Reinforcement of Natural Rubber Latex Film by Ultrafine Calcium Carbonate

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ABSTRACT: Using ultrafine calcium carbonate to reinforce natural rubber latex film, the effect of its content on latex properties such as surface tension, viscosity, mechanical stability, and heat stability and the physical properties of latex film before and after aging such as tear strength, modulus, and tensile strength were investigated. The results showed that the surface tension of natural rubber latex reinforced by ultrafine calcium carbonate only changed slightly; when the content of calcium carbonate was less than 20%, the change of viscosity was not obvious, but when the content was greater than 20%, the viscosity significantly lowered. Ultrafine calcium carbonate could effectively improve the tear strength, tensile strength, and modulus of the natural rubber latex film. The modulus increased with the increment of the calcium carbonate. When the content of calcium carbonate was less than 15%, the tear strength and tensile strength increased with the increments of calcium carbonate, but when the content was greater than 15%, the above-mentioned properties decreased with the increment of calcium carbonate. By comprehensive consideration, the best reinforcing effect was obtained at a content of 15% ultrafine calcium carbonate. The particle diameters of calcium carbonate and their distribution in the calcium carbonate emulsion and in the rubber film were analyzed with SEM and a laser particle size tester, which showed that the distribution of calcium carbonate in the latex film was even and that it could effectively reinforce natural rubber latex film.
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Key words: calcium carbonate; natural rubber latex; reinforcement; latex film

INTRODUCTION

Natural rubber latex possesses excellent comprehensive properties, but it also has some inadequacies.[1] For example, the tear strength of glove made from natural rubber latex cannot meet the requirements during application. So it is essential to reinforce natural rubber latex. Direct reinforcement of natural rubber latex is one of the most important problems in latex product industry. Effective and commonly used reinforcing agents for dry rubber such as carbon black only act as a filler for natural rubber latex without any reinforcing effect.[2] Some reports on direct reinforcement of natural rubber latex by methyl-methacrylate-grafted natural rubber (MG rubber) latex, vinyl acetate/vinyl chloride/ethylene terpolymer, vinyl acetate/ethylene copolymer, polystyrene, resins, and so forth have been reported.[3–7] By blending MG rubber latex with natural rubber latex, tensile strength, tear strength, and puncture strength can be improved. Blended with 20% MG rubber latex, tear strength can be increased by 100%, whereas puncture strength is increased by 200%. By adding vinyl acetate/vinyl chloride/ethylene terpolymer, vinyl acetate/ethylene copolymer, and polystyrene into natural rubber latex, tensile strength remains the same, but tear strength can be increased. When blending with 30% vinyl acetate/vinyl chloride/ethylene terpolymer, the tearing pattern shifted from the original "filiform" type to the "zigzag" type, indicating that tear strength was increased significantly. Incorporating resin such as polystyrene and polyvinyl chloride into natural rubber latex increased tear strength with the increment of the amount added until the added amount reached 20%, when tear strength decreased. The optimum amount for resin is 10%–15%. The aim of this study was to reinforce natural rubber latex by inorganic reinforcing agent—ultrafine calcium carbonate and to improve the physical properties of latex film such as tear strength.

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EXPERIMENTAL

Materials

Calcium carbonate emulsion was supplied by South China Tropical Agricultural Product Processing Research Institute. Natural rubber latex concentrate was obtained from a local rubber plantation. The reinforced latex was prepared as follows: the latex concentrate was first prevulcanized at room temperature for 2 days with the following recipe: rubber (dry weight) 100; sulfur 1.5; accelerator PX 1.2; accelerator ZDC 0.8; zinc oxide 1.5, and an appropriate amount of

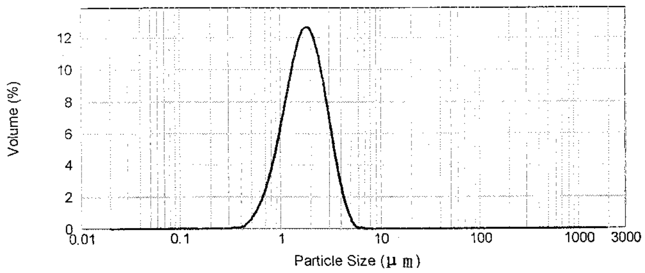

Figure 1 The distribution curve of calcium carbonate particle size.

stabilizer. Then 0%–30% calcium carbonate emulsion (based on dry weight) was added as required. The reinforced latex was cast on a glass plate and dried in an oven at 85°C. After leaching and drying, the reinforced latex film was formed.

Testing methods

The particle size was determined by a MasterSizer 2000 laser particle size tester. Latex film reinforced by 10% ultrafine calcium carbonate was analyzed by scanning electron microscopy (SEM), using a PHILIPS XL30. The samples were gilded for 2 min by a Hitachi E-1010 sputtering device. The heat stability time (HST) was determined by a latex heat stability tester at a temperature of 80°C. The viscosity was determined by a viscometer at a constant temperature of 25°C. The mechanical stability time (MST) was determined according to GB/T8301-1987 by using a KLAXON HMSUB2 mechanical stability tester. The surface tension was determined according to ISO1409:1995 "Plastics/Rubber—Polymer Dispersions and Rubber Lattices (Natural and Synthetic)—Determination of Surface Tension by the Ring Method" by using a JYW-200A automatic interfacial tension tester. The physical properties was determined according to GB/T528-1998, GB3512-1983, and GB/T2941-1991. The condition for aging was: 100°C × 22 h. The tear strength was determined according to GB/T529-1991. The test pieces were cut by a right-angle-type cutter.

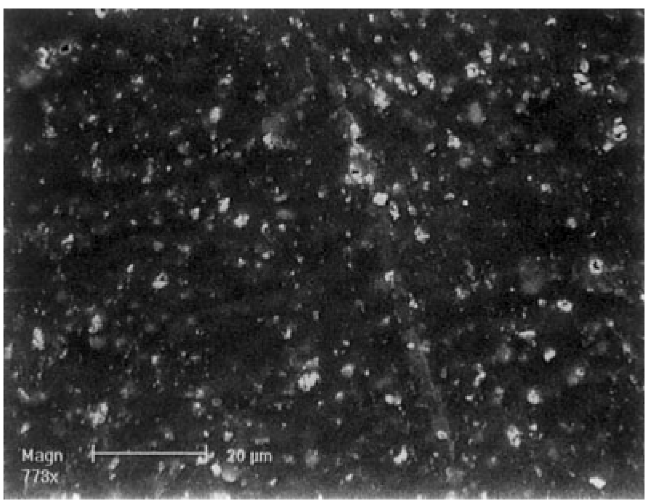

Figure 2 The SEM graph of latex film reinforced by 10% calcium carbonate.

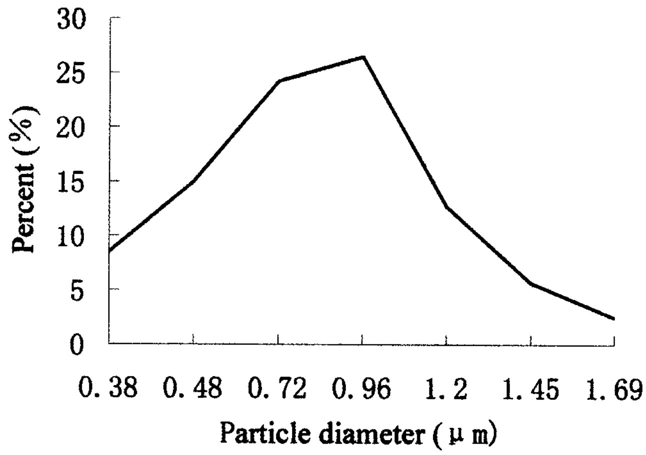

Figure 3 The distribution curve of particle diameter of calcium carbonate in latex film.

RESULTS AND DISCUSSION

Particle diameters of calcium carbonate and their distribution

Figure 1 is the distribution curve of particle size in calcium carbonate emulsion. The results show that the particle sizes of calcium carbonate were in the range of 0.356–6.3 μm, where particles with a diameter of 0.356–0.926μm, 0.356–1.775 μm and 0.356–3.153 μm accounted for 10%, 50%, and 90%, respectively. The average particle diameter of calcium carbonate was 1.551 μm, and there was a normal-type distribution of particle diameter size of calcium carbonate.

Particle diameters of calcium carbonate in latex film and their distribution

Figure 2 is the SEM graph of latex film reinforced by 10% calcium carbonate, and Figure 3 is the distribution curve of particle diameter of calcium carbonate in

TABLE I
Effect of Calcium Carbonate Content on Latex Properties

Content of calcium carbonate (%)	Viscosity (mPa · s)	MST (s)	HST (s)	Surface tension (mN/m)
0	19	414	49.0	44.3
5	21.8	680	30.2	44.5
10	22.5	750	29.8	44.7
15	23.0	>1200	27.6	44.9
20	24.3	>1200	23.4	44.8
30	10	>1200	20.1	46.1

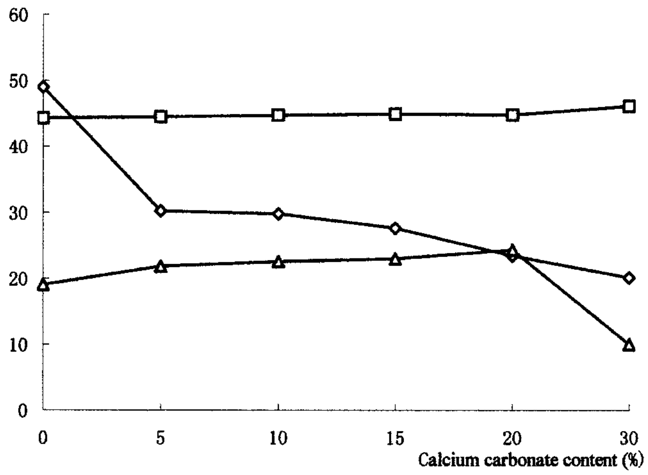

Figure 4 The effect of calcium carbonate content on latex properties (□: surface tension, mN/m; ◇: HST, s; △: Viscosity, mPa · s).

latex film. The statistical analysis shows that the average particle diameter of calcium carbonate was 1.08 μm, which is close to that of calcium carbonate emulsion and the distribution of particle diameter is also at a normal distribution type. It can be seen from Figures 2 and 3 that the distribution of calcium carbonate in latex film was even, resulting in a reinforcing effect on the latex film.

Effect of calcium carbonate on latex properties

It can be seen from Table I that the viscosity of latex increased slightly with the increment of calcium carbonate, but when its content was greater than 20%, there was an obvious decrease in viscosity (Fig. 4). The main reason for this is that with the increment of calcium carbonate, the diffusion movement of latex particles is inhibited, which causes viscosity to increase. But when the amount of calcium carbonate increases continuously to a liminal value, the dilution effect of calcium carbonate is greater than its inhibitory action on the diffusion movement of the latex particles. Then the calcium carbonate acts as a diluent for latex, which causes the viscosity to decrease. It can be seen from the surface tension test result that with an increase in calcium carbonate, the surface tension increases slightly. This occurs because the calcium carbonate that filled in the free volume of latex has a similar particle diameter to that of the latex, and so the variation of the particle sizes in latex is not apparent. With an increase in the amount that calcium carbonate fills, the free volume in latex tends to be saturated, and the surface tension increases slightly under the action of the calcium carbonate particles. The significant increasing of MST and obvious decreasing of HST is caused by KOH existing in the calcium carbonate emulsion, which can increase the negative charge of the rubber particles, causing a significant increasing of MST. At the same time, KOH hydrolyzes the protein in the protective layer of the rubber particles, causing the breakdown of the hydrated membranes on the surface of the rubber particles and lowers the HST.

Effect of calcium carbonate content on physical properties of latex film

It can be seen from Table II that with the increase in calcium carbonate content, the modulus of latex film increased accordingly, whereas tensile strength and tear strength were increased at the beginning and reached a peak value when calcium carbonate content as 15% and then decreased (Figs. 5 and 6). The elongations at break tended to gradually decrease. It is apparent that calcium carbonate has a good reinforcing effect on latex film. When the amount of calcium carbonate was 15%, the comprehensive efficacy was optimum; when it was greater than 15%, the reinforcing effect was decreased; and when it reached 30%, there was no more reinforcing effect.

When the latex was reinforced with filler, the particle diameter of the reinforcing agent was the main factor for its reinforcing ability. The smaller the particle diameter, the better the diffusion efficacy became, its matching effect with the free volume of rubber tending to be stronger, its role as an impurity weaker, and its ability to inhibit the microcrack expansion

TABLE II
Effect of Calcium Carbonate Content on Physical Properties of Natural Rubber Latex Film

Content of calcium carbonate (%)	700% modulus (MPa)		Elongation at break (%)		Tensile strength (MPa)		Tear strength (kN/m)	
	Before aging	After aging	Before aging	After aging	Before aging	After aging	Before aging	After aging
0	2.4	1.8	2000	1590	18.8	13.2	48.1	17.5
5	2.0	1.5	1960	1480	24.4	15.8	65.0	20.0
10	5.2	3.8	1720	1640	24.8	17.5	70.0	24.7
15	5.2	4.6	1660	1520	26.3	19.0	72.3	29.2
20	7.3	6.1	1320	1360	22.7	17.7	64.8	19.2
30	7.4	7.3	1440	1320	21.0	15.0	56.2	17.9

higher. In addition, with the micronization of particles, the filler particles became the aggregates of a limited amount of atoms, which exhibited a special surface effect. The smaller the particle, the greater the specific surface area became. with the surface effect tending to be stronger, which increased the contact area between the filler and rubber particles and ensured the formation of physical tangles. At the same time, the ability to inhibit the movement of macromolecules and the carrying efficiency increased, resulting in a good reinforcing effect. But when the amount of reinforcing agent exceeded a critical value, the contact of rubber particles with reinforcing-agent particles tended to be saturated. If the amount of reinforcing agent continued to increase, the aggregates became larger, and the distance between the rubber particles increased, which broke down the monolithic construction of the material, making the reinforcing effect poorer.

It can be seen from the aging properties that the quantity of calcium carbonate did not have a great effect on the aging properties (Fig. 6). The aging coefficient was around 20%.

CONCLUSIONS

The size of the particle diameters of ultrafine calcium carbonate are in the range of 0.356–6.3 μm, among which the particles with a diameter of 0.356–0.926 μm accounted for 10%, and the average particle diameter was 1.551 μm. The calcium carbonate particles were evenly distributed in natural rubber latex film reinforced by ultrafine calcium carbonate, which can effectively reinforce natural rubber latex. Calcium carbonate had no obvious effect on the surface tension of reinforced latex. When the amount of calcium carbonate was less than 20%, there was no great effect on viscosity; but when the amount was above 20%, the viscosity of latex decreased significantly. Calcium carbonate had a significant effect on the physical properties of latex film. The modulus increased with an increase in calcium carbonate, whereas the elongation at break had a tendency to be reduced with an increase in calcium carbonate; both tensile strength and tear strength improved when the amount of calcium carbonate was less than 15%; but when the amount of calcium carbonate was above 15%, these two properties decreased gradually. From comprehensive consideration, the reinforcing effect was found to be optimum at a content of 15% calcium carbonate.

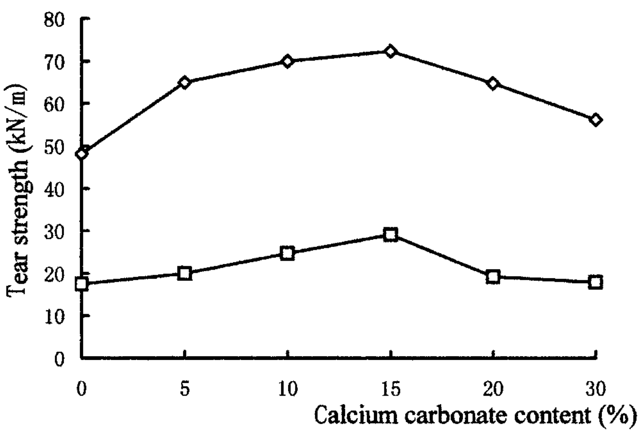

Figure 5 The effect of calcium carbonate content on tear strength (◇: before aging, □: after aging).

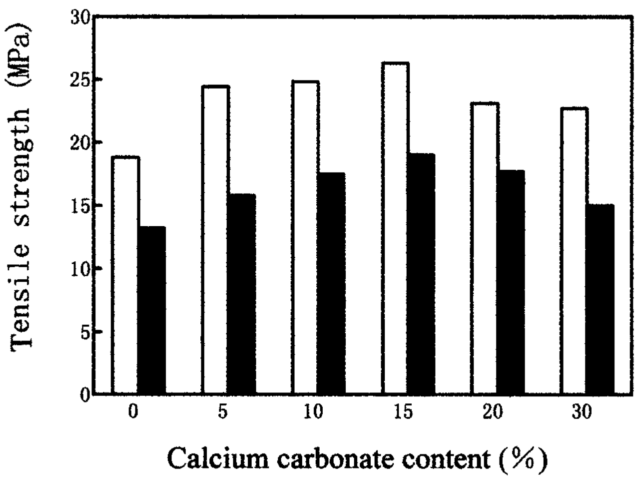

Figure 6 The effect of calcium carbonate content on aging properties (□: before aging; ■: after aging).

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