

Improving interfacial adhesion in aramid-fiber-reinforced rubber composites

Zhu Luo, Weilong Chen, Zhong Jin, Fuping Dong, Le Yang, and Qiang Zheng

An anhydride and multifunctional epoxy are grafted onto liquid polybutadiene in a novel compatibilizer that has a high grafting degree and very low gel rate.

In recent years, short fibers have emerged as effective components for improving the strength and stiffness of rubber materials. In particular, aramid fibers (AFs)—because of their exceptional durability—have a substantially greater reinforcing effect compared with other fiber materials.¹ The use of AFs in rubber, however, does come with some disadvantages. For example, the smooth surfaces, high crystallinity, and low chemical activity of AFs means that there is a weak interfacial adhesion between the fibers and the rubber matrices. Currently, therefore, there is a large amount of interest in developing novel technology to modify and improve the interfacial adhesion, and to thus prepare high-performance AF-reinforced rubber composites.

In the past few years, two general methods—physical and chemical—have been used for AF modification (i.e., to increase the interfacial adhesion properties). Examples of the physical method include surface modification through the use of plasma,² ultrasonic infiltration,³ surface emulsion coating,⁴ and high-energy radiation.⁵ In addition, the chemical methods include surface etching,⁶ surface grafting or covalent modification,⁷ and surface oxidation.⁸ Of particular note, grafted products have already been used extensively as compatibilizers (to improve the bonding of non-polar rubbers with surface-treated fibers). The grafting degree (GD) of these products, however, is generally low, and considerable amounts of undesirable by-products are produced during the grafting process.

In this work,⁹ we have therefore investigated a new preparation method to produce grafting liquid rubber that has a high GD and very low gel rate (GR). In this way we hope to improve the mechanical properties of fiber-reinforced rubber composites. Specifically, we have used a solution method to synthesize a novel compatibilizer—LPB-g-MA, i.e., liquid polybutadiene (LPB) with a high GD of maleic anhydride

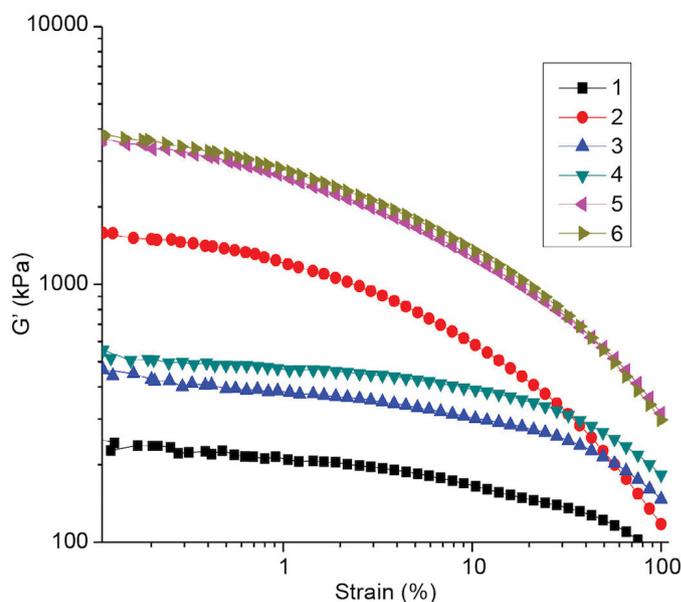


Figure 1. Measured storage modulus (G') of a variety of rubber samples (1–6), shown as a function of strain. 1: Natural rubber (NR). 2: NR/carbon black (CB). 3: NR/aramid fiber (AF). 4: NR/AF/liquid polybutadiene grafted with maleic anhydride (LPB-g-MA). 5: NR/AF/CB. 6: NR/AF/CB/LPB-g-MA.

(MA)—which has a very low GR. We also used this compatibilizer to prepare a set of natural rubber/aramid fiber/carbon black (NR/AF/CB) composites.

We synthesized the LPB-g-MA in a xylene solution at 95°C by using benzoyl peroxide as the initiator and a mixture of acetanilide and a bisphenol-A-type epoxy resin (E51) as the anti-gelling agent. To find the optimal solution, we studied the effect of adding these components in different concentrations (see Table 1). Overall, we find that the GD of our products increases with, and the GR is suppressed by, the ad-

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Table 1. The grafting degree (GD) and gel rate (GR) of the compatibilizer LPB-g-MA synthesized (over 2.5 hours) in a solution of xylene, where benzoyl peroxide (BPO) was used as the initiator and a mixture of different epoxy resin (E51) and acetanilide (in different concentrations) as the anti-gelling agent.

LPB (g)	MA (g)	Xylene (ml)	Acetanilide (g)	BPO (g)	E51 (g)	GD (%)	GR (%)
20	6	150	0.0	0.2	0	4.7	49.91
20	6	150	0.1	0.2	0	7.7	12.63
20	6	150	0.1	0.2	1	7.93	1.10
20	6	150	0.1	0.2	2	8.42	0.65
20	6	150	0.1	0.2	3	9.55	0.52
20	6	150	0.1	0.2	4	9.84	0.48
20	6	150	0.1	0.2	5	9.79	0.49

dition of the acetanilide.¹⁰ Moreover, even when we add acetanilide alone to the solution, the GR is still greater than 10%. We therefore tried adding the E51 into the reaction system in the presence of acetanilide, to further reduce the GR and increase the GD. This resulted in an obvious synergistic effect, which is caused by the epoxy resin and the acetanilide. In addition, from Fourier transform IR measurements, we observe that a small part of the multifunctional epoxy resin was also grafted onto the molecular chain of the LPB (through reaction with the MA).

In another aspect of our methodology, we used a simple thermal oxidation approach (rather than previously employed complicated AF-modification techniques, such as the plasma,² ultrasonic infiltration,³ high-energy radiation,⁵ surface etching,⁶ or surface grafting⁷ methods) to increase the oxygen content on the surface of the AFs. To verify the success of our method, we made scanning electron microscope (i.e., x-ray) measurements of our samples. We found that the oxygen content of the AF surfaces after heat oxidation in air is significantly higher than those fibers that did not undergo the heat treatment. The oxygen groups that form in this way on the fiber surfaces help to improve the level of bonding between the fibers and the LPB-g-MA.

We have also studied the mechanical properties of our vulcanized rubber samples. For instance, we found that the strength of a composite containing 4 parts per hundred rubber (phr) AF, 50phr CB, and 4.5phr LPB-g-MA increased when the E51 content in the compatibilizer was greater. This is because there is an enhanced level of bonding between the fibers and the matrix. In addition, we show the strain-storage modulus results for a variety of our rubber samples in Figure 1. These results indicate that a synergistic action between the AF and CB causes NR to be reinforced, and that NR without CB can be effectively enhanced with the addition of a small amount of AF (4phr) and LPB-g-MA. When the strain is greater than 50%, the storage modulus of the NR sample rein-

forced with 4phr AF and 4.5phr LPB-g-MA is greater than that of the NR sample reinforced with 50phr CB.

The low gel content and good dispersibility of our LPB-g-MA products means that they form strong bonds with our thermally modified AF. Furthermore, because the LPB-g-MA has a similar backbone structure to NR, there is good compatibility between the two. The LPB-g-MA thus participates in a crosslinking reaction with NR during our curing process, which serves to also increase the compatibility between NR and AF in our composites.¹¹

In summary, we have used a novel technique to simultaneously graft two different polar groups (an anhydride and a multifunctional epoxy) onto the molecular chain of LPB. We have thus demonstrated a new compatibilizer that has a high grafting degree and very low gel rate, and that can be used to improve interfacial adhesion in AF-reinforced rubber composites. In the next step of our work, we plan to focus on regulating the proportion of the two monomers that are grafted on the LPB molecular chain. We will achieve this by adding an accelerator (e.g., imidazole), and we will study the compatibilizing effect of the two co-grafted polar monomers.

Author Information

Zhu Luo, Weilong Chen, Zhong Jin, Fuping Dong, Le Yang, and Qiang Zheng

Department of Polymer Materials and Engineering
Guizhou University
Guiyang, China

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