Macromolecules **2001,** *34,* 3725−3729

Probing Thermoplastic Matrix−Carbon Fiber Interphases. 1. Preferential Segregation of Low Molar Mass Chains to the Interface

V. Carlier,*,† M. Sclavons,† A. M. Jonas,† R. Jérôme,‡ and R. Legras†

Unité de Physique et de Chimie des hauts Polymères, Université catholique de Louvain, Croix du Sud, 1-B-1348 Louvain-la-Neuve, Belgium, and Center for Education and Research on Macromolecules (CERM), University of Liège, Sart-Tilman B6 B-4000 Liège, Belgium

Received March 6, 2000; Revised Manuscript Received February 5, 2001

ABSTRACT: The molecular mobility of polystyrene (PS) chains near the surface of carbon fibers was investigated. The glass transition temperature of very thin coatings deposited on carbon fibers was measured by supported DMTA in order to probe the properties of the thermoplastic interphase. Depending on the fiber impregnation method from the melt or from solution, T_g changed in an opposite way for the thinnest coatings, decreasing with coating thickness in the case of impregnation in the melt and increasing when a polymer solution was used. This observation is explained by degradation of PS in the melt and subsequent preferential segregation of low molar mass chains to the interface. This conclusion is supported by the study of the T_g of coatings made from a bimodal molar mass distribution.

Introduction

Probing the interphase properties in composite materials remains a challenge.[1] For instance, the assessment of the molecular mobility of the matrix nearby the fiber might help to provide a better understanding of the stress transfer mechanism, this allowing a better tailoring of such materials. The present paper is part of a larger study aimed at probing interphase mobility through the in-situ measurement of interphase matrix glass transition temperatures, our ultimate goal being to correlate this transition with the intensity of interfacial interactions of varying nature (low interaction, polar interaction, and covalent bonding) and, finally, with reinforcement efficiency. Interfacial glass transition temperatures are approached by comparing the glass transition of composites of strongly decreasing matrix content, which permits to deduce the interface effect on this transition.

To reach this goal, a technique for measuring thermal transitions of polymer coatings was required. Dynamic mechanical analyses in dual cantilever bending mode appeared[2] surprisingly sensitive to thin coatings on various supports, when using a specifically designed clamping device. Modeling of such composite samples by sandwich samples built up by alternatively stacking rigid support plates and polymer films showed[2] that this sample configuration gives rise to a shear stress within the soft polymer coating, which is the reason for the measured DMA loss. Calculation of the shear modulus of such sandwich samples indicates that it is strongly related to the shear modulus of the films (or coatings): A multiplication factor which increases exponentially with decreasing coating thickness amplifies the shear modulus of the polymer in the overall shear modulus of the sandwich. This calculation explains why sensitivities to coatings as thin as a few nanometers are possible with this technique, even though thicker coatings are also measurable. This technique was therefore selected for our study.

In addition, to minimize unwanted interferences on the glass transition temperature resulting from other sources than the presence of the interface, sample preparation was carefully considered. First we selected as polymer polystyrene despite its low industrial interest, since it eliminates parameters such as crystallinity, reactivity, and polarity. The possible monodisperse molar mass distribution of this polymer when obtained by anionic synthesis was also of interest in the framework of the overall study. Second, we used carbon fibers as reinforcement in order to be as close as possible to real systems. However, the fibers were intensively washed[3,4] to remove their proprietary coating which would otherwise affect the properties of the studied coating (plasticizing effects, etc.). This also allowed us to recover the actual carbon fiber surface and functionalities. Finally, two impregnation methods were used (in the melt or in solution) so as to detect any influence of sample preparation, in particular possible effects related to sample degradation during processing.

In the present paper, we will precisely concentrate on segregation of low molar mass species generated during composite processing. It is therefore appropriate to briefly review the issue of preferential segregation of low molar mass molecules to an interface.[5,8−13] Such a segregation may arise simply because larger chains experience a higher entropic loss due to a larger decrease of conformational freedom in the vicinity of the surface, which favors accumulation of the low molar mass molecule preferentially to the interface.[5] This entropic partitioning is expected to be quite low, with an excess quantity of shorter chains at the surface of about 1% or lower in the case of a truly macromolecular system.[5]

Contrasting with this purely entropic effect, Kumar et al.[6] also reported that very small differences in chemical structures between components may affect dramatically surface segregation of chains. In this case, minimization of the surface free energy is the dominating factor. Complete wetting of the surface by one of the components can be even predicted for strong segregations. Experimental confirmations of these findings were reported by Jones et al.,[7] who observed a prefer-

---

[†] Université catholique de Louvain, Croix du Sud.

[‡] University of Liège.

[*] Corresponding author. Phone (32) 10 47 35 60; Fax (32) 10 45 15 93; E-mail carlier@poly.ucl.ac.be.

10.1021/ma000404b CCC: $20.00

ential segregation of deuterated PS to the air interface when studying a deuterated-PS/protonated-PS blend despite the small energetic difference between both isotopic forms.

Further neutron reflectivity (NR) studies by Kumar et al.[8] of isotopic polystyrene blends of disparate molar masses indicated that it is possible to balance at a free surface this energetic preference with entropic effects.

Later on, Kajiyama and co-workers[9−11] also contributed to this issue. They observed[9] by scanning force microscopy (SFM) the preferential segregation of low molar mass molecules to the air/polymer interface on films of proton-terminated PS of bimodal or trimodal molar mass distribution. This was explained by the preferential segregation of chain ends to the surface. More recently,[10] these results were confirmed by a NR study of a PS of bimodal molar mass distribution deposited on oxidized silicon wafer: low molar mass molecules are preferentially segregated to both interfaces (air/polymer, polymer/substrate), forming 13.5 and 9.5 nm thick interphases, respectively.

Kajiyama and co-workers[11] also reported a possible balance between energetic and entropic effects when studying a blend of low molar mass PMMA with high molar mass PS. For such blends, PMMA is preferentially segregated to the film surface even tough PMMA has higher free energy than PS.

Similar segregation effects were also reported by Pangelinan[12] and on less model systems by Drzal et al.[13] working on thermoplastic composites.

Before closing this section, we mention that the way we have elected to study in this paper the interfacial glass transition of polymers in composites, i.e., by comparing glass transitions of coatings of varying thickness deposited onto fiber also addresses a very intense[14−21] and previously controversial research topic which is the glass transition of thin polymer films. Our present results observed on an unreactive and unpolar polymer will be discussed in the light of the presently published consensus:[16] glass transitions temperatures of thin polymer films on weakly interacting substrates are reduced from bulk values.

Materials and Method

Carbon Fibers (CF). The carbon fibers were PAN-based CF, AS4.6K supplied by Hercules.

Wash Procedure. The carbon fibers were carefully wound around a glass frame and washed in Soxhlet's extractors. Eighty hours of extraction in methylene chloride was followed by 48 h of extraction in methanol (10 g of fibers for 100 mL of solvent). The washed carbon fibers were then dried for 24 h in open air and for 2 h under vacuum at room temperature. The washed carbon fibers were stored before use in a cleaned aluminum sheet in a sealed polyethylene bag.

Polystyrene. Different polystyrene grades were used in this study. (1) The polystyrene (PS) "PS 143 E" was supplied by BASF ($M_w = 263\,000$, $M_n = 81\,000$). (2) A PS powder (particle diameter of about 200 mesh) was generated by grinding PS143E pellets cooled in liquid nitrogen. (3) Degraded PS was obtained by mixing molten PS143E in a Brabender Plasticorder. The PS was introduced under nitrogen at 270 °C, and the roller speed was fixed at 75 rpm. The mixing was carried out for 1 h. The collected PS was ground coarsely prior to use. (4) Anionic PS. The anionic synthesis of PS was performed in glassware previously flamed under vacuum, flushed with nitrogen, and kept under nitrogen overpressure. Liquid compounds were transferred through syringe or stainless steel cannula stored in an oven and flamed under nitrogen flow prior to use.

Tetrahydrofuran (distilled over Na/benzophenone complex) was added to the polymerization flask and kept at −78 °C. α-Methylstyrene (0.5 mL) was added to the medium followed by the dropwise addition of *sec*-BuLi until a slight red color characteristic of the α-methylstyryl anion was observed. The required amounts of *sec*-BuLi and styrene were sequentially added, the styrene concentration being 5% (w/v) in THF. The polymerization was carried out for 2 h at −78 °C. The living chains were deactivated by addition of a few drops of acidic methanol. The final polystyrene was recovered by precipitation in a large volume of methanol, and the polymer was dried at 60 °C under vacuum.

Composite Preparation. Melt and solution fiber impregnations were carried out as described below.

1. Melt Impregnation of Washed Fibers. A bundle of unidirectional washed fibers was first inserted into a cylindrical vertical oven closed with a slit die. The fibers were then pulled from the feeding zone of the oven through the die. Inside and in the middle of the oven, the bundle was threaded through several staggered rungs of a ladder with the goal of applying a stress to open the bundle as much as possible. The oven temperature was raised to 250 °C under argon, and then 200 g of the selected PS powder was added. The bundle was then mechanically pulled out at a rate of 0.0167 m/s through the slit die. The temperature of the molten matrix in the middle of the oven ranged between 200 and 210 °C while the contact time between fibers and polymer was about 15 s. At the oven exit, the impregnated carbon fibers were gathered together to form a tape with a cross section of 5×1 mm^2.

2. Solution Impregnation. Impregnations were prepared under agitation in solutions of varying concentrations: 30, 10, 7.5, 5, 2.5, 1, 0.75, 0.5, 0.25, 0.1, 0.05, and 0.01 g of PS per liter of methylene chloride. A bundle of unidirectional washed fibers was put into contact with the solution using a metallic ladder. The impregnation was carried out by unwinding a carbon fiber roll at a speed of 0.0167 m/s. The contact time within the solution was about 10 s. The fibers were dried at the bath exit in an air flow.

Another impregnation was carried out in a cyclohexane solution at 34 °C (Θ solvent of PS). In this case, the PS polymer was made soluble at 65 °C before cooling the solution to its Θ temperature.

3. Controlled Dissolution of Previously Impregnated Carbon Fibers. Melt impregnated coatings were thinned by solvent dissolution. A similar treatment was also carried out onto solution (30 g/L) impregnated bundles for control experiments. The bundles were cut into pieces of 10 cm length. The ends of each pieces were clamped for avoiding bundles opening and were introduced into a methylene chloride solution under gentle mixing for times ranging from a few seconds to 2 h. The methylene chloride solution was changed for each dissolution time. The clamped samples were then hung and dried for 24 h in open air and for 2 h in an oven at 50 °C. The samples were immediately cut to the dimensions of DMTA samples, packed individually in clean aluminum sheets, and saved in a vacuum vessel before analysis.

Characterization Techniques. *(i) Thermal Gravimetric Analyzer (TGA).* The matrix weight loss was recorded by TGA in order to assess the fiber weight ratio in the sample. TGA's were carried out under nitrogen with a Perkin-Elmer TGS-2 thermogravimetric analyzer model TADS-101. A heat ramp from 30 to 650 °C at a heating rate of 10 °C/min was performed on about 10 mg samples.

(ii) Supported Dynamic Mechanical Properties (DMTA). A Rheometrics mechanical spectrometer (model RSA II, Rheometric, Inc.) was used for determining the glass transition temperature of the PS matrix in the composite. A dual cantilever deformation at a frequency of 10 Hz was applied. The dynamic measurements were performed with a strain amplitude of 0.1%. All samples were heated from 40 to 300 °C at a heating rate of about 2 °C/min. Measurements were performed over five cycles of deformation every 2 °C, after a thermal stabilization of 0.3 min. Temperature resolution of the technique is about 2 °C.

The bundles were clamped by a special grip device previously reported.[2]

T_g was defined as the temperature corresponding to the maximal value of $\tan\delta$. Nevertheless, attention was paid that temperature variations of maximum E'' are correlated with maximum $\tan\delta$ observed ones. Moreover, it is to mention that the damping peak ($\tan\delta$) occurs at low frequencies at 15−20 °C above the glass transition temperature as measured by dilatometry or differential scanning calorimetry (DSC).[22]

(iii) Size Exclusion Chromatography (SEC). The measurements were carried out at room temperature with a HPLC 590 Waters module, equipped with five Ultrastyragel Waters columns (10^5, 10^4, 10^3, 10^2, and 50 nm). An UV detector coupled with a Digital MicroVAX computer was used for data acquisitions and treatments. THF was the permeation solvent and the sample diluent. Samples ranged in concentration from 2 to 3 mg/mL. Injection volume was 120 μL. Parameters of the molar mass distribution were calculated with the help of a specific calibration using anionic PS standards.

(iv) Ellipsometry. A digisel rotating compensator ellipsometer from Jobin-Yvon/Sofie instruments was used. It is a single wavelength ellipsometer working at 632.8 nm (He−Ne laser). To compensate some systematic errors (imperfections and residual misalignment of the optical components), measurements have been carried out with the analyzer at +45° and −45° (with respect to the plane of incidence). The refractive index of silicon was taken to be 3.84-j0.017. The refractive index of the PS film was fixed to 1.59. The presence of an oxide layer on top of the silicon substrate does not influence the effective index but results in an overestimation of the film thickness by about 1.5 nm.

Results and Discussion

The ultimate goal of this study being the assessment of the polymer molecular mobility near carbon fiber interface, the glass transition temperature (T_g) of polymer coatings of different thickness, thus of different ratio of interface to bulk volumes, was measured in order to deduce the effect of the interface on this transition. Nevertheless, it has to be kept in mind that a simple relation between glass transition temperature and chain mobility does not exist in the case of thin films.[16]

After melt impregnating the fibers by the polymer, the matrix weight content was in the range of about 70% as determined by TGA. Since only a narrow range of fiber coating thickness was attainable when the impregnations were carried out in the melt, the impregnated mesh were soaked in a solvent of the PS matrix for increasing time periods, to remove part of the matrix. The so-obtained fiber-richer bundles were then analyzed by TGA in view to assess the polymer content and by SDMTA to measure the T_g of the polymer. Control samples were realized by impregnating bundles in a concentrated PS solution (30 g/L), giving a matrix weight content of about 40%. Those samples were similarly decoated and analyzed.

Figure 1 shows how T_g depends on matrix weight content for both impregnation methods. For both impregnations techniques, the glass transition temperature increases slighty when decreasing the PS content. However, for the lower PS contents (<2%), experimental dependencies are completely different. T_g goes on increasing slightly with decreasing PS content, thus increasing interfacial content, for solution-impregnated bundles, while it strongly decreases for melt-impregnated ones. The coating thickness related to this behavior change might be roughly estimated to be about 110 nm, from fiber[23] and matrix densities (1.7936 and 1 g/m^3, respectively), and considering 6000 fibers in each bundle. This estimation assumes that the fibers are perfect cylinders of 7 μm diameter, covered by a coating of uniform thickness.

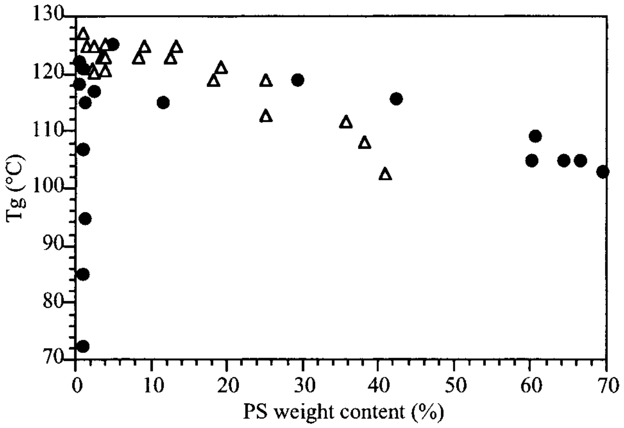

Figure 1. Variation of the glass transition of a PS matrix deposited from the melt (●) or from methylene chloride solution (△) on washed carbon fibers vs the matrix weight content in the composite.

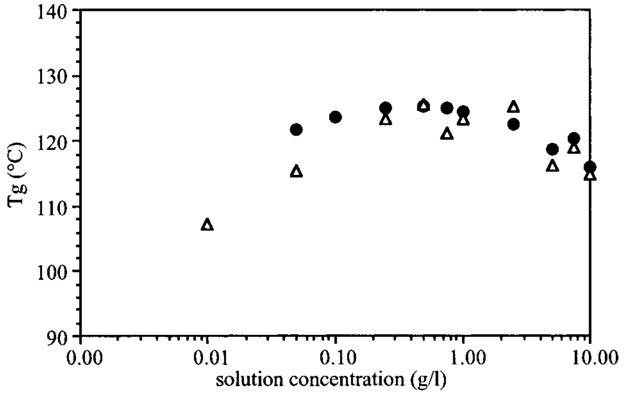

Figure 2. Variation of the glass transition of a PS matrix deposited from methylene chloride solutions (●) or from Θ solutions (cyclohexane at 34 °C) (△) on washed carbon fibers vs the concentration of the impregnation solution.

To check the effect of the impregnation solvent quality on the deposited coating, fibers were impregnated in a cyclohexane solution at 34 °C, which are the Θ conditions for PS. In this series of experiments, fiber bundles were impregnated from increasingly more dilute PS solutions rather than by progressive dissolutions of a precoating. Matrix/fiber weight ratios of 0.65, 0.55, 0.45, 0.25, and 0.05% were measured out by TGA for the sample impregnated in 10, 7.5, 5, 2.5, and 1 g/L solutions, respectively. However, more dilute solutions gave matrix contents that could not be measured accurately by TGA anymore while measurements of T_g by SDMTA remains reliable. To get an estimation for coating thickness, a study was carried out by ellipsometry on PS films deposited onto a flat surface. As cleaved highly oriented pyrollitic graphite (HOPG) substrates were found not to be sufficiently flat for ellipsometry, we turned to silicon wafers as model substrates. Dipping these wafers into decreasingly dilute solutions of 10, 1, and 0.1 g/L led to decreasing ellipsometric thicknesses of 113 ± 47, 22 ± 7, and 8 ± 1 nm, respectively. This clearly shows that, although not linearly correlated, the thickness of the coating evolves similarly to the solution concentration.

Figure 2 compares T_g measured for bundles impregnated in solutions in good and Θ solvents, respectively.

Table 1. Molar Mass Data Measured by SEC for the PS Samples

	M_n	M_w	H
polydisperse PS	81 000	263 000	3.25
degraded polydisperse PS	45 000	190 000	4.2
monodisperse PS (2000)	1 950	2 200	1.13
monodisperse PS (100 000)	86 900	89 500	1.03

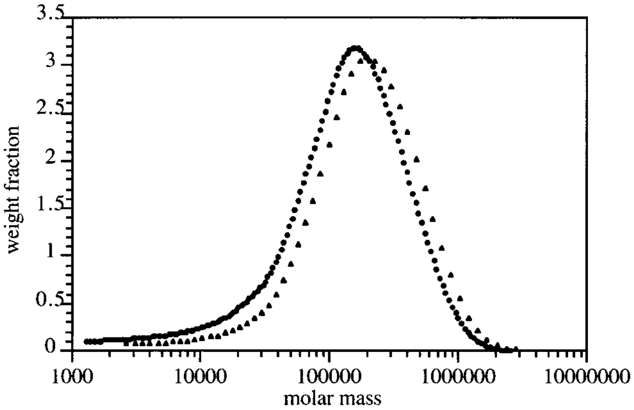

Figure 3. Distribution curves of polydisperse PS (△) and of degraded PS (●).

The curves are practically identical, and the sharp decrease in T_g observed for the melt impregnated samples (Figure 1) is not reproduced when a Θ-solvent is used in the impregnation procedure.

At this stage, the reproducibility of glass transition measurement was also checked. Six samples prepared from bundles impregnated in 1 and 0.1 g/L solutions of methylene chloride were studied by SDMTA. The reproducibility of the glass transition temperature was observed to be within 2 °C for both sets of samples.

Another explanation of the discrepancy between melt and solution impregnation methods could be the thermal degradation of PS in the melt[24] followed by preferential segregation of the released low-T_g oligomers to the interface.

To confirm this hypothesis, PS was degraded in a melt mixer at 270 °C and then used in solution for bundle impregnation. Degradation resulted in a decrease about 2 of molar masses and a significant increase of polydispersity as measured by SEC and reported in Table 1. The distribution curve presented in Figure 3 confirms a drop in molar masses and an enrichment in low molar mass chains. Using this degraded PS, an important decrease in T_g with coating thickness was observed (Figure 4) for both cyclohexane and methylene chloride solutions. This experiment strongly suggests that the presence of chain of lower mass in the PS is responsible for the decrease of T_g observed for the thinner coatings.

A more convincing evidence of the preferential accumulation of low molar mass chains at the interface was obtained in the case of bundles impregnated by a 90/10 (w/w) mixture of two fractions of quasi-monodisperse PS of quite different molar mass, i.e., M_n = 1950 (M_w/M_n = 1.13) and 87 000 (M_w/M_n = 1.03) (Table 1). The PS mixture again shows a decrease of T_g with thickness of the polymer coating (Figure 5), with the T_g of the low molar mass fraction being measured for the thinnest coatings.

Out of the scope of the present paper but quite interestingly for the relaxation dynamics understanding of thin polymer films is the complete reversed dependence of T_g on coating thickness, observed when the molecular weight of PS is decreased from 87 000 to 1950. For the low molar mass chains, the T_g increases near the interface altough it decreases in the case of high molar mass chains.

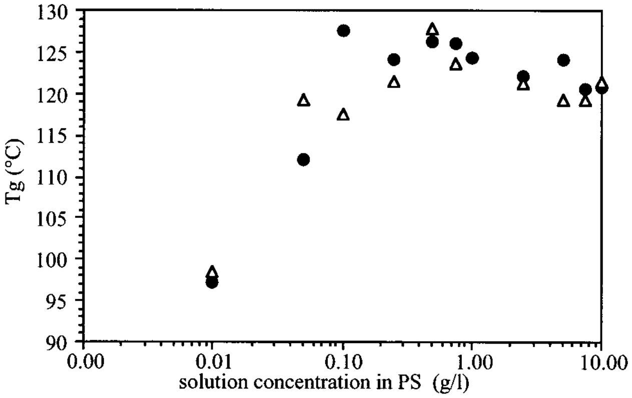

Figure 4. Variation of the glass transition of a PS matrix previously degraded in a melt mixer and then deposited from a methylene chloride solution (●) or from a Θ solvent (△) on washed carbon fibers vs the concentration of the impregnation solution.

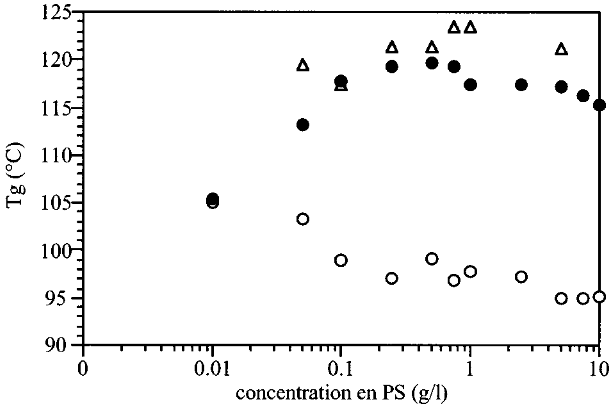

Figure 5. Variation of the glass transition for homodiperse PS of M_n = 1950 (○), of M_n = 87 000 (△), and of their 90/10 (87 000/1950) mixture (●) deposited from methylene chloride solutions on washed carbon fibers vs the concentration of the impregnation solution.

Conclusions

Contrasting with most previous studies in the field, when model substrates have to be used in order to apply techniques such as ellipsometry, X-ray reflectivity (XRR), NR, etc., we have elected to use a mechanical technique allowing to study samples closer to real materials, without artifacts due to chain tagging, etc. The selected technique is DMTA, by which we succeeded to measure the T_g of increasingly thinner polymer coatings on carbon fibers.

For the thinner coatings, we found a completely different behavior between PS coatings made by impregnation from the melt or from solution. The results were not sensitive to solvent quality. To explain this observation, we propose that a degradation of the PS occurs in the melt followed by preferential segregation of the so-formed low molar mass chains to the interface. Solution impregnations of previously degraded PS and of a PS of bimodal molar mass distribution confirm this hypothesis. In a paper to come, we will report a similar T_g study on interactive and reactive monodisperse PS chains, showing a completely different behavior from unreactive PS chains of the present report.

Acknowledgment. The authors acknowledge the "Région Wallonne" (programme Multimatériaux) and the "Services Fédéraux des Affaires Scientifiques, Techniques et Culturelles" ("Pôle d'attraction interuniversitaire": 3/41 and 4/11), for financial support and Dr. X. Arys for performing the ellipsometric measurements.

References and Notes

(1) Fink, B. K.; McCullough, R. L. *Composites*: *Part A* **1999**, *30*, 1.

(2) Carlier, V.; Sclavons, M.; Legras, R. *Polymer* **2001**, *42*, 5327.

(3) Carlier, V.; Sclavons, M.; Adam, F.; Legras, R. In *Proceedings of International Conference on Composites Engineering (ICCE/1)*, New Orleans, LA, Aug 28−31, 1994; pp 653−654.

(4) Carlier, V.; Sclavons, M.; Franquinet, P.; Legras, R.; Poleunis, C.; Weng, L. T.; Bertrand, P. In *Proceedings of International Conference on Composites Engineering (ICCE/1)*, New Orleans, LA, Aug 28−31, 1994; pp 831−832.

(5) Weng, L. T.; Poleunis, C.; Bertrand, P.; Carlier, V.; Sclavons, M.; Franquinet, P.; Legras, R. *J. Adhes. Sci. Technol.* **1995**, *9*, 859.

(6) Hariharan, A.; Kumar, S. K.; Russell, T. P. *Macromolecules* **1990**, *23*, 3584.

(7) Hariharan, A.; Kumar, S. K.; Russell, T. P. *Macromolecules* **1991**, *24*, 4909.

(8) Jones, R. A. L.; Kramer, E. J.; Rafailovich, M. L.; Sokolov, J.; Schwarz, S. A. *Phys. Rev. Lett*. **1988**, *62*, 2801.

(9) Hariharan, A.; Kumar, S. K.; Russell, T. P. *J. Chem. Phys.* **1993**, *98*, 4163.

(10) Tanaka, K.; Takahara, A.; Kajiyama, T. *Macromolecules* **1997**, *30*, 6626.

(11) Kajiyama, T.; Tanaka, K.; Takahara, A.; Tasaki, S.; Ebisawa, T.; Matsushita, Y. *JAERI Rev.* **1999**, *99−007*, 209.

(12) Tanaka, K.; Takahara, A.; Kajiyama, T. *Macromolecules* **1998**, *31*, 863.

(13) Pangelinan, A. B. Ph.D. Thesis, University of Delaware, 1991.

(14) Drzal, L. T.; Raghavendran, V. *53rd Annu. Technol. Conf. Soc. Plast. Eng.* **1995**, *2*, 2877−2881.

(15) Keddie, J. L.; Jones, R. A. L. *Europhys. Lett*. **1994**, *27*, 59−64.

(16) Keddie, J. L.; Jones, R. A. L.; Cory, R. A. *Faraday Discuss*. **1995**, *98*, 219−230.

(17) Jones, R. A. L. *Colloid Interface Sci.* **1999**, *4*, 153−158.

(18) Van Zanten, J. H.; Wallace, W. E.; Wu, W. L. *Phys. Rev. E* **1996**, *53*, R2053−R2056.

(19) Forrest, J. A.; Dalnoki-Veress, K.; Stevens, J. R.; Dutcher, J. R. *Phys. Rev. Lett*. **1996**, *77*, 2002−2005.

(20) Forrest, J. A.; Dalnoki-Veress, K.; Dutcher, J. R. *Phys. Rev. E* **1997**, *56*, 5705−5716.

(21) Danolki-Veress, K.; Forrest, J. A.; de Gennes, P. G.; Dutcher, J. R. *J. Phys. IV* **2000**, *10* (P7), 221−226.

(22) Forrest, J. A.; Jones, R. A. L. In *Polymer Surfaces Interfaces and Thin Films*; Karim, A., Kumar, S., Eds.; World Scientific Publishing: Singapore, 2000.

(23) Nielsen, L. E.; Vandel, R. F. *Mechanical Properties of Polymers and Composites*, 2nd ed.; Marcel Dekker: NewYork, 1994; p 141.

(24) Hercules data sheet.

(25) Daoust, D.; Bormann, S.; Legras, R.; Mercier, J. P. *Polym. Eng. Sci.* **1981**, *21*, 721.

MA000404B