High Efficient Grafting Polymerization of Styrene on Surface of NBR Latex and Physical Properties of NBR/NBR-g-PSt Composite

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The grafting polymerization of styrene on the surface of commercial available vulcanized acrylonitrile butadiene rubber (NBR) latex was initiated by the heat decomposing cleavage of dormant groups of semipinacol (SP) immobilized firstly under UV irradiation. Extremely high grafting efficiency in the range from about 90% to nearly 100% could be achieved. Certain factors affinitive to the grafting polymerization, such as the concentration of monomer, the UV irradiation time taking on the immobilization of SP groups, and concentration of NBR latex containing SP groups, were investigated.

It was noted that there was the highest conversion when the weight ratio of NBR and St was 4:6; the grafting polymerization had a constant grafting efficiency that was almost not affected by polymerization time and the ratio of NBR-SP/St.

Furthermore, the morphologies of the thermal compression molded composites of NBR/NBR-g-PSt were observed by TEM and the thermal properties as well as tensile behaviors were examined. Obviously rubber-plastic transition could be displayed with the increasing of grafting yield. When the grafting yield was controlled at about 50%, the strength of modified rubbers increased significantly without losing its elongation.

KEY WORDS: NBR / Grafting Polymerization / Surface /

Chemical modification of rubber aims at improving its mechanical properties and enlarging its applications.[1–3] Vulcanization and grafting polymerization are some of the viable techniques for modifying the properties of rubbers.

The grafting copolymerization of vinyl monomer such as styrene and acrylates onto rubber has been studied extensively. The resultant composites comprising an inner soft rubber sphere (the "core") and an outer hard grafting polymer brushes (the "shell") could be expected to enhance the mechanical properties, especially the impact-resistance properties of materials greatly.[4] Also, the core-shell structure with two different components could be used as favourable compatibilizer.[5,6]

The most economical and practical method to produce rubber with grafted polymer brushes is possibly latex modification.[7–10] Generally, the grafting of a second polymer in latex can be completed *via* a conventional well-established technique of seed emulsion polymerization and the grafting copolymerization is usually initiated by thermal means, a redox system, or high energy irradiation. The substantially unavoidable homopolymerization triggered by radicals created on monomers leads to low grafting efficiency and additional post-treatment.[11]

Abbasian *et al.*[12] prepared styrene butadiene rubber (SBR) with 2,2,6,6-tetramethyl-piperidinyloxy (TEMPO) in their study of "living" radical grafting polymerization of styrene onto SBR. With this TEMPO-terminated SBR as macroinitiator, the radical sites at which initiation may proceed were limited on the backbone of SBR, which is preferred to achieve high grafting efficiency. However, the preparation of macroinitiator was quite complicated, including multiple-steps of synthesis.

It is known that the grafting polymerization initiated by benzophone (BP) in a two steps is of great interest in reducing homopolymer byproduct and achieving high grafting efficiency because of the reactive sites are left on the backbone of macromolecules.[13,14] Recently, our research group has explored the possibility of utilizing this sequential initiated grafting polymerization method for preparing composite core-shell particles with a commercially available vulcanized acrylonitrile butadiene rubber (NBR) emulsion as model latex.[12] The obtained results reveal that a high grafting efficiency (greater than 90%) and a facility in the fabrication process of composite core-shell particles can be achieved.

In the present work, the grafting polymerization of St on the NBR surface in the seeded emulsion was performed in a procedure comprising UV irradiation to allow SP groups coupled with NBR before thermal re-initiated grafting polymerization. The influences of various parameters on grafting polymerization occurred on the vulcanized NBR core surface were investigated. The morphology and the mechanical property of the NBR with grafted polystyrene were also examined.

EXPERIMENTAL

Materials

Acrylonitrile butadiene rubber (NBR) latex (dry rubber content 50 wt %, gel content 80 wt %, AN content 26%, average particle diameter 111 nm, d (0.1): 72 nm, d (0.5) 101 nm, d (0.9) 159 nm) was generously donated by Lanzhou Chemical Plant, China. Activator, trimethylpropane triacrylate (TMPTA)

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was obtained from Tianjin Chemical Reagent Co. and used as received. Styrene (St) was purchased from Beijing Chemical Reagents Company and purified by distillation to remove any inhibitors. Benzophenone (BP) was obtained from Shanghai Chemical Reagents Co. Ltd. China and used as received.

Synthesis of NBR Latex Containing Dormant SP Groups (NBR-SP)

The synthesis of NBR latex containing dormant SP groups is same to our earlier report.[15] A mixture of BP (5 g) dissolved in TMPTA (4 g) was added drop-wise into the NBR latex (200 g) under vigorous stirring for at least 1 h. 50 mL of the reaction mixture was placed in a pyrex beaker (with dimesions 5 cm (Φ) $\times$ 9 cm (h)) that was sealed with a thin film of biaxially oriented polypropylene (BOPP) and purged with nitrogen for 30 min. The mixture was then subjected to UV irradiation (with a 375-W high pressure mercury lamp as a polyspectrum light source emitting light primarily at wavelength of 254 nm and 365 nm, and a light intensity is retained at 45 w/m²) for 1 h whilst keeping a low flow of nitrogen. Stable latex was obtained during the irradiation.

Preparation of NBR Latex with Surface Grafted Polystyrene (NBR/NBR-g-PSt)

A given amount of the latex derived from the irradiation, carrying dormant SP groups (NBR-SP), was diluted with water, and charged into a 250 mL four-necked round-bottom flask assembled with a mechanical stirrer, thermometer, nitrogen inlet tube and condenser. After degassing for 30 min, the flask was placed in a thermostat preheated to 85 °C, and St was dripped into it in 15 min. The flask was incubated at 85 °C for several hours to complete the grafting polymerization.

The resultant NBR/NBR-g-PSt latex were precipitated in a 2% calcium chloride aqueous solution, washed with hot water at least 5 times, dried at 50 °C for 24 h, placed in a vacuum oven at 50 °C until a constant weight was reached, and finally extracted with 2-butanone to remove trace amounts of homopolymer.

The monomer conversion (C), grafting yield (GY, *i.e.* the ratio of the weight of grafted polymer to the weight of the NBR particles) and grafting efficiency (GE, *i.e.* the ratio of the weight of grafted PSt to the weight of polymerized PSt) were calculated according to the following equations:

$$\text{Conversion: } (C, \%) = \frac{W_p}{W_0} \times 100 \tag{1}$$

$$\text{Grafting yield: } (GY, \%) = \frac{W_g}{W_r} \times 100 \tag{2}$$

$$\text{Grafting efficiency: } (GE, \%) = \frac{W_g}{W_p} \times 100 \tag{3}$$

Here, W_p was the weight of the polymerized monomers. W_0 was the weight of the added monomer, W_g was the weight of the grafted polymers and W_r was the weight of the NBR used.

TEM, SEM Observation

The treated NBR/NBR-g-PSt composites powder was thermally compressed at 120 °C for 30 min and cut with a diamond knife at low temperature to obtain thin sections of $\sim$50 nm in thickness, and then stained in the vapor of 2 wt % OsO₄ aqueous solution for 20 min. The stained samples were observed under the transmission electron microscopy (TEM, HITACHI H-800).

The thermal compression molded samples were immerged in liquid nitrogen for 10 min and then were broken immediately. The freeze-fractured surfaces were observed using a S250MK3 scanning electron microscope at an accelerate voltage of 19 kV. All surfaces were coated with a thin layer of gold prior to SEM examination.

Thermal Property

Samples of approximately 5–10 mg in an aluminum pan were measured on a differential scanning calorimeter (DSC, NETZSCH DSC 204 F1) from −100 °C to 150 °C at 10 °C/min. The data obtained from the scan was used to determine T_g of NBR/NBR-g-PSt copolymer.

Mechanical Property

The thermal compression molded samples with standard size were tested by an Instron Materials Testing Machine (Instron 1185), following a method described in ASTM D638-81, with a crosshead speed of 5 cm/min. All tests were carried out at room temperature, and the data reported were averages of at least five measurements.

RESULTS AND DISCUSSION

Effect of Styrene Concentration

Figure 1 plots the conversion of St *vs.* reaction time curves under constant concentration of NBR-SP (C_{NBR}) and various concentration of styrene (C_{St}) added in grafting polymerization. It shows that both the grafting polymerization rate and conversion had an ascending tendency when the concentration
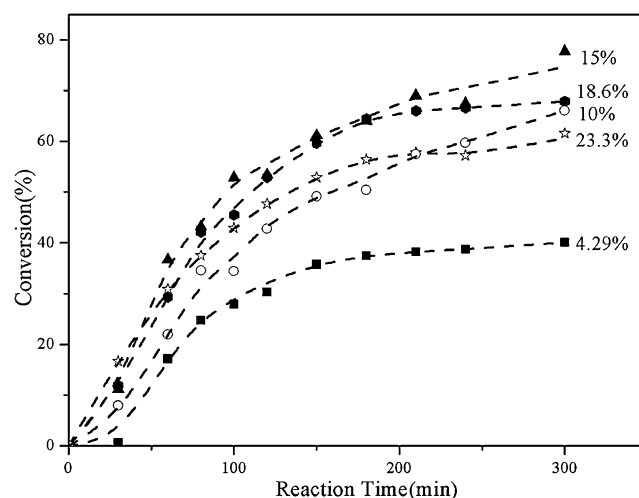

Figure 1. Monomer conversion *vs.* reaction time with different St concentration, C_{NBR} = 10% (wt), at 85 °C.

of St is on the increase, but the descending appeared when the concentration of St is above 15%. It is known that the active radicals on the NBR backbone yielded by the cleavage of the weak C-C bond formed between dormant SP groups and NBR could initiate the grafting polymerization of St. With higher concentration of monomer presents in the system, more monomers will diffuse to the vicinity of latex surface and accelerate the grafting polymerization. While the concentration of St exceeds 15%, even more styrene was added, the concentration of styrene on micelle surface would not increase any more and then the grafted monomer would not increase in a given time. The St conversion calculated from formula (1) would be decreased with St concentration exceeds 15%. On the other hand, more monomer presented in the system would promote it diffusing to the center of NBR core in which little active sites were generated. This would have some negative effects on the enhancement of conversion. It is reported that BP semi-pinacol radicals could induce a "living" grafting polymerization,[14,16,17] however, in the present heterogeneous system, the grafting polymerization initiated by the macro-initiator on NBR-SP latex surface could not be a real "living" reaction. The consuming of surface active sites by termination or transfer of other impurities or monomer might also be responsible for the decrease of conversion at concentration of St greater than 15%.

The grafting efficiency was calculated as the ratio of the amount of grafted PSt chains to the total amount of St polymerized. For the NBR-SP/St ratio varied from 5:5 to 3:7, an almost constant and considerably high level of GE could be achieved (Figure 2). The reasons could be attributed to that the reactive sites could only be generated on the backbone of NBR and the growth of grafting chains was limited to the surface of NBR-SP latex. Homopolymer was hardly to produce for the lack of active radicals in monomers drops. Furthermore, with the polymerization prolonging, the grafting efficiency almost kept invariable. This phenomenon was not consistent with some other's research. Arayapranee[18] found that the grafting

efficiency increased gradually over the range of conversion of 10–80%. In their system, the increasing grafting efficiency was resulted from an encapsulation of un-grafted chains on seed latex particle. In the present system, active radicals were mainly limited on the backbone of NBR-SP to start grafting chains propagation. Only trace of homopolymer might be formed due to chain transfer reaction which could be controlled by the intrinsic characteristics of radicals, monomer and solvent. So, the grafting efficiency kept at a high level during polymerization.

On the other hand, it was noted that the grafting efficiency increased first and then decreased with the reduction of NBR-SP/St feed ratio from 5:5 to 3:7. This might be due to the copolymerization of PSt and NBR chains. The main polymerization place was the surface and the subsurface of NBR particles. There existed not only PSt grafted chain, and St monomer, but also the NBR chain. As we knew, there were some double bonds in NBR-SP chains. Some of homopolymerized PSt chain would copolymerized with NBR chains, by which PSt homopolymerized PSt chains immobilized on NBR. Thus, the grafting efficiency increased. When the NBR-SP/St ratio reduced from 4:6 to 3:7, the double bonds in NBR-SP was not enough to copolymerize with the generated homopolymer which leading to a little slide of grafting efficiency.

Effect of UV Irradiation Time in the First Step

In order to get the grafting polymerization of St onto NBR-SP latex preceded smoothly, more dormant groups coupled on the surface of NBR-SP latex were desirable. The UV irradiation time in synthesizing NBR-SP latex containing dormant SP groups would have a great effect on the amount of dormant groups coupled on NBR surface, which would consequently affect the grafting polymerization of St.

Figure 3 exhibits the effect of UV irradiation time in the first step on the conversion of St at the end of grafting polymerization. It can be seen that the conversion of St improves within a longer irradiation time, indicating more dormant groups
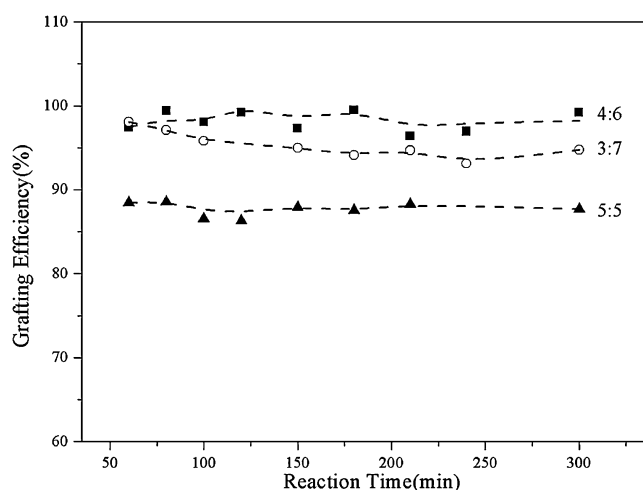

Figure 2. Relationship between grafting efficiency and the ratio of NBR-SP/St.
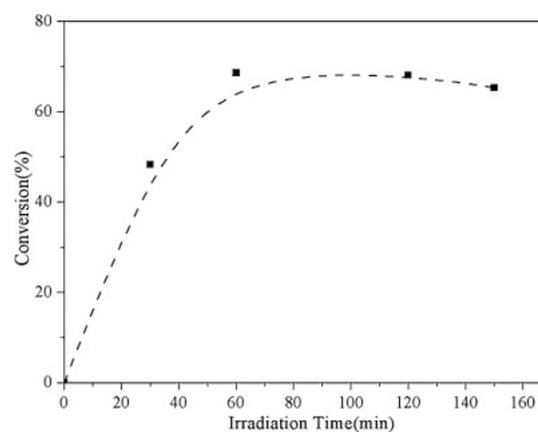

Figure 3. Relationship between irradiate time in step 1 and the followed grafting conversion, $C_{NBR} = 2.5\%$, $C_{St} = 10\%$, polymerized at 85 °C for 10 h.

could be coupled on the NBR surface through the combination of semi-pinacol free radicals and surface alkyl free radicals resulted from hydrogen abstraction of BP, *i.e.*, more active sites could be produced for the grafting polymerization. This would provide an improvement to the subsequent grafting polymerization. However, after about 60 min irradiation, a little bit decrease is shown in the conversion of St. This phenomenon might be attributed to the termination of radicals under over exposure to UV light, which actually reduce the active sites ready for the grafting polymerization.

Effect of the Concentration of NBR Latex Containing Dormant SP Groups

In the process of grafting polymerization of styrene, the NBR-SP latex containing dormant SP groups on its surface could be considered as a macroinitiator. Increasing the concentration of this macroinitiator from 4.3% to 10.0% allows more active sites produced on the surface of NBR-SP latex, leading to the elevation of the grafting polymerization rate and the conversion of St, as shown in Figure 4. While, a greater concentration than 10.0% of this macroinitiator resulted in a decrease of the grafting polymerization rate and the conversion of St. During polymerization, St exist not only on the surface but also in the center of NBR-SP latex where the St would not be involve in the grafting polymerization for the lack of living groups. When the NBR-SP feeding amount increased, the excesses of macroinitiator are likely to reproduce plentiful radicals by the cleavage of the formed weak C-C bonds and the possibility of radicals terminated by other components or impurity in system tends to be magnified. As a result, the real
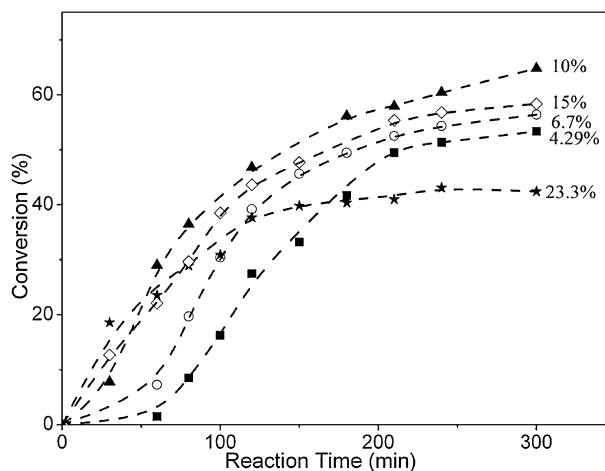

Figure 4. Monomer conversion *vs.* reaction time with different macroinitiator concentration, $C_{St} = 10\%$ (wt), at 85 °C.

initiation efficient might be reduced. Furthermore, the increasing of the amount of NBR-SP latex might absorb more monomer in its center which would not be helpful to the grafting polymerization. As a result, the values of C_{NBR} beyond 10% gave a reduced conversion of monomer.

Morphology Observations of NBR/NBR-g-PSt

The TEM photographs of the thermal compression molded NBR/NBR-g-PSt composites with different grafting yields were shown in Figure 5. The darker region was NBR and the lighter region was PSt grafted. Because the NBR region was of
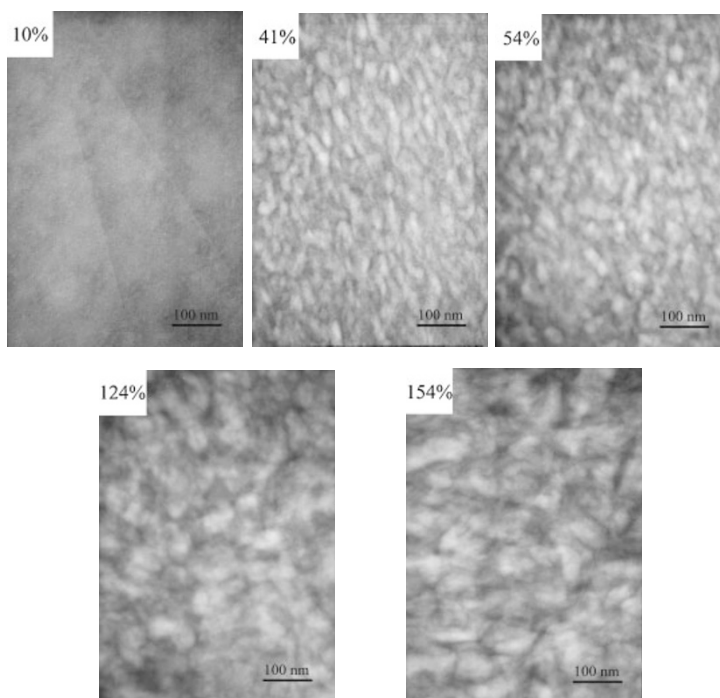

Figure 5. TEM photographs of NBR/NBR-g-PSt composites with different grafting yield at a magnification of 100 k. Polymerized conditions: $C_{NBR} = 4.3\%$ (wt), $C_{St} = 10\%$, at 85 °C for 5 h. Samples were stained with OsO$_4$.

cross-linking structure, it will not deformed during the thermal process.

When the composite contained NBR/NBR-g-PSt copolymer with a low grafting yield of 10%, it appeared that no NBR and PSt regions could be discerned clearly, that is, the composite was completely homogeneous, similar to an identical NBR phase.

When the grafting yield improved to a mediate value, quite small domains of PSt were distributed uniformly in the phase of NBR. And when the grafting yield was above 100%, similar with Yang's report,[19] large domains of PSt formed. It might be agglomerated with small PSt region during thermal compression. Some PSt region were connected together to produce a double continuous-phase. In addition, no legible boundary could be seen, indicating that there was a mixed phase or a flexible layer at the interface between PSt and NBR phases.

Thermal Properties of NBR/NBR-g-PSt

The glass transition temperatures (T_g) of the NBR/NBR-g-PSt composites with grafting yields ranging from 9.8% to 142% were measured by DSC analysis, as summarized in Table I.

It was noted that the prime NBR had a low T_g of about −7.8 °C, and with the grafting yields increased, the T_g of the composite shifted to a higher temperature gradually. The movement limitation of NBR chains by the introduction of rigid chains of plastic polystyrene could contribute to the change of T_g. The more the rigid chains of polystyrene introduced, the higher T_g of composites would be obtained. Furthermore, when the grafting yields exceed 41%, T_g of the composites appeared at a temperature of around 106 °C, approaching to the T_g of PSt homopolymer. This phenomenon confirms the presence of mixed phase or flexible layer at the interface between the PSt and NBR phases.

Mechanical Properties of NBR/NBR-g-PSt

Table II and Figure 6 shows us the mechanism properties of NBR/NBR-g-PSt composites with various grafting yields of PSt. It seems that the specimen did not experience an obvious yield. Apparently, the tensile strength (the maximum stress developed during a tensile test) and elastic modules (the slope of the stress-strain curves in elastic region) of the composites
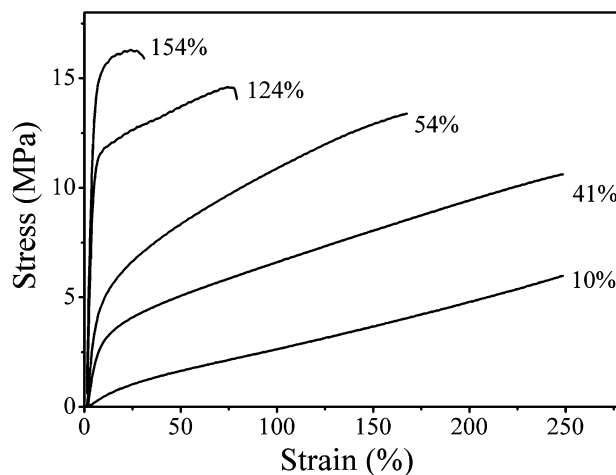

Figure 6. Stress-Strain curves for the modified NBR with different grafting yield.

enhanced greatly with the increasing of grafting yields of PSt, while the elongation percentage of the composites dropped substantially, especially in a grafting yield of PSt above 100%.

The tensile behaviors of the NBR/NBR-g-PSt composites with grafting yields ranging from 10% to 54% exhibit the toughness of the composites, and much like an elastomer, the high elongation could be developed under a relatively low stress. As observed in Figure 5, when the grafting yield was 10%, no distinguished PSt phase formed to reinforced the composite, the tensile strength and elastic modulus was quite low. When the grafting yield reached at a level of 40–50%, separated PSt phase acted as a reinforcement, accordingly, the tensile strength and elastic modulus of composites increased greatly. However, when the grafting yield exceeded 100%, double continuous-phase was formed, the fracture of composites occurred at a low elongation percentage, displaying the brittle of the composite like a plastic. At a grafting yield of about 40–50%, a balance between the toughness and strength could be achieved, displaying optimum properties of the composites reinforced by a plastic.

The morphology observation of the freeze-fractured surfaces at liquid nitrogen temperature confirmed the above described evolvement from ductile to brittle composite along with the improvement of the grafting yields of PSt. Figure 7 presents the morphologies of the freeze-fractured surfaces of composites with different grafting yields of PSt. It revealed that the fractured surface of NBR was very clean and some ridges arose, like a fractured-surfaces of a brittle polymer. At a liquid nitrogen temperature, the NBR fractured in a similar way of a brittle material. But, as a typically ductile material, the specimen of NBR possessed high elasticity and resilience. The immediate rebound of molecular chain of NBR after fracture occurred could result in the formation of ridges.

With the introduction of grafted polymer and the increase of grafting yield, fractured surfaces presented more roughness and cavities companying some close-grained rumples, especially for the samples containing more grafted copolymer with
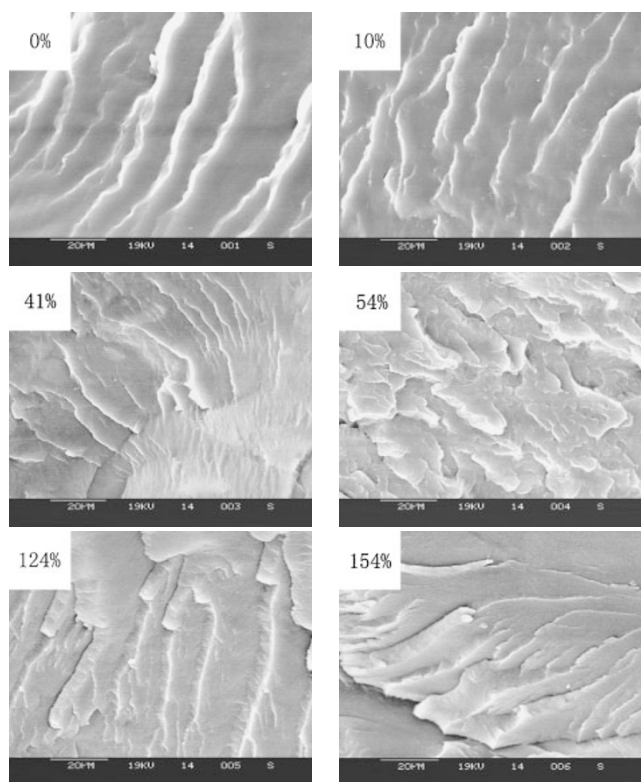
Table I. DSC text of NBR/NBR-g-PSt copolymer with different grafting yield

Grafting Yield (%)	0	10	41	84	154
T_{g1} (°C)	−7.8	−7	6.3	—	—
T_{g2} (°C)	—	—	106	106	106

Table II. Mechanism properties of NBR/NBR-g-PSt composites with different grafting yield

Grafting Yield (%)	0*	10	41	54	124	154
Modulus (MPa)	1.5	4.3	30	60	216	273
Tensile strength (MPa)	0.9	5.9	10.6	13.4	14.6	16.2
Elongation at break (%)	1380	247	248	167	76	27

*Sample was prepared *via* casting method.

Figure 7. Scanning electron micrographs of NBR/NBR-g-PSt copolymer with different grafting yield, C_{NBR} = 4.3%, CSt = 10%, at 85 °C.

grafting yields in the range of 40–50%. This accidental morphology of the fractured surfaces of composites suggested the presence of plastic deformation of samples. Under an extraordinarily high grafting yield, the composites became a plastic toughed by NBR in essence and a completely brittle fracture occurred, leading to crackles could not be relaxed even under room temperature.

CONCLUTION

The results obtained in this work show that the vulcanized NBR latex can be modified by grafting St using surface dormant active group as initiator. By this method, grafting modification can be carried with quite high grafting efficiency. When the NBR-SP (irradiated for 60 min) concentration 10% and St concentration 15%, the highest grafting efficiency and final conversion would obtained. The NBR grafted composite behaves gradually like plastic when grafting yield increased. When the grafting yield was about 40%, the strength of modified NBR doubled without losing its elongation.

REFERENCES

1. V. Vijayabaskar and A. K. Bhowmick, *J. Appl. Polym. Sci.*, **95**, 435 (2005).
2. P. S. Majumder and A. K. Bhowmick, *J. Appl. Polym. Sci.*, **77**, 323 (2000).
3. F. Abbasi, H. Mirzadeh, and A. A. Katbab, *Polym. Int.*, **51**, 882 (2002).
4. W. Arayapranee, P. Prasassarakich, and G. L. Rempel, *J. Appl. Polym. Sci.*, **89**, 63 (2003).
5. C. F. Lee, Y. H. Chen, and W. Y. Chiu, *Polym. J.*, **32**, 629 (2000).
6. C. F. Lee, *Polym. J.*, **32**, 642 (2000).
7. J. Q. Zhao, H. G. Yuan, and Z. R. Pan, *J. Appl. Polym. Sci.*, **53**, 1447 (1994).
8. K. Zhang, H. T. Chen, X. Chen, Z. M. Chen, Z. C. Cui, and B. Yang, *Macromol. Mater. Eng.*, **288**, 380 (2003).
9. Y. Luo, M. Z. Rong, M. Q. Zhang, and K. Friedrich, *J. Polym. Sci., Part B: Polym Chem.*, **42**, 3842 (2004).
10. P. Prasassarakich, P. Sintoorahat, and N. Wongwisetsirikul, *J. Chem. Eng. Jpn*, **34**, 49 (2001).
11. W. Arayapranee, P. Prasassarakich, and G. L. Rempel, *J. Appl. Polym. Sci.*, **83**, 2993 (2002).
12. M. Abbasian, H. Namazi, and A. Entezami, *Polym. Adv. Technol.*, **15**, 606 (2004).
13. J. Deng and W. Yang, *J. Appl. Polym. Sci.*, **95**, 903 (2005).
14. W. T. Yang and B. Rånby, *Macromolecules*, **29**, 3308 (1996).
15. Q. Wang, L. Liu, and W. Yang, *Polymer*, **48**, 6581 (2007).
16. H. Ma, R. H. Davis, and C. N. Bowman, *Macromolecules*, **33**, 331 (2000).
17. K. Yamamoto, S. Kyouzuka, and S. Shimada, *Macromolecules*, **37**, 86 (2004).
18. W. Arayapranee, P. Prasassarakich, and G. L. Rempel, *J. Appl. Polym. Sci.*, **89**, 63 (2003).
19. J. Yang and J. J. Liu, *Polym. J.* **33**, 952 (2001).