

Blends of Natural Rubber Latex and Methyl Methacrylate-Grafted Rubber Latex

GUANG LU, ZHI-FENG LI, SI-DONG LI, JIAN XIE

Agriculture Ministry Key Laboratory of Natural Rubber Processing, South China Tropical Agricultural Product Processing Research Institute, P.O. Box 318, Zhanjiang 524001, People's Republic of China

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ABSTRACT: By mixing natural rubber latex uniformly with methyl methacrylate-grafted natural rubber latex and then carrying out prevulcanization, we obtained blends with stable viscosities. Under certain blending ratios, the blends maintained good basic properties, and the heat stability time (T_{HS}) of the blend increased with the increment of percent content of MG49 latex (C). The relationship between T_{HS} and C was $T_{HS} = 0.36C + 33.0$, whereas, the mechanical stability time (T_{MS}) was slightly decreased, and the relationship between T_{MS} and C was $T_{MS} = -1.33C + 772.0$; The modulus, antiaging properties, and tear strength of the films of the blends increased with the increment of C ; the tensile strengths fluctuated on a small scope; the Shore A hardness (H) and breaking set (B_S) both increased with the increment of C ; their relationships were $H = 0.66C + 40.0$ and $B_S = 0.46C + 8.0$, respectively. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1736–1741, 2002

Key words: natural rubber latex; methyl methacrylate-grafted rubber latex; graft copolymer; blends; compatibility; latex property; mechanical property

INTRODUCTION

Methyl methacrylate-grafted (MG) natural rubber latex (NRL), which is referred to as methyl methacrylate rubber latex (MGL), is a kind of specialty latex produced by chemical modification of NRL. Methyl methacrylate monomer is graft copolymerized with NRL under the action of a free-radical catalyst to produce MGL. The industrialized graft copolymer of MG rubber contains 49% poly(methyl methacrylate) and is referred to as MG49. Because the rigid chains of poly(methyl methacrylate) are grafted onto the flexible chains of natural rubber, this characteristic molecular

geometry gives MG rubber self-reinforcing properties,¹ but MG rubber is poor in film-forming properties and processability. NRL possesses excellent film-forming properties^{2,3} and has been widely used in the manufacture of dipping products such as gloves, condoms, and catheters, but the hardness of this film is lower, and the tear strength of this film is comparatively poor. Collins and Gorton⁴ incorporated a certain amount of MG49 latex to increase the modulus in the production of NRL thread. Gorton⁵ added MG49 latex to NRL to improve the tear strength and puncture strength of NRL, but systematic study on blends of NRL and MGL and the properties of the blends seems to be scarce. In this study, we aimed to investigate the basic properties and film-forming properties of the blends and the mechanical properties of films by blending NRL with different amounts of MG49 latex and systematically study-

Correspondence to: S.-D. Li (lisidong@pub.zhanjiang.gd.cn).

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Table I η (mPa s) Changes of the Blends of Prevulcanized NRL and Prevulcanized MGL During the Storage Periods

C (%)	Storage Time (Days)					
	1	2	3	5	7	9
10	25.0	32.0	40.0	43.0	50.0	Seriously thickened
15	28.0	35.0	41.0	45.0	52.0	Seriously thickened
30	30.0	36.0	43.0	47.0	56.0	Seriously thickened

ing the property changes of the blends of NRL and MG49 latex.

EXPERIMENTAL

Materials

NRL, with a total solid content of 62%, was obtained from a local rubber plantation. MGL, or MG49 latex, with a total solid content of 48%, was a product of the South China Tropical Agricultural Product Processing Research Institute (Zhanjiang, China); the remaining materials were commercial products.

Sample Preparation

NRL was mixed uniformly with MGL according to the following blending ratios: 100:0, 95:5, 90:10, 85:15, 80:20, 75:25, 70:30, and 65:35 (w/w; based on dry rubber weight). Blends were obtained with the following percent contents of MGL (C_s): 0, 5, 10, 15, 20, 25, 30, and 35, respectively. The blends were prevulcanized in a water bath at 60°C for 2 h with of the following recipe: 100 rubber (dry weight); 1.0 sulfur; 1.0 vulcanization accelerator tetramethylthiuram disulfide; 1.0 zinc oxide; 1.0 antioxidant

2,5-di-*tert*-butylhydroquinone, and the prevulcanized blends were obtained. The films of prevulcanized blends were formed by a dipping process with a 20% calcium nitrate ethanol solution as a coagulant.

Testing Methods

The total solid content was determined according to GB/T8298-1987. The alkalinity was determined according to GB/T8300-1987. The mechanical stability time (T_{MS}) was determined according to GB/T8301-1987. The Shore A hardness (H) was determined according to GB/T531-1992. The 500% modulus, elongation at break, tensile strength, and breaking set (B_S) were determined according to GB/T528-1992. The tear strength was determined according to GB/T529-1991. The viscosity (η) was determined with a DNJ-79 type rotating viscometer (Tongji University, Shanghai, China) under the following conditions: the temperature of the water was 30°C, the total solid content was adjusted to $55 \pm 0.1\%$, and a No. 1 rotor was used. The heat stability time (T_{HS}) was determined with a RWY-1 type latex heat stability tester (Tongji University) under the following conditions: the temperature of the water was 70°C, the total solid content was adjusted to $55 \pm 0.1\%$, and a No. 1 rotor was used.

Table II η (mPa s) Changes of the Prevulcanized Blends of NRL and MGL During the Storage Period

C (%)	Storage Time (Days)								
	1	2	3	5	7	9	15	30	Average
0	18.0	18.0	18.0	18.5	18.0	18.0	18.5	19.0	18.3
15	18.5	18.5	18.5	19.0	18.5	18.5	19.5	19.5	18.9
30	19.0	19.0	19.0	19.5	19.5	19.0	19.0	19.5	19.2

Table III Basic Properties of the Pre vulcanized Blends

C (%)	Property		
	Solid Content (%)	η (mPa s)	Alkalinity (%)
0	50.0	18.0	0.35
5	50.0	18.5	0.35
10	50.1	18.0	0.36
15	50.1	19.0	0.37
20	50.2	18.5	0.36
25	50.0	19.0	0.37
30	50.1	19.5	0.35
35	50.2	19.0	0.37

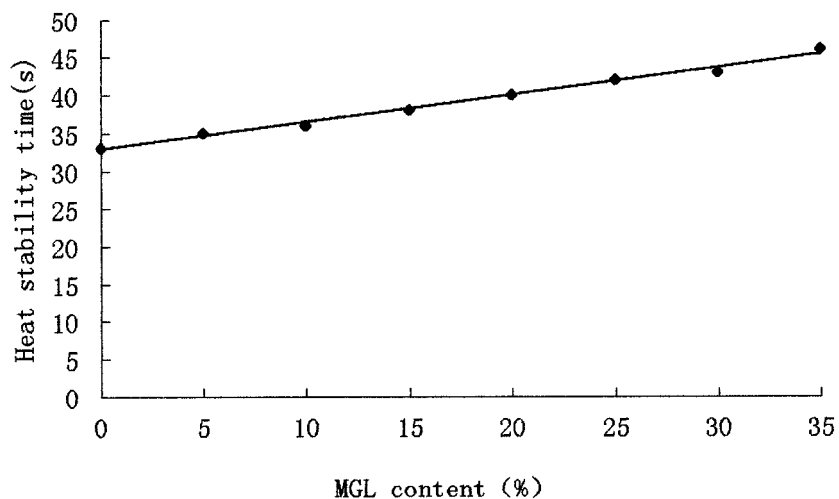


Figure 1 Relationship between C and T_{HS} .

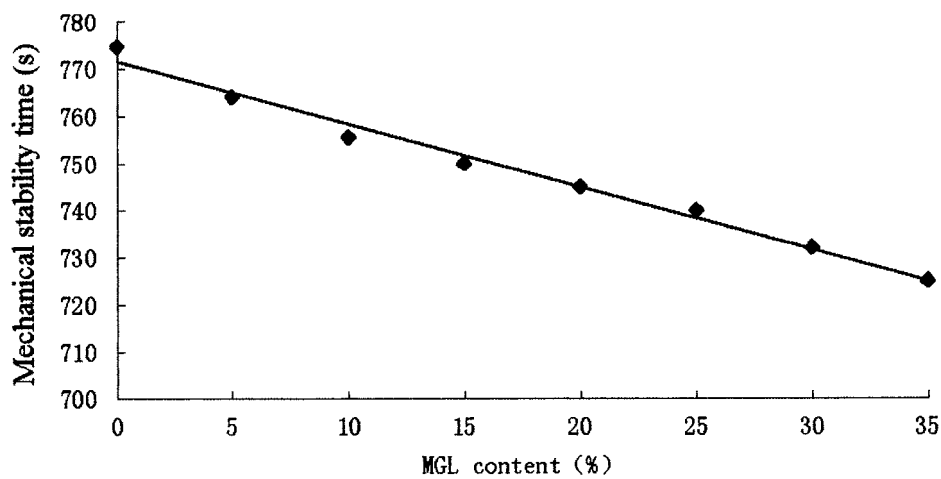


Figure 2 Relationship between C and T_{MS} .

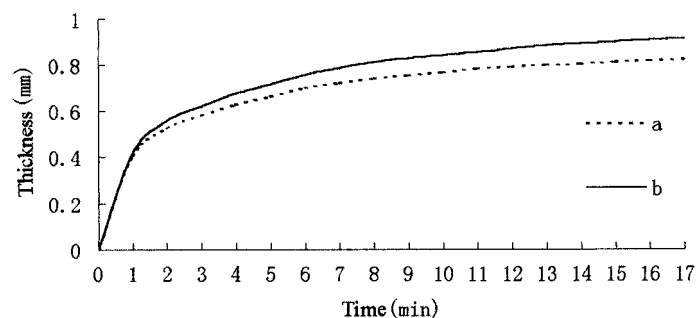


Figure 3 Relationship between dipping time and film thickness: (a) NRL and (b) MGL; C is 30%.

RESULTS AND DISCUSSION

Determination of the Blending Method for NRL and MGL

Table I shows the η changes during the storage period of the blends of pre-vulcanized NRL and pre-vulcanized MGL. It can be seen from Table I that the η s were in unstable states and increased along with increasing storage time. By 9 days, the blends were all seriously thickened, which may have been caused by the poor compatibility of pre-vulcanized NRL and pre-vulcanized MGL.

Table II shows the η changes during the storage period of the pre-vulcanized blends of NRL and MGL that were mixed uniformly before vulcanization. Table II shows that after NRL has been mixed uniformly with MGL and then subjected to pre-vulcanization, the viscosities of pre-vulcanized blends are only slightly different from

that of pre-vulcanized NRL and keep approximately stable during storage period, indicating that this way is suitable for blending.

Basic Properties of the Pre-vulcanized Blends

The basic properties of the pre-vulcanized blends of different C s are shown in Table III and Figures 1 and 2.

It can be seen from Table III that the η , total solid content, and alkalinity of the pre-vulcanized blends were only a little different than that of pre-vulcanized NRL; Figures 1 and 2 show that with the increment in C in the pre-vulcanized blends, T_{HS} increased, but T_{MS} decreased, both in a linear relation. Their relationships were $T_{HS} = 0.36C + 33.0$ and $T_{MS} = -1.33C + 772.0$, respectively. Results obtained by comprehensive analysis indicated that the pre-vulcanized blends

Table IV Mechanical Property Changes of the Films

C (%)	500% Modulus (MPa)	Property					Tear Strength (N/m $\times 10^3$)
		Elongation at Break (%)		Tensile Strength (MPa)			
		Before Aging	After 70°C $\times 72$ h Aging	Before Aging	After 70°C $\times 72$ h Aging		
0	1.8	1064	960	29.0	27.8	25.0	
5	2.0	960	912	28.0	28.0	45.0	
10	2.1	928	884	29.0	32.0	55.0	
15	3.4	900	844	24.0	26.0	56.0	
20	4.2	860	840	26.0	28.0	58.0	
25	4.8	840	835	28.5	29.0	59.0	
30	5.7	816	820	26.4	30.8	62.0	
35	5.8	828	800	29.0	30.0	48.0	

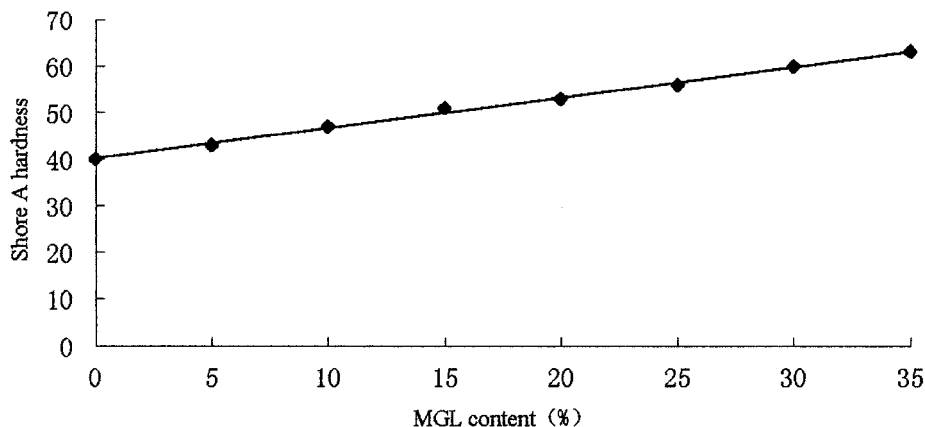


Figure 4 Relationship between C and H .

still possessed good basic properties that were similar to that of preulcanized NRL and that the heat stabilities of the blends improved.

Film-Forming Properties of the Preulcanized Blend

When the film-forming properties of preulcanized NRL and the preulcanized blend containing 30% MGL were compared, the results indicated that all of these had good flowability, were evenly deposited on the mold, and had films of good consistency. The relationship between film thickness and dipping time is shown in Figure 3.

It can be seen from Figure 3 that the film thickness increased quickly in the early part of the film-forming period, especially in the beginning 3 min, both for the preulcanized NRL and the preulcanized blend containing 30% MGL.

However, after 7 min, the thickness increased at a gentle speed, and the film-forming rate of the preulcanized blend was slightly faster than that of preulcanized NRL. It can be concluded from this result that the preulcanized blend still possessed excellent film-forming properties similar to those of preulcanized NRL.

Mechanical Properties of the Films

The mechanical properties of the films of the preulcanized blends containing different amounts of MGL are shown in Table IV and Figures 4 and 5.

It can be seen from Table IV that the 500% modulus increased with the increment of C and the increasing degree became bigger and bigger; for elongation at break, there was a decreasing trend with the increment of C . Tensile strength fluctuated on a small scope. The elongation at

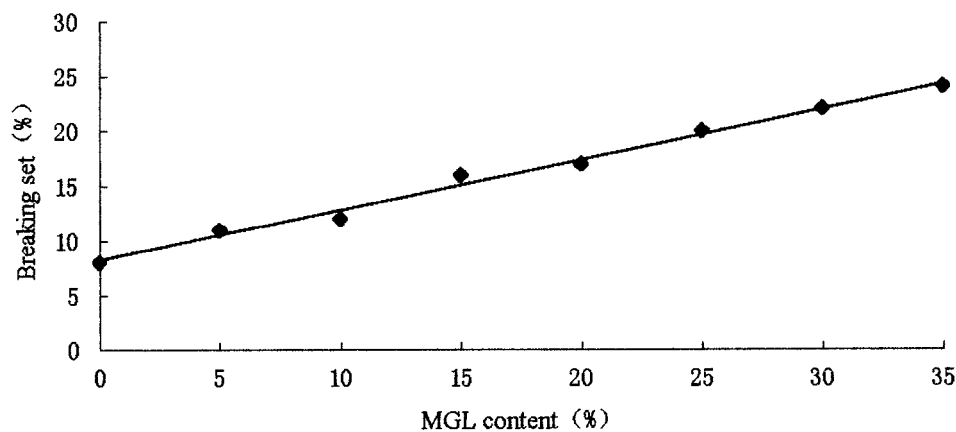


Figure 5 Relationship between C and B_s .

break slightly decreased, and the tensile strength increased after aging, which indicates that the films of the prevulcanized blends maintained good antiaging properties. Tear strength increased with the increment of C . Even for the prevulcanized blend containing 5% MGL, the tear strength increased by almost 200%. However, as C increased to 35%, the tear strength decreased sharply, but it was still higher than that of prevulcanized NRL. This proves that the blending of NRL and MGL can increase the tear strength of the films.

Figure 4 shows that H increased linearly with the increment of C ; their relationship was : $H = 0.66C + 40.0$. Figure 5 shows that the B_s also increased linearly with the increment of C ; their relationship was $B_s = 0.46C + 8.0$.

CONCLUSIONS

By mixing NRL uniformly with MGL and then carrying out prevulcanization, we obtained pre-

vulcanized blends with similar basic properties to that of prevulcanized NRL and improved the heat stability.

The prevulcanized blend of NRL and MGL possessed excellent film-forming properties.

By blending NRL with MGL, we increased the hardness and modulus of film and improved its antiaging properties, and there was no adverse effect on the tensile strength, whereas the elongation at break decreased and B_s increased.

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