

Molecular Design of Damping Rubber Based on Polyacrylate-Containing Silicone

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ABSTRACT: A series of damping rubbers based on poly(meth)acrylate and poly(meth)acrylate-containing silicone rubbers has been prepared. The dynamical mechanical properties were evaluated by using a dynamic mechanical viscoelastometer (DMA). A detailed investigation is reported on the relationship of the damping capability of the poly(meth)acrylate rubbers with their composition and macromolecular architecture. Also discussed is the effect of two kinds of silicone elastomers on the damping performance of the polyacrylate-containing silicone rubber. The results indicate that, in vulcanized rubber systems, both statistical copolymerization for multiple monomers and blending between immiscible polymers with close T_g s facilitate broadening the glass transition peaks. Furthermore, the molecular design is quite an effective approach in which the multiple monomers whose polymers have a ladder-changing T_g are used to synthesize the damping rubber with the broad effective functional area. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 746–751, 2002

Key words: polysiloxanes; poly(meth)acrylate; rubber

INTRODUCTION

Because of their wide applications in military fields and civil products, polymeric damping materials have received increasing interest. However, since most homogeneous polymers often possess narrow glass transition regions serving as the high damping function areas, the application of polymer damping materials from much wider fields is limited.^{1–3}

Recently, considerable attention has focused on broadening the glass transition regions of damping materials. Much of the literature has reported the achievements in the interpenetrating polymer net-

works of polyurethane with vinyl polymers, such as poly(meth)acrylate and polystyrene,^{4–9} but little research has involved damping rubber derived from vulcanization. However, it might be a project with potential to prepare a rubber with a broad absorbant energy temperature band, because the vulcanized rubber used for a wider field possesses striking advantages of dimension stability, lower deformation set for elongation and compression, as well as fatigue resistance, etc. Simultaneously, to broaden the damping functional domain from vulcanized rubber still has quite a few difficulties.

Poly(meth)acrylate has the capability of high damping above ambient temperature and is known for its good oil resistance and mechanical properties, while silicone rubber is of remarkably high and low temperature resistance, water resistance and permeability, though its damping value is low. If the poly(meth)acrylate damping rubber prepared via special molecular design is combined

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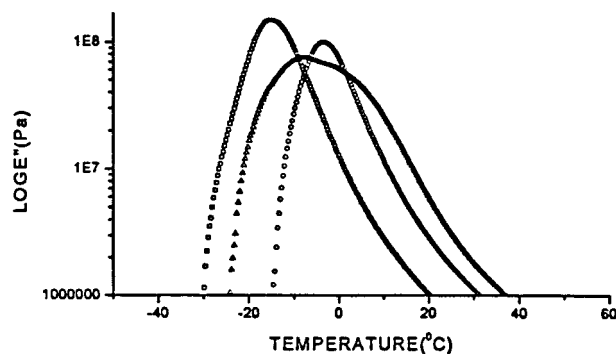


Figure 1 Plots of $\log E''$ vs temperature of poly(meth)acrylate rubber. \square : No.33 sample from homopolymer; \circ : No. 34 sample from copolymer of two monomers, \triangle : 27-8 sample from copolymer-containing MMA monomeric unit.

with silicone rubber, it will be possible to broaden the damping function region in the lower temperature band for polyacrylate rubber, and to heighten damping value for silicone rubber in the high temperature region, and moreover, to come to a balance of excellent properties in the novel damping rubber.

We have synthesized such materials. In this paper, the research results are first presented, and an effective method of molecular design and some interesting phenomena are discussed.

EXPERIMENTAL

Materials

Various monomers applied to synthesize the poly(meth)acrylates are ethyl acrylate (EA), butyl acrylate (BA), 2-ethylhexyl acrylate (HEA), methyl methacrylate (MMA), acrylonitrile (AN), styrene (ST), and a diene monomer such as dicyclopentadiene and its dimer, etc. They were distilled under reduced pressure or treated by column chromatography using neutral alumina for eliminating inhibitor.

Polymethylphenylsiloxane (PMPS), with the trade name of MPVQ 1201, and polydimethylsiloxane, with the trade name of MVQ 1102 supplied by Jieling Chemistry Institute and Cheng Guang Chemistry Institute of China, respectively, were used.

Synthesis and Preparation of the Samples

Poly(meth)acrylate damping rubber was synthesized by the method of emulsion copolymerization

from the above-mentioned monomers. The polymeric reaction was performed in a reactor equipped the N_2 protection, a stirrer, feed funnels, and a thermometer when the temperature was maintained at $25 \pm 2^\circ\text{C}$. After about 3 h of the reaction, the elastomers with ~ 14 iodine value was obtained through breaking emulsion, coacervating, rinsing, and drying. Then it was blended with 0.8 phr hexane peroxide or with the two kinds of silicone elastomers mentioned above and the peroxide on a two-roll mill and at a controlled temperature such as 100°C 5 ~ 7 min and 25°C ~ 10 min. Then the blend was vulcanized at $160 \sim 170^\circ\text{C}$ under a pressure of about 5.0 ~ 10 MPa.

Dynamic Mechanical Spectroscopy

A dynamic viscoelastomer, 7e (Perkin Elmer Co.), was used to evaluate the dynamic mechanical properties of the samples with the diameter of 5 mm and height of ~ 2 mm. The measurements were made at a heating rate of $1^\circ\text{C}/\text{min}$ and a frequency of 1 Hz by selecting a compression mode.

RESULTS AND DISCUSSION

The damping capability of rubber is dominated by its glass transition region, while the latter is determined the flexibility of the backbone, the size and flexibility of the side groups, and the structure of the vulcanized network. In this article, keeping the vulcanized system constant, we concentrate on the relationship of different chemical

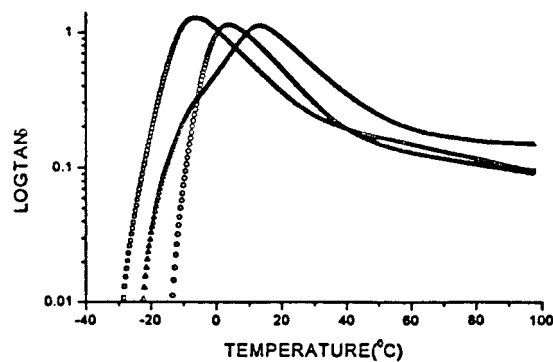


Figure 2 Plots of $\text{Logtan}\delta$ vs temperature of poly(meth)acrylate rubber. \square : No. 33 sample from homopolymer; \circ : No. 34 sample from copolymer of two monomers; \triangle : No.27-8 sample from copolymer-containing MMA monomeric unit.

Table I Dynamic Mechanical Viscoelastometer (DMA) Data of Damping Rubber of Poly(meth)acrylate

Sample No.	E''				$T_g \delta$			
	LA (Pa \times Min)	T_g ($^{\circ}$ C)	Peak Width ($^{\circ}$ C)	E''_{\max}	Area ($T_g \delta \sim T$)	T_g ($^{\circ}$ C)	Peak Width ($^{\circ}$ C)	$T_g \delta_{\max}$
34	1.2567×10^8	-4	14	1.0483×10^8	35.84	3.67	84	1.14
33	2.009×10^8	-16	25	1.5746×10^8	44.42	-5.83	93	1.27
27-8	1.8242×10^8	-9	50	7.8389×10^7	45.12	12.21	115	1.12
27-9	1.5269×10^8	-9	66	6.2385×10^7	48.84	9.11	125	1.02
27-6-5	1.3792×10^8	-17	36	1.0342×10^8	40.93	-5.50	100	1.17

groups and backbone with damping performance, and on the molecular design of the damping rubber made from poly(meth)acrylate- and polyacrylate-containing silicone rubber.

Molecular Design of the Poly(meth)acrylate Rubber

As shown in Figure 1, only Sample No. 34 exhibits a very narrow loss modulus (E'') transition peak. Number 33 displays a wider one, its E'' peak width being 1.3 times the size of No. 34. Compared with them, No. 27-8 shows the widest E'' peak, which is 2.25 times as much as that of No. 34. From Figure 2 and Table I, it can be seen that the same tendency appears in the loss factor vs temperature ($T_g \delta - T$) diagram.

The fact mentioned above demonstrates that even if, in the poly(meth)acrylate rubber vulcanizing system, the degree of microphase separation, to considerable extent, is still governed by the structure at diverse levels, such as the structural groups in poly(meth)acrylate repeating units, and the microheterogeneity of the aggregate state of the statistical copolymer or polymer blend. Number 34 exhibits the narrowest E'' peak, for it was synthesized only from ethyl acrylate, EA, displaying a typical dynamic mechanical behavior of a homopolymer. Comparatively, No. 33 was prepared by copolymerization of the monomers EA and EHA, and therefore the width of the E'' peak shows an evident increase, but no peak splitting is found, confirming how microphase separation can be induced by incorporation of different repeat units via copolymerization. In the same way, the molecular architecture of No. 27-8 was designed on the idea that the homopolymers compounding the statistical copolymer had ladder-changing T_g s that were fully arranged on dis-

cussed temperature range. Consequently, in the case of No. 27-8, only a single broad loss modulus transition peak emerges. Furthermore, because of the combination of each transition region with its neighboring ones, the $T_g \delta$ transition peak also keeps a higher value.

According to Chang and Sperling,⁸⁻¹⁰ LA , the area under the loss modulus vs temperature curve, is a measure of the magnitude of damping capability of interpenetrating polymer networks, and it can be determined from the additive value of the molar loss constant Gi of unit weight of repeating unit $LA = \Gamma_i^n = \sum Gi/Mi$. In a composite system, it is equal to a summation of LAI on its weight fraction, $LA = \sum \Gamma_i^n = \sum WiLAI$, where LAI stands for the loss modulus of respective homopolymer components. As seen in Table I, our experimental results indicate that, with the increase of components constituting the damping

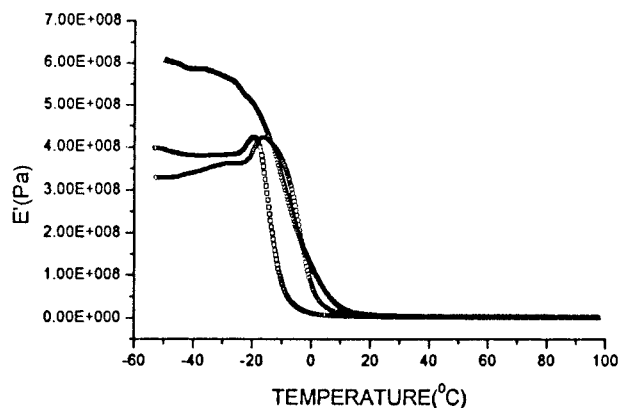


Figure 3 Plots of E' vs temperature of poly(meth)acrylate damping rubber. \square : No. 33 sample from homopolymer; \circ : No. 34 sample from copolymer of two monomers; \triangle : No. 27-8 sample of copolymer-containing MMA monomeric unit.

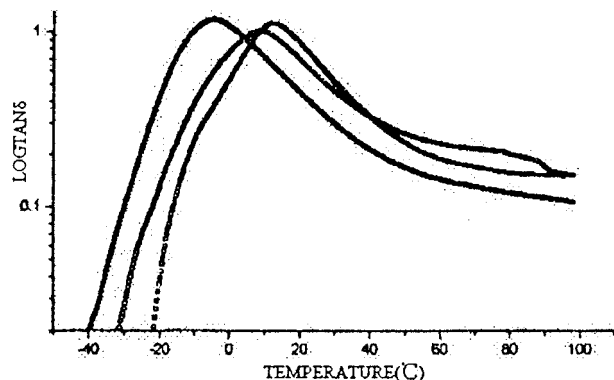


Figure 4 Fig 4 Plots of $\text{Log}T_g\delta$ vs temperature for poly(meth)acrylate damping rubber. \square : No. 27-6-5 sample from copolymer-containing AN monomeric unit; \circ : No. 27-8 sample from copolymer-containing MMA monomeric unit; \triangle : No. 27-9 sample from copolymer-containing St monomeric unit.

rubber, the change of LA reflects directly both the magnitude of an additive value resulting from LA_i of different poly(meth)acrylates and of their microphase structure, which have the same tendency with Sperling's,⁸ though, for different crosslinking systems and adopting diverse measuring instruments and methods, the value of LA is very different from his. However, in this work, it is significant to know how to realize its change for LA . As a matter of fact, a common and certain effect derived from combining multiple T_g s is that the width of transition peaks has been increased.

As shown in Figure 3, in the glass transition region, E' of the 27-8 sample has the highest value among the three and drops down more slowly in the region of the rubbery plateau. It reveals that in 27-8, some hard segments consisting of the copolymer participate in the relaxation of the chain segments of the rubber molecules. What is worth mentioning is that, from the practical point of view, the value of E' is not the higher the better. Figure 4 exhibits the semilogarithmic curves of the loss factor vs the temperature of another group of poly(meth)acrylate rubber of No. 27-8, No. 27-9, and No. 27-6-5. The curves of $T_g\delta - T$ all show a single peak with a wider absorbing band, but their $T_g\delta$ peaks have diverse shapes. Why the curves have different shapes could be interpreted in terms of the miscibility between hard segments and the basic polyacrylate system. When the three kinds of vinyl monomers, MMA, ST, and AN, were used to prepare respective samples, being of better miscibility for PMMA with its homologue, the transition peak of 27-8 is nar-

rower than that of 27-9. On the other hand, the phenomenon that 27-9 exhibits the widest $T_g\delta$ transition peak indicates that PSt and polyacrylate have the worst miscibility among them.

Incorporation of Poly(meth)acrylate and Polysiloxane Damping Rubber

The poly(meth)acrylate-containing silicone damping rubber was obtained by blending and covulcanizing both the poly(meth)acrylate rubber prepared via the special molecular design, and silicone rubber including methyl phenyl silicone rubber (PMPS) and poly(dimethylsiloxane) rubber (PDMS). Figure 5, Table II, Figure 6, and Table III exhibit their dynamical mechanical behavior, where two kinds of silicone elastomers have distinctly different influence on the damping behavior of the materials. According to the group contribution analysis,⁸ the phenyl groups possess the highest E'' value over all other structural groups. Therefore, it can be reasoned that silicone elastomer containing the phenyl groups has stronger damping capability than that of PDMS. As expected, it is confirmed by comparing the LA data in Table II and Table III. However, it is unexpected, as seen in Figure 5, in the blending rubber at a rate of 50/50 for PMPS and poly(meth)acrylate, that two independent glass transition peaks appear: one lies in -114°C , and the other emerges in -7°C , assuming that the former stands for the glass transition of PMPS rubber, and the latter for the glass transition of polyacrylate rubber. This illustrates that in the system two transition peaks fail to be combined, in spite of the T_g of the polyacrylate rubber having a shift

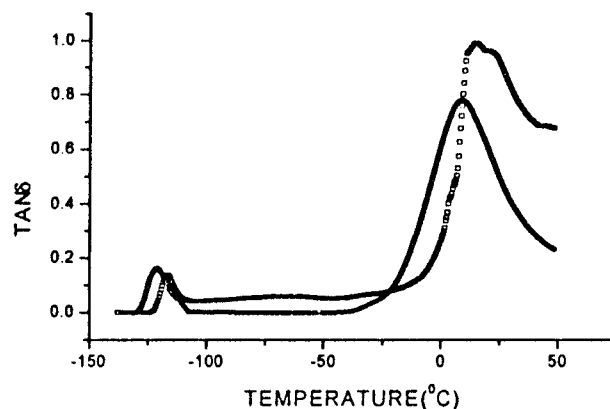


Figure 5 Plots of $T_g\delta$ vs temperature of poly(meth)acrylate/PMPS damping rubber. \circ : 50/50; \square : 70/30.

Table II DMA Data of Damping Rubber for Poly(meth)acrylate/PMPS

Polyacrylate/ PMPS	Poly(meth)acrylate				PMPS			
	Area ($T_g\delta \sim T$)	T_g ($T_g\delta$, °C)	$T_g\delta_{\max}$	LA (Pa \times min)	Area ($T_g \delta \sim T$)	T_g ($T_g\delta$, °C)	$T_g\delta_{\max}$	LA (Pa \times min)
100/0	45.12	23	1.34	1.8012×10^9				
70/30	39.18	19	0.99	1.2228×10^9	2.94	109	0.15	6.3953×10^8
50/50	38.15	17	0.78	9.1196×10^8	3.89	-115	0.17	3.6118×10^8
40/60	35.32	9	0.74	1.2240×10^9				
0/100					29.71	-118	1.01	7.389×10^8

toward lower temperature. Note that with the elevated rate of C_6H_5 -/Si in PMPS, the glass transition peak of the PMPS shifts toward higher temperature, and consequently, as shown in our recent experimental result, both transition peaks of poly(meth)acrylate and PMPS can well be combined.

In contrast, in the system of the blending materials of PDMS with poly(meth)acrylate, only a single glass temperature transition peak be found (the smaller peak might be the crystallizing melting peak of PDMS,¹⁵ which we will specially discuss later), but as seen in Figure 6, at low temperature the value of $T_g\delta$ is lower, which suggests the influence of PDMS with lower damping value. With the increase of the PDMS component in the blending rubber, the onset temperature of loss modulus peak shifts to lower temperature. As revealed in Figure 6 and Table III, when the rubber contains 60% PDMS, the onset transition temperature can reach -60°C , whereas the onset temperature only reaches -19°C when it contains 0% PDMS.

The results strongly suggest that in vulcanized rubber of poly(meth)acrylate, the idea of T_g s with an even and full arrangement in certain temperature ranges is advantageous for combining the glass temperature transition peaks of homopolymers. For immiscible blending rubbers, only when their T_g s are closer to each other, or overlapping, can the two kinds of transition peaks of the polymers be incorporated.

CONCLUSION

From the above discussion, the main conclusions can be summarized as follows:

1. By adopting the idea that multiple (meth)acrylate monomers whose polymers

have different T_g s are used to prepare the poly(meth)acrylate damping rubber via statistical copolymerization so as to make the transition peaks incorporate mutually with their neighboring ones, and elevate the microheterogeneous level of the system, damping functional area can be broadened to about 100°C , in the case the vulcanized system keeps constant.

2. In a covulcanized system, the transition peaks of two immiscibility components of polyacrylate and silicone rubber can be combined, and might be a superposition, only when their T_g s are closer to each other. If the T_g s separates further, the peak splitting will be found.
3. Through a suitable molecular design, the damping rubber of polyacrylate-containing silicone rubber will exhibit striking damping capability. Its value of $T_g\delta$ can be controlled in the range of $0.7 \sim 1.1$, the lowest onset temperature reaches $\sim 60^\circ\text{C}$ and the spanning temperature reaches $\sim 150^\circ\text{C}$.

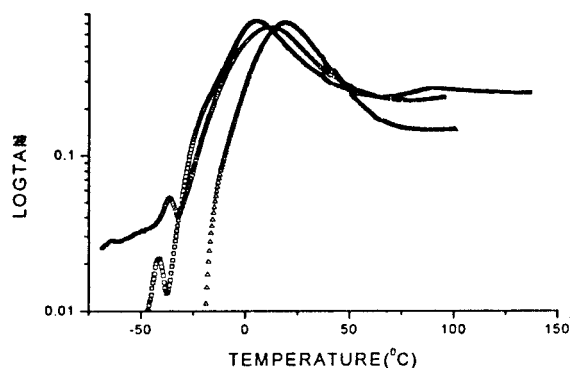


Figure 6 Plots of $\text{Log}T_g\delta$ vs temperature of poly(meth)acrylate/PDMS damping rubber. Δ : 100/0; \square : 50/50; \circ : 40/60.

Table III DMA Data of Damping Rubber of Poly(meth)acrylate/PDMS

Polyacrylate/ PDMS	LA (Pa × min)	Area ($T_g\delta \sim T$)	T_g ($T_g\delta$ °C)	$T_g\delta_{\max}$	Temperature Range (°C)		
					Onset	End	ΔT
100/0	8.8753×10^8	37.79	20	0.7	-20	60	80
60/40	9.4687×10^8	39.15	6	0.63	-30	60	90
50/50	1.0632×10^9	55.11	5	0.72	-50	100	150
40/60	1.2492×10^9	39.29	0	0.66	-60	100	160
0/100	4.5864×10^8	21.37		0.2	-100	150	250

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