the polymer blend interface, even though the excess of interface is not determined quantitatively.[5,21–23]

Plasma is a partly ionized gas and can be defined as a quasi-neutral particle system in the form of gaseous or fluid-like mixtures of free electrons, ions, and radicals, generally also containing neutral and excited particles (atoms, molecules).[24] Thus, the components of functional groups on the plasma-modified polymer surface were very complicated, such as C—O, C=O, C—OOH and even active radicals, and
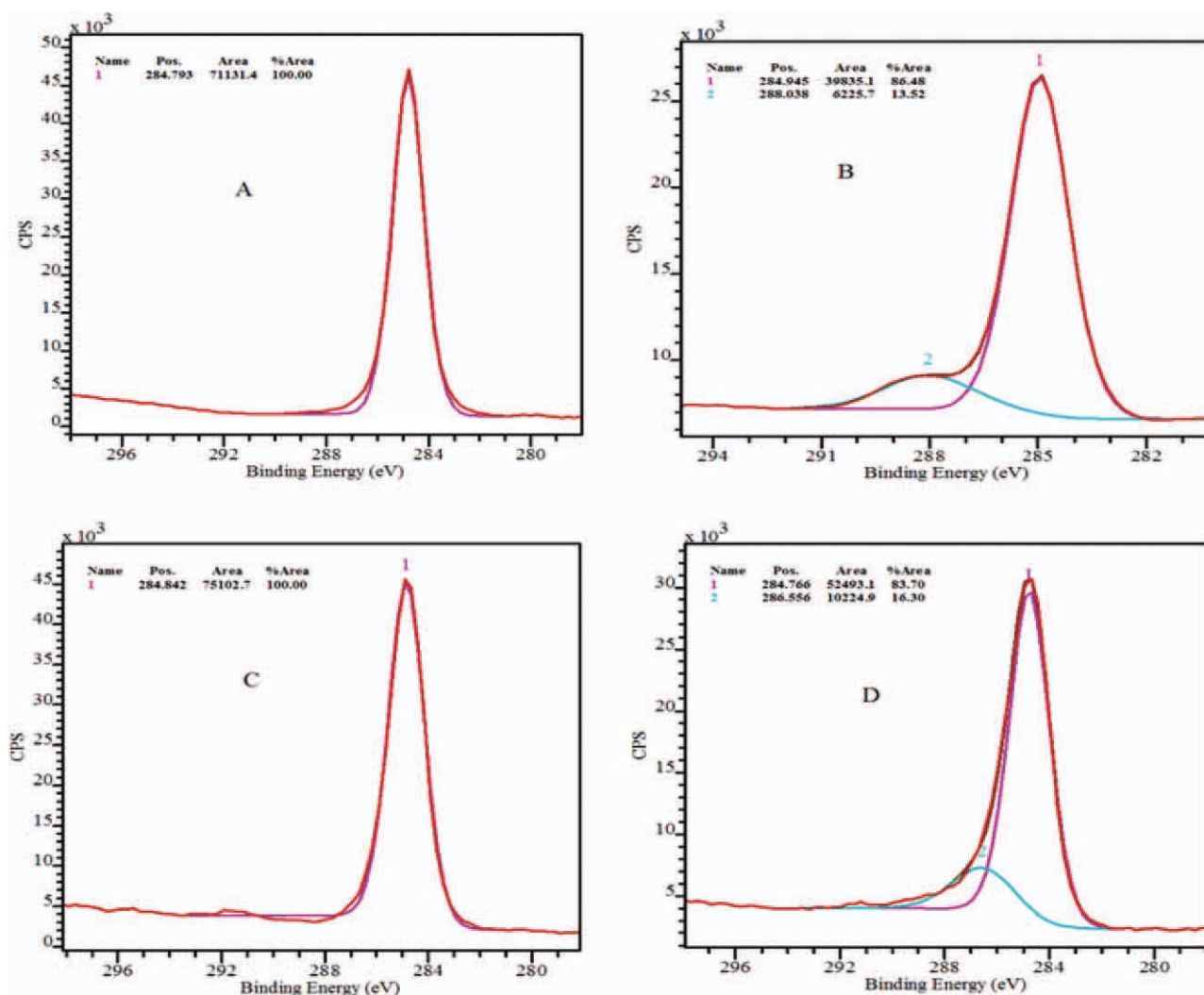
Figure 1 XPS spectra of untreated and plasma-treated PP and PS [(A): untreated PP; (B): plasma-treated PP; (C): untreated PS; (D): plasma-treated PS]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the quantity of functional groups on the surface was indeterminate. Unlike the common reactive blends, it was very difficult to monitor the reaction kinetics at the interface of plasma-modified polymer plates due to the wide varieties and uncertain quantities of active radicals and functional groups. In this article, we introduce a rheological method to evaluate the interfacial reaction of surface-modified PP/PS sand- wich geometry plates (SGP). Reactive groups were introduced on the surface of PP and PS by Ar plasma. The reaction between them occurred easily during the test at high temperature, giving the *in situ* graft copolymers of PP-*g*-PS, and the changes of complex viscosity could be studied by a rotational rheometer to reflect the reaction kinetics at the interface. To our knowledge, this is the first system- atic study where a series of reactive kinetics at the interface of Ar plasma-modified PP and PS was reported.

EXPERIMENTS

Materials

PP (1300) and PS (666D) were purchased from Yan- shan Petrochemical (Beijing, China). Ar at the purity of 99.995% was purchased from Qiaofeng chemical factory in Longkou city (Shandong, China). Ethanol and water were bought from Kewei Company (Tian- jin, China).

PP and PS particles were washed 30 min in the ultrasonic washing with ethanol, then washed three cycles by distilled water, and then were dried at 40°C in a vacuum oven for 24 h. PP and PS plates were prepared by compression molding on polytet- rafluoroethylene plate at 200°C for 20 min to make sure that the surface of each plate was smooth. The thicknesses of PP and PS plate were 0.1 mm and 0.5 mm, respectively. All of the plates were washed 30 min in the ultrasonic washing with ethanol, then
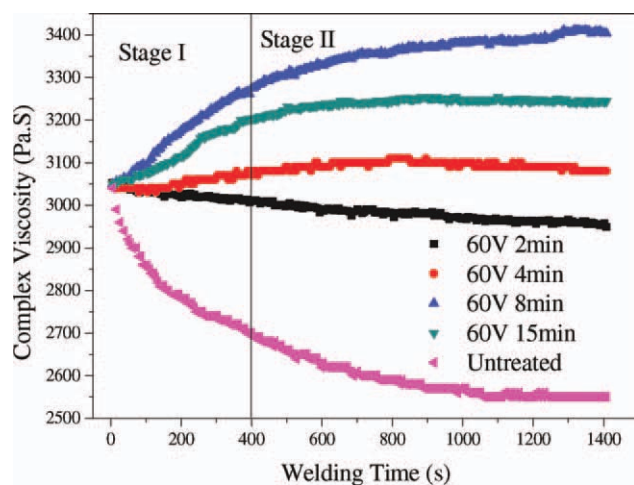
Figure 2 Relationship of η* versus time of Ar plasma treatment for different time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

washed three cycles by distilled water, and later they were dried at 40°C in a vacuum for 24 h.

Plasma surface modification

PP and PS plates were exposed to the low pressure radio-frequency (RF) plasma treatment for surface modification. Plates were attached to a metal plate holder located in the middle of the two electrodes to ensure samples could be treated uniformly. After loading the samples, the internal pressure of the chamber first reached less than 1 Pa, and then Ar was directly injected into the chamber from the top of samples. When the system pressure reached to 67 Pa, an RF power (13.56 MHz, self-made generator) was applied for the generation of plasma and maintained for a set time. The base slab temperature was 25°C. The gas flow rate was 60 mL/min.

Surface characteristics

XPS spectra were recorded on a PHI-1600 X-ray photoelectron spectroscopy (Perkin-Elmer) at pass energy of 1253.6 eV with Mg Kα excitation (250 W). The base pressure was 1.1×10^{-8} Pa and the pass energy was 20 eV during the analysis. The XPS spectra were referenced to the main component of the C1s peak at a binding energy of 285.0 eV.

Rheological properties

The pure and plasma-treated PP and PS plates with a sandwich structure, which included two PP plates at the bottom and top and a PS plate as middle layer, were put into the rheometer (STRESSTECH, Rheological Instruments AB, Sweden) at 200°C under a nitrogen environment. The polymer sand-

wich was then slightly compressed. The measurement was started after 3 min required for thermal equilibrium to avoid the slip between plates. The complex viscosity was monitored with time while the frequency at 1 rad/s and a strain of 1% were supplied during the measurement.

## RESULTS AND DISCUSSION

XPS analysis

The structure of modified surface of PP and PS plates treated by Ar plasma was measured by XPS and the results of C1s spectra are shown in Figure 1. Obviously, C—C and/or C—H (at 284.98–285.09 eV) groups were present on these results. It was interesting to notice that two additional peaks, which corresponded to C—O (at 286.6 eV) and C=O (at 288.0 eV), were observed on the plasma-modified plates. It is well known that Ar is inert gas in plasma treatment, and could not form a coating or graft on the surface of polymer directly. But the excited Ar atom and high energy electrons could generate active radicals as a substitute of functional groups during the treatment. The appearance of O meant that O_2 could react with some free radicals and form reactive groups when plasma-treated plates were exposed to the air.[13]

Rheology analysis

The complex viscosity (η*) of the PP/PS SGP were studied and the results are shown in Figures 2 and 3. η* of plasma-modified PP/PS SGP, which was much higher than that of untreated PP/PS SGP, increased with welding time and reached a final value.
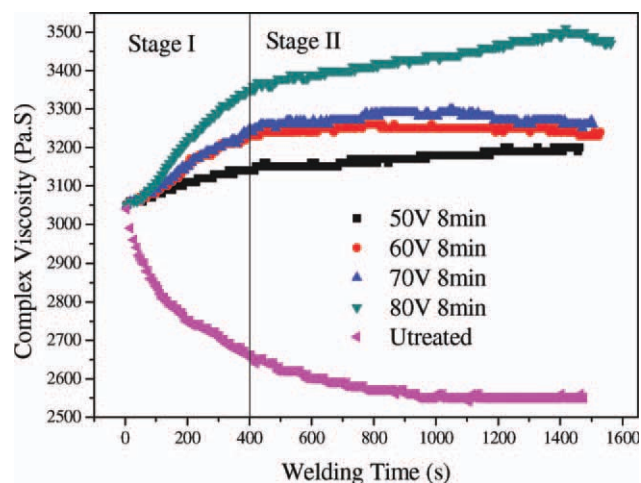

Figure 3 Relationship of η* versus time of Ar plasma treatment for different voltage. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]
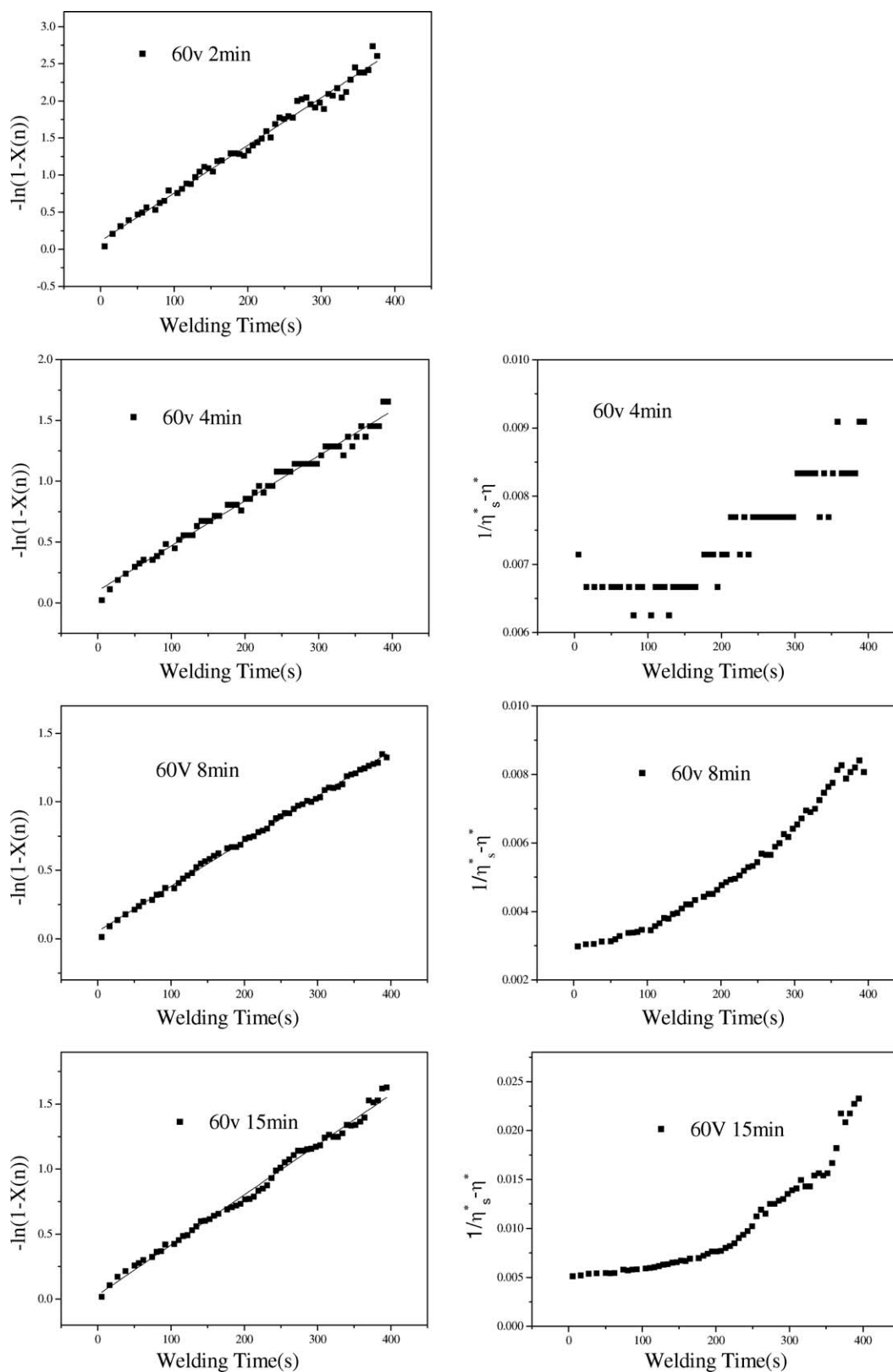
Figure 4 Plot of conversion versus welding time of Ar plasma treatment for different time based on the first-order reaction kinetics (left) and second-order equations (right).

In the welding process, the chains of two polymer could be mixed within their interface and the interface was thickened, which caused η^* to

increase. Since untreated PP/PS SGP were thermodynamically incompatible and could not mix completely, the interface thickness should be finite
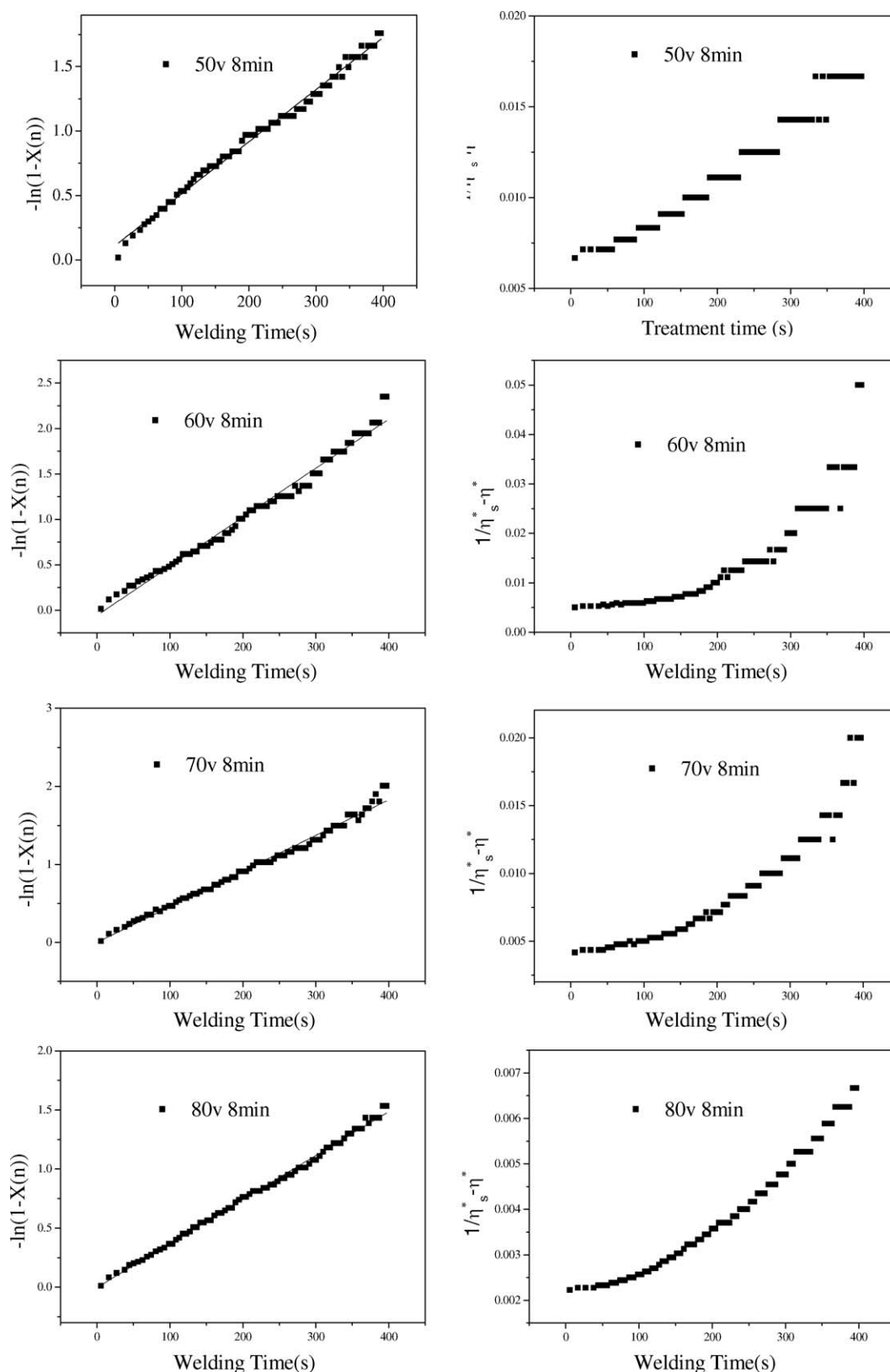
Figure 5 Plots of conversion versus welding time of Ar plasma treatment for different voltage based on the first-order reaction kinetics (left) and second-order equations (right).

due to the small Flory's interaction parameter,[25] resulting in little increase of η^*. In this article, η^* of untreated PP/PS SGP decreased slightly with welding time, suggesting that shear thinning and oxidative degradation prevailed in this process.

TABLE I
Values of k_1

Treatment conditions	60 V, 2 min	60 V, 4 min	60 V, 8 min	60 V, 15 min	50 V, 8 min	60 V, 8 min	70 V, 8 min	80 V, 8 min
$k_1(=10^{-3}\text{ s}^{-1})$	6.4	3.9	3.4	4.0	4.2	5.4	4.6	3.7

When there was a tight contact of the plasma-modified PP and PS plates, reactions between the active radicals and reactive groups, such as C=O, C—O, and C—OOH, occurred at the interface, resulting in the graft reaction between PP and PS chains that induced the increase in the molecular weight of graft copolymer and the enhancement in the compatibility of the interface. The root-mean-square roughness of the interface increased, and η^* increased accordingly. Thus, η^* was related to the amount of the *in situ* formed graft copolymers for a reactive blend.[22]

From the results of Figures 2 and 3, the whole process should be divided into two stages. Stage I, η^* increased rapidly with the welding time at the beginning; Stage II, η^* increased slowly with the welding time then reached a plateau value.

During Stage I, reactions occurred between active radicals and functional groups near the interface. If the supply of both reactive groups was sufficient at the interface in the reaction time scale, the reaction rate would vary proportionally to the vacant sites available for the reaction.[26] We used this equation to correlate the change of η^* with the conversion $[X(t)]$ of the *in situ* formed graft copolymers as follows[21]:

$$X(t) = \frac{\eta^*(t) - E^*(0)}{\eta^*(t, \text{sat}) - \eta^*(0, \text{sat})} \qquad (1)$$

where $\eta^*(t, \text{sat})$ was the plateau value of $\eta^*(t)$ of plasma-modified PP/PS SGP, $\eta^*(0, \text{sat})$ was the plateau value of $\eta^*(0)$ of plasma untreated PP/PS SGP.

To determine the relationships between the change of η^* with the reaction conversion $X(t)$ of plasma-modified PP/PS SGP, the reaction kinetics were carried out the first and the second-order analysis.

$$-\ln[1 - X(t)] = k_1 t \qquad (2)$$

For the first-order reaction kinetics, k_1 was the reaction constant.

$$\frac{1}{\eta^*(t, \text{sat}) - \eta^*(t)} = k_2 t \qquad (3)$$

For the second-order reaction kinetics, k_2 was the reaction constant.

From Figures 4 and 5, it was concluded that the reaction between plasma-modified PP and PS plates

at Stage I could be described by the first-order reaction kinetics. In Table I, the values of k_1 under different plasma treatment conditions were almost unchanged, suggesting that the growth mechanism was reaction-controlled kinetics. Diffusion-controlled reaction regime could occur after the interface was covered by the monolayer of the *in situ* formed graft copolymer.[21] During this stage, graft reactions were fast at the interfacial region and η^* increased rapidly. Most of the active radicals and reactive groups were consumed in this process.

At Stage II, the interface was densely occupied by *in situ* formed graft copolymers, or the active radicals and functional groups were consumed, η^* increased slowly. The decrease of slopes of η^* indicated that the effect of the diffusion became as important as the reaction. Although *in situ* formed copolymer would be graft type rather than block type for this system, the diffusion of active radicals and functional groups into graft copolymer layer would be much more retarded than that into neat PP–PS interface.[21] Another reason might be the quantitative limitation of active radicals and reactive groups. The plasma-treated depth of PP or PS was no more than 100 nanometers, and the surface active radicals and functional groups might have less of an effect than expected.[10] As the interface was totally occupied by the graft copolymers, the roughness increased at Stage II, and η^*, which was correlated with increased interface thickness, increased steadily due to the continuing reaction.
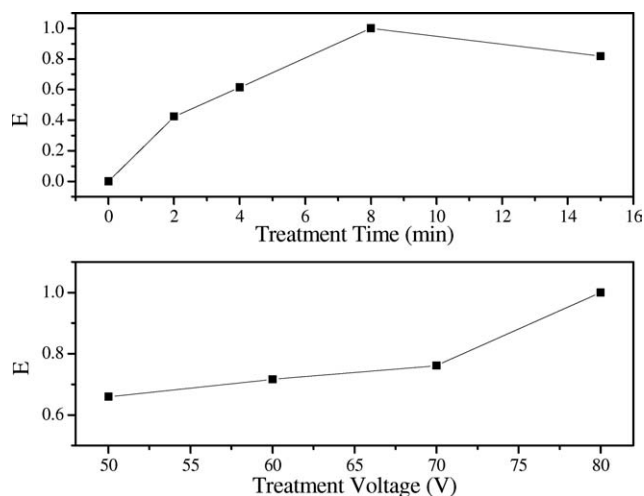

Figure 6 Effects of Ar plasma treatment for different time and voltage.

To analyze the effects of plasma treatment under different conditions, an index, E, was defined as follows:

$$E = \frac{\eta_n^*(t, \mathrm{sat}) - \eta^*(0, \mathrm{sat})}{\left[\eta_n^*(t, \mathrm{sat}) - \eta^*(0, \mathrm{sat})\right]_{\max}} \quad (4)$$

where $\eta_n^*(t, \mathrm{sat})$ was the $\eta^*(t, \mathrm{sat})$ under different plasma treatment conditions.

The index, E, was for qualitative trends but should not be an absolute method. From Figure 6, the effects of plasma modification were improved by prolonging the treatment time and raising the plasma voltage. When plasma treatment time went up to 15 min, E decreased. The reason would be that interfacial reaction was blocked because of the very slow diffusion of the graft copolymer away from the interface and arduous penetration of active radicals and functional groups to the interface.[1]

CONCLUSIONS

In this article, the effects of low temperature Ar glow discharge plasma modification of PP and PS on the surface and interface were studied. The results of XPS spectra showed that functional groups, such as C—O and C=O, had been introduced into the surfaces of PP and PS plates, the formation of reactive groups might be due to the reaction of O_2 with some free radicals when plasma-treated plates were exposed to the air. In the rheology study, because of the increase of interfacial adhesion strength due to the coupling reaction between the reactive groups at the interface, η^* increased with welding time. The whole process could be divided into two stages. In Stage I, η^* increased rapidly. The growth mechanism of interface was reaction-controlled, and was diffusion-controlled later. The first-order was suitable to analyze the kinetics. In Stage II, η^* increased slowly due to the retarded diffusion and the quantitative limitation of functional groups and copolymers at PP–PS interface.

References

1. Seo, Y.; Lee, J.; Kang, T. J.; Choi, H. J.; Kim, J. Macromolecules 2007, 40, 5953.
2. Kim, H. J.; Lee, K. J.; Seo, Y. Macromolecules 2002, 35, 1267.
3. Seoa, Y.; Tran, N. H. Polymer 2004, 45, 8573.
4. Sailer, C.; Handge, U. A. Macromolecules 2008, 41, 4258.
5. Qiu, H.; Bousmina, M. Macromolecules 2000, 33, 6588.
6. Qiu, H.; Bousmina, M. J Rheol 1999, 43, 551.
7. Shi, D.; Ke, Z.; Yang, J.; Gao, Y.; Wu, J.; Yin, J. Macromolecules 2002, 35, 8005.
8. Omonov, T. S.; Harrats, C.; Groeninckx, G.; Moldenaers, P. Polymer 2007, 48, 5289.
9. Kim, H. J.; Lee, K. J.; Seo, Y.; Kwak, S.; Koh, S. K. Macromolecules 2001, 34, 2546.
10. Kim, S.; Lee, K. J.; Seo, Y. Langmuir 2002, 18, 6185.
11. Kim, H. J.; Seo, Y. Langmuir 2003, 19, 2696.
12. Mirabedini, S. M.; Arabi, H.; Salema, A.; Asiaban, S. Prog Org Coat 2007, 60, 105.
13. Pascu, M.; Vasile, C.; Gheorghiu, M. Mater Chem Phys 2003, 80, 548.
14. Poncin-Epaillard, F.; Brosse, J. C.; Falher, T. Macromolecules 1997, 30, 4415.
15. Evenson, S. A.; Fail, C. A.; Badyal, J. P. S. Chem Mater 2000, 12, 3038.
16. Basarir, F.; Choi, E. Y.; Moon, S. H.; Song, K. C.; Yoon, T. H. J Membr Sci 2005, 260, 66.
17. Warren, J. M.; Mather, R. R.; Neville, A.; Robson, D. J Mater Sci 2005, 40, 5373.
18. Dhamodharan, R.; Nisha, A.; Pushkala, K. Langmuir 2001, 17, 3368.
19. Liu, Z. M.; Tingry, S.; Innocent, C.; Durand, J.; Xu, Z. K.; Seta, P. Enzyme Microb Tech 2006, 39, 868.
20. Wang, C. Q.; He, X. N. Surf Coat Technol 2006, 201, 3377.
21. Kim, H. Y.; Jeong, U.; Kim, J. K. Macromolecules 2003, 36, 1594.
22. Wu, Y.; Yu, X.; Yang, Y.; Li, B.; Han, Y. Polymer 2005, 46, 2365.
23. Bousmina, M.; Qiu, H.; Grmela, M.; Klemberg-Sapieha, J. E. Macromolecules 1998, 31, 8273.
24. Desmet, T.; Morent, R.; Geyter, N. D.; Leys, C.; Schacht, E.; Dubruel, P. Biomacromolecules 2009, 10, 2351.
25. Russell, T. P.; Menelle, A.; Hamilton, W. A.; Smith, G. S.; Satija, S. K.; Majkrzak, C. F. Macromolecules 1991, 24, 5721.
26. Oyama, H. T.; Ougizawa, T.; Inoue, T.; Weber, M.; Tamaru, K. Macromolecules 2001, 34, 7017.