Enhancing the Air Impermeability of a Biobased Poly(di-isoamyl itaconate-*co*-isoprene) Elastomer via the Cocoagulation of Latex and Natural Layered Silicates

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ABSTRACT: The gas-barrier properties of elastomer are of particular importance, especially for airtight applications. Poly(di-isoamyl itaconate-*co*-isoprene) (PDII) is a newly invented and respectable biobased elastomer, but the barrier properties of PDII and its composites with carbon black and silica are not satisfying at all. Because there are abundant ester groups in PDII macromolecules and these groups can contribute to the homogeneous dispersion of layer silicates, we applied layered silicates, including montmorillonite (MMT) and rectorite (REC), into the PDII matrix to improve the air impermeability. MMT/PDII and REC/PDII composites were prepared by a cocoagulation method, and the air impermeability of the PDII elastomer was highly improved. The smallest gas permeability index reached 1.7×10^{-17} m^2 Pa^{-1} s^{-1} at an REC content of 80 phr; this implied a reduction of 85.5%. A comparison of the two types of silicate/PDII composites showed that the MMT/PDII composites had better properties at low filler contents, whereas the REC/PDII composites had better mechanical and gas-barrier properties at high filler contents. Other structures and properties of the composites were investigated by X-ray diffraction, transmission electron microscopy, and dynamic mechanical rheology. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40682.

INTRODUCTION

Because of its special and outstandingly high elasticity, rubber has been taken as an irreplaceable material and is widely applied in our daily life and in industry, scientific research, and national defense. However, natural rubber trees have rigorous growth conditions that are not suitable for most districts. The basic building blocks of synthetic rubber are derived from crude oil, which is an unrenewable resource. It is urgent for us to work out some coping strategies. Emerging as the times require, the concept of biobased engineering elastomers was first demonstrated in 2010.[1] These are a new generation of synthesized elastomers with particular significance because they are synthesized from monomers derived from biomass by routes that are suitable for large-scale production, and they exhibit thermomechanical properties that are equivalent to current commercial petrochemical-derived elastomers.

In our previous study, we prepared poly(di-isoamyl itaconate-*co*-isoprene) (PDII) as one kind of biobased engineering elastomer by emulsion polymerization on the basis of itaconic acid, isoamyl alcohol, and isoprene.[2] PDII elastomers have a high molecular weight (number-average molecular weight > 300,000) and a low glass-transition temperature ($T_g < -30°C$). Silica and carbon black were used as fillers to reinforce the mechanical properties of the PDII elastomers.[3] However, the air impermeabilities of the pristine PDII, PDII/carbon black composite, and PDII/silica composite were not satisfactory. We plan to use other fillers in the PDII matrix to improve the air impermeability of this novel biobased elastomer.

In recent years, natural layered silicate/rubber composites have attracted great interest because they offer remarkably better material properties, including better tensile strength and modulus,[4] gas-barrier,[5,6] thermostability,[7] ionic conductivity,[8] flammability, [9,10]
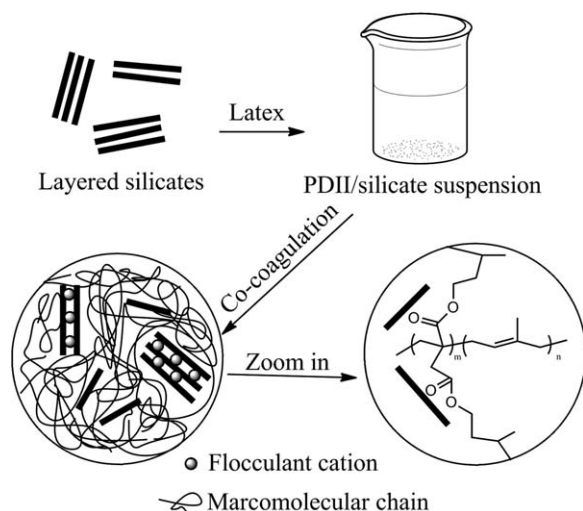
Figure 1. Sketch of the designed cocoagulation method.

and wear-resistance[11] properties, than virgin rubber or conventional microcomposites and macrocomposites.[12] Among these properties, the improvement in the gas-barrier properties is the most outstanding for layered silicate/rubber composites because of the high-aspect-ratio characteristics of the silicate monolayers. The high aspect ratio could improve the gas barrier of composites by prolonging the gas paths and hindering the diffusion of gas and other small molecules in the matrix. The dispersion of layered silicates in the polymer matrix profoundly affects the various properties of composites.

Latex cocoagulation is a promising method for the preparation of layered silicate/rubber composites and has been used to prepare composites, such as clay/NR,[13] rectorite (REC)/styrene butadiene rubber (SBR),[14] organoclay/natural rubber (NR)/NBR[15] and clay/carboxylated acrylonitrile-butadiene rubber (CNBR).[16] Most rubbers have their own latex forms, and pristine layered silicates can easily take water as a dissociation medium. Additionally, the process, which does not involve a complicated chemical reaction or solution and has a low energy cost, is inexpensive and environmentally friendly for both industrial production and scientific research.[17,18] Moreover, the basal spacing range of rubber composites prepared by latex compounding is 1.37–1.57 nm; this is much smaller than that of composites with intercalated structures (generally > 3.3 nm) and even smaller than that of organoclay (>1.7 nm).

In this study, we aimed to prepare layered silicate/PDII composites with high air impermeabilities by a cocoagulation method. Because with plenty of polar ester groups PDII has a good compatibility with layered silicates through relatively strong boundary interactions (see Figure 1), we supposed that the silicate/PDII composites would have excellent gas-barrier properties if the layered silicates were dispersed well in the polymer matrix.[19] Two types of layered silicates, including montmorillonite (MMT) and REC, were investigated in this study. MMT and REC are both 2:1 type layered silicates, but they have different constitutions and aspect ratios. The results of this study are expected to provide a new method for the preparation of environmentally friendly composites from renewable resources with excellent air impermeability and to enhance our understanding of the difference between composites filled with MMT and REC.

EXPERIMENTAL

Materials

PDII latex, which was synthesized by a previous method, consisted of 80 wt % di-isoamyl itaconate and 20 wt % isoprene.[2] The average particle size of the latex was 57.7 nm, and the dispersion index was 1.33. Sodium montmorillonite (Na$^+$ MMT; CET 78), with a cation-exchange capacity of 78 mequiv/100 g, was purchased from Siping Liufangzi MMT Co. (Jilin Province, China). REC (CET 45), with a cation-exchange capacity of 45 mequiv/100 g, was purchased from Hubei Celebrities Rectorite Technology Co., Ltd. (Hubei Province, China). The other compounding agents used in this study were commercially available.

Preparation of MMT/PDII and REC/PDII Composites

A certain amount (which varied according to the layered silicate content in the composite) of a 5% clay aqueous suspension or 2% REC aqueous suspension was mixed with the PDII latex under vigorous stirring for 20 min. Then, the mixture was cocoagulated in the electrolyte solution (a 1% calcium chloride aqueous solution), washed with deionized water until its pH was close to 7, and dried at 60°C in an air oven and at 60°C in a vacuum oven for 12 h each to obtain MMT/PDII and REC/PDII compounds.

The curing characteristics of the neat PDII and PDII composites were measured at 150°C with an oscillating disc rheometer (P3555B2, Beijing University of Chemical Technology).

The vulcanizing ingredients and other additives were mixed into the nanocompound with a 6-in. two-roll mill. The recipe of layered silicate/PDII is shown in Table I. Next, the compounds were vulcanized in a standard mold at 150°C for the optimum curing time; this was determined by a torque rheometer manufactured by Beijing Huanfeng Mechanical Factory. The vulcanizates were referred to as the MMT/PDII and REC/PDII composites.

Characterization

X-ray diffraction (XRD) analyses of various samples were carried out on a Rigaku D/Max 2500VBZt/PC X-ray diffractometer (Japan) with Cu Kα radiation operating at 40 kV and 200 mA and scanning from 0.5 to 10°. Transmission electron microscopy

Table I. Recipes for the MMT/PDII and REC/PDII Composites

LS/PDII (nanocompound; phr)	100
LS (phr)	Variable
Zinc oxide (phr)	5
Stearic acid (phr)	0.5
Sulfur (phr)	1
Accelerator CZ (phr)[a]	1
Accelerator M (phr)[b]	0.7

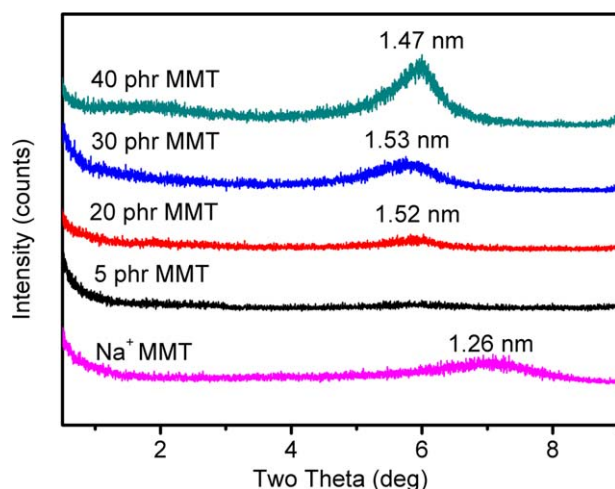LS, layered silicate; CZ, N-cycolhexyl-2-benzothiazole; M, 2-mercaptobenzothiazole.

Figure 2. XRD patterns of the MMT/PDII composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(TEM) micrographs were taken of ultrathin sections of the composites with an H-800 TEM manufactured by Hitachi, Ltd. (Japan) at an acceleration voltage of 200 kV. Strain sweep experiments in the strain range 0.1–400% were performed on uncured compounds with an RPA 2000 rubber process analyzer (Alpha Technologies) at 60°C and 1 Hz. The tensile behavior of the composites was characterized according to ASTM D 412 with a CMT4104 electrical tensile tester (SANS, Shenzhen, China). An XY-1 rubber hardness apparatus (4th Chemical Industry Machine Factory, Shanghai) was used to measure the Shore A hardness of the layered silicate/PDII composites according to ASTM D 2240. The permeation of nitrogen experiments were carried out with a gas permeability measurement apparatus. The pressure on one face of the sheet (ca. 1 mm in thickness and 8 cm in diameter) was kept at 0.57 MPa, and the other face was at zero pressure. Then, nitrogen was allowed to permeate through the sheet. Gas chromatography was used to obtain the rate of permeation of nitrogen at 40°C from which the nitrogen permeability was calculated.

RESULTS AND DISCUSSION

Morphology and Structure of the MMT/PDII and REC/PDII Composites

The XRD patterns of the Na^+ MMT and MMT/PDII composites with different MMT contents are shown in Figure 2. Na^+ MMT is a 2:1 type phyllosilicate, which consists of layers made up of two tetrahedrally coordinated silicon atoms fused to an edge-shared octahedral sheet of aluminum hydroxide. The d_{001} of Na^+ MMT appeared at 6.8° and corresponded to a basal spacing of 1.26 nm. The PDII composite with 5-phr MMT showed no diffraction peaks, whereas all of other samples showed single peaks at 2θ values of about 6°; this corresponded to a basal spacing of 1.5 nm. Usually, the layers of an exfoliated composite such as MMT (5 phr)/PDII are almost randomly distributed so that no diffraction peak appears in the XRD pattern. The diffraction peaks of the PDII composites with higher contents of MMT were located at lower 2θ angles and corresponded to basal spacings larger than a value of 1.26 nm for Na^+ MMT.

All of these intergallery distances were larger than the basal spacing of Na^+ MMT (1.25 nm). As the radius of Ca^{2+} was about 0.10 nm and according to our previous studies, the small expansion was derived from the intercalation of Ca^{2+} from calcium chloride aqueous solution during cocoagulation (see Figure 1).[19]

REC also belongs to the general family of 2:1 type phyllosilicates and has a structure similar to that of MMT. In contrast to MMT, REC has a 1:1 type of layer structure arranged regularly with alternating dioctahedral mica layers and dioctahedral smectite layers. As a result, REC's layers are thicker than MMT's. The thicker layers and larger size endow REC with mechanical and gas-barrier properties before MMT. Figure 3 presents the XRD patterns of the pristine REC powder and PDII composites with different REC contents. The peaks of the pristine REC powder at 4 and 8° were distinct, and the bipeak phenomenon agreed with the 1:1 constitution. All of REC/PDII composites, except the one with 10-phr REC, showed peaks around 3.6°; the second peak was not distinct in these composites. When we compared the patterns of both types of composites, there were some conclusions we could draw. At low contents of layered silicate, the composites had exfoliated structures. As the silicate content increased, the composites evolved into different structures containing both single layers and multiple layers, and the peak intensity increased. The basal spacing of the 40-, 60-, and 80-phr composites were all about 0.45 nm larger than that of pristine Na^+ REC. The expansions were derived from the intercalation of the Ca^{2+} flocculant.

Furthermore, by comparing the XRD pattern status of MMT/PDII and REC/PDII at a filler content of 40 phr, we inferred that REC could be used at higher contents than MMT because of REC's larger size, which was verified in the permeability test.

As shown in Figure 4, the dark lines are the intersections of MMT. The MMT layers in the composite with 5-phr MMT existed in single-layer form, but the other composites with high contents of MMT contained not only single layers but also multiple layers, which came from the intercalated structures of
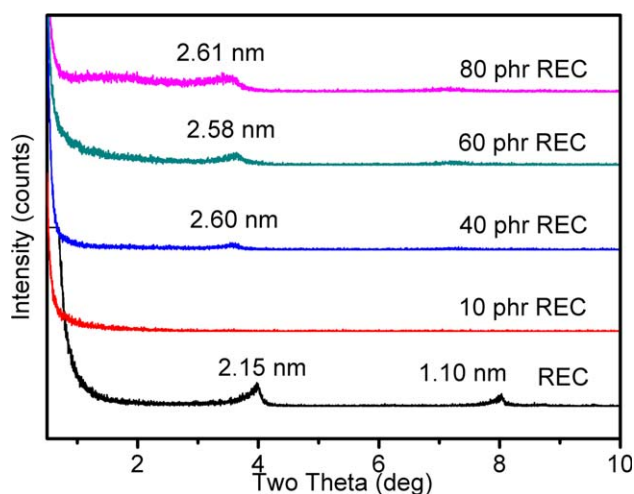

Figure 3. XRD patterns of the REC/PDII composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
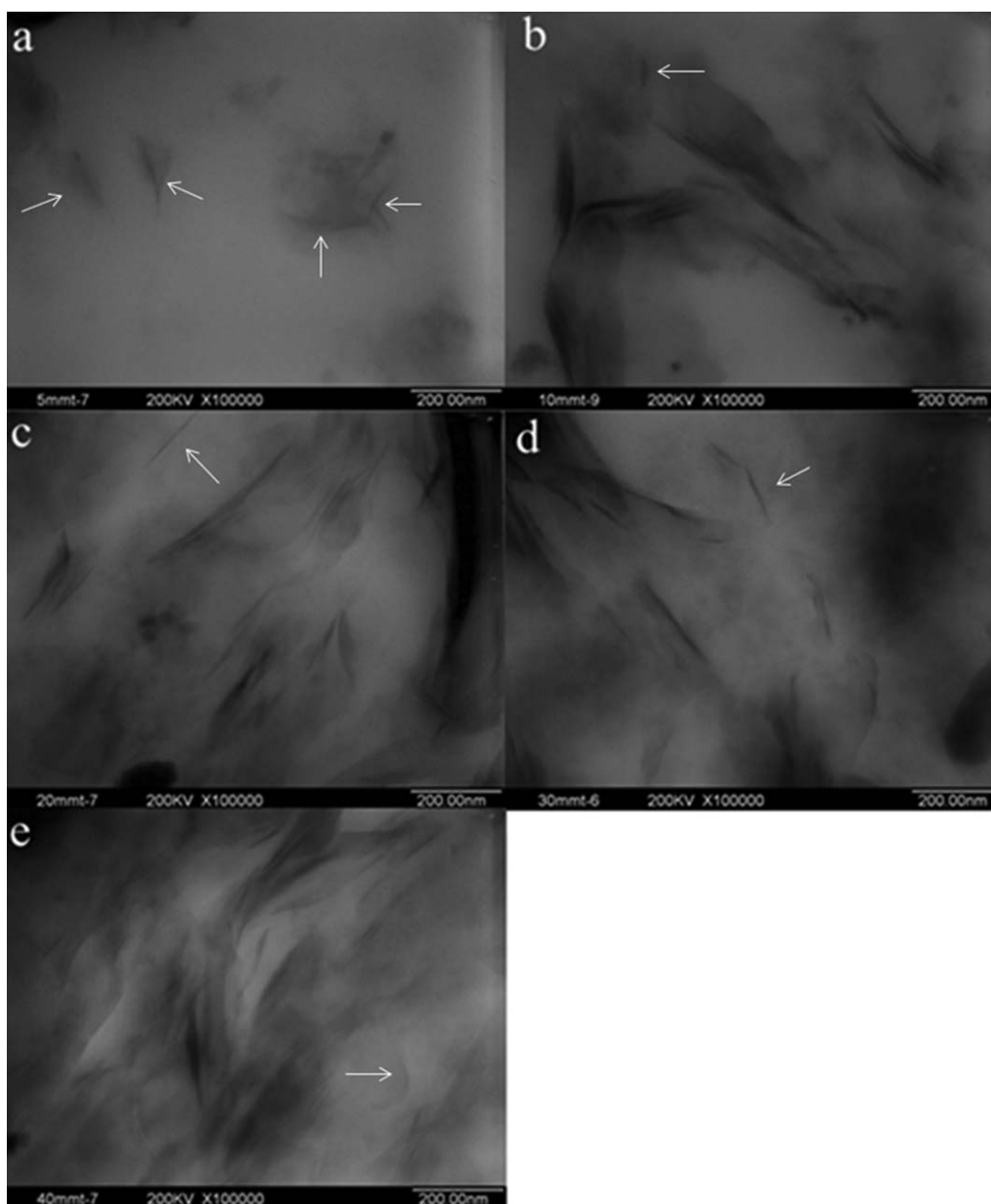
Figure 4. TEM micrographs of the MMT/PDII composites with different MMT contents: (a) 5, (b) 10, (c) 20, (d) 30, and (e) 40 phr.

MMT. The thicknesses of the multiple layers were between 10 and 30 nm. It is worthwhile to note that the dispersion of MMT in each of the PDII matrices was homogeneous. TEM observation clearly showed that MMT dispersed in the PDII matrix at a nanometer level, and the XRD diffraction peaks shifted to smaller angles compared to those with the pristine MMT. On the basis of these results, we assumed that these composites contained both exfoliated and intercalated structures.

The TEM micrographs of the REC/PDII composites also confirmed the XRD results. From Figure 5, we can see that the REC/PDII composites changed from an exfoliated structure into an intercalated structure as the REC content increased. In addition, REC showed a more uniform distribution than MMT in the PDII composites. The superiority of REC was due to its larger layer area and thickness. The larger size of REC also increased its Shore A hardness and air impermeability.

Networks of the MMT/PDII and REC/PDII Composites

The storage, or elastic, modulus (G') of rubber changes with increasing strain, which presents a strong strain dependence. Under external forces, the filler network in a rubber composite breaks down and reforms at the same time. As the strain amplitude reaches a critical value, G' sharply decreases; this is an indication that the continuous filler network is broken, until the minimum modulus is obtained. This strong strain dependence of G' is known as the *Payne effect*,[20] and it reflects the situation of the filler network in the composite. Figures 6 and 7 show the dependence of G' of the uncured MMT/PDII and
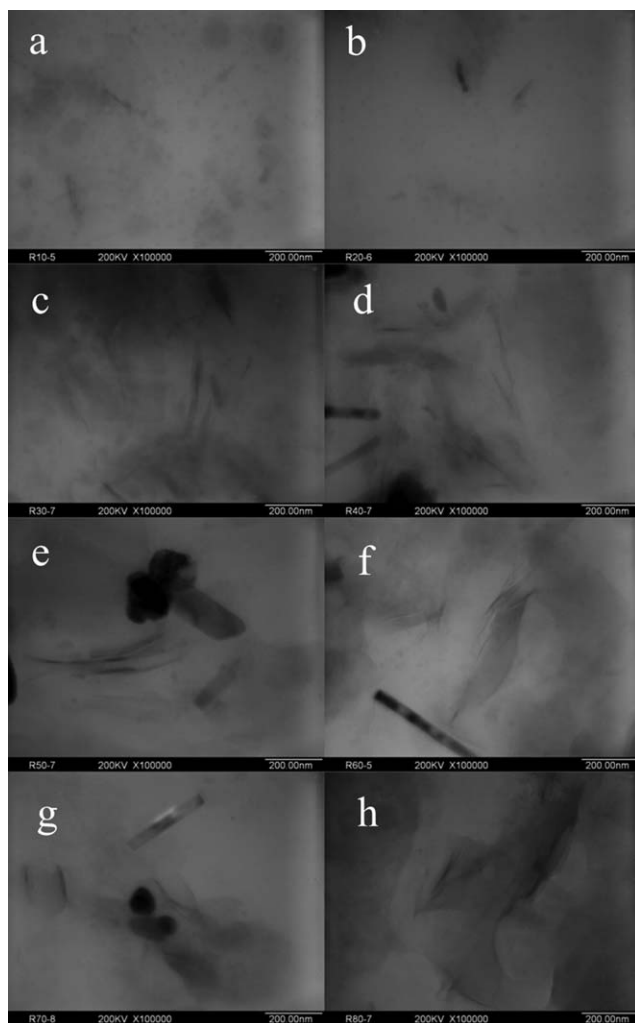
Figure 5. TEM micrographs of the REC/PDII composites with different REC contents: (a) 10, (b) 20, (c) 30, (d) 40, (e) 50, (f) 60, (g) 70, and (h) 80 phr.
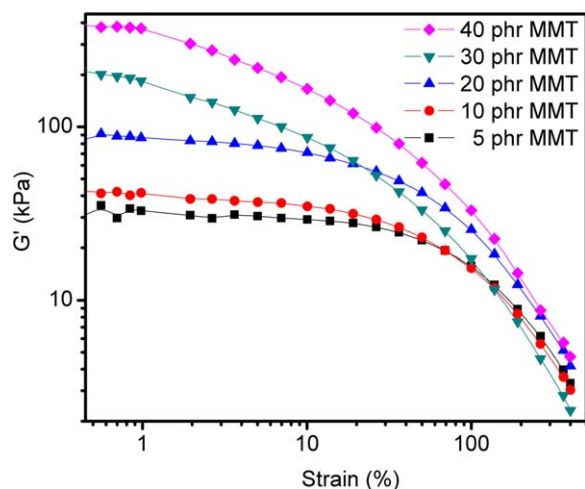
REC/PDII nanocompounds on the strain amplitude. A highly nonlinear behavior was observed for each material. First, the composites all showed a much higher modulus than the pristine PDII rubber because of the reinforcement of the nanofillers. With an increasing filler content, the initial G' increased. This means that stronger and more compact filler networks formed; they came from both the interaction between the polar ester groups of the elastomer and the layered silicates and filler–filler network. Furthermore, the nanocompounds with 30–40-phr MMT or 80-phr REC did not show a plateau in the G' versus strain curve; this was an indication that the compact filler network was broken down within the compound. It is noteworthy that a compact filler network makes it difficult for even gas and other small molecules to pass through.

Mechanical Properties of the MMT/PDII and REC/PDII Composites

The mechanical properties of the composites are summarized in Tables II and III. The mechanical properties of the unfilled PDII were pretty low. Its tensile strength was only 0.9 MPa, and its Shore A hardness was 23. However, the incorporation of 5-phr MMT into the PDII increased the tensile strength to 1.3 MPa, an increase of almost 50%.

As the amount of layered silicates increased, the tensile strength, tensile stress at 100% strain, and Shore A hardness of the composites increased, and both the elongation at break and the permanent set increased first, reached a maximum, and then decreased. It is well known that the distribution of fillers in the matrix and the interfacial interaction both affected the mechanical properties of the composites. The abundant ester polar groups in PDII provided good compatibility of the elastomer with the layered silicates. At low filler contents, a uniform distribution of the layers was easily obtained through latex compounding. However, because of their nanosize and large aspect ratio, the layered silicates tended to self-aggregate in the matrix at high filler contents; this led to no further improvement in the mechanical properties. In addition, the rigidity of the fillers confined the movement of macromolecular chains so that the
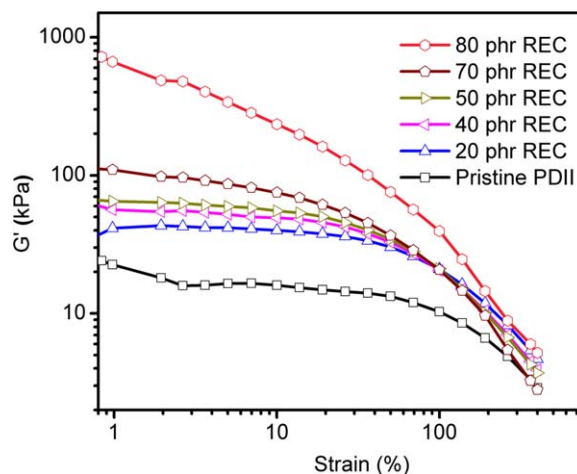

Figure 6. G' as a function of the strain of the uncured MMT/PDII nanocompounds. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 7. G' as a function of the strain of the uncured REC/PDII nanocompounds. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Mechanical Properties of the MMT/PDII Composites

MMT content (phr)	0	5	10	20	30	40
Stress at 100% strain (MPa)	0.2	0.6	0.8	1.4	1.8	2.5
Tensile strength (MPa)	0.9	1.3	2.2	2.8	2.8	3.1
Elongation at break (%)	205	228	350	354	240	213
Permanent set (%)	0	4	25	33	24	22
Hardness (Shore A)	23	40	51	61	66	74

Table III. Mechanical Properties of the REC/PDII Composites

REC content (phr)	10	20	30	40	60	70	80
Stress at 100% strain (MPa)	0.3	0.4	0.6	0.7	0.8	1.7	—
Stress at 300% strain (MPa)	0.7	0.9	1.4	1.6	1.6	2.4	—
Tensile strength (MPa)	1.6	1.8	2.3	2.3	2.4	2.6	3.9
Elongation at break (%)	536	548	557	570	621	433	91
Permanent set (%)	20	36	44	56	68	64	20
Hardness (Shore A)	26	35	35	42	51	60	78

elongation at break and permanent set both decreased at high filler contents. Moreover, it was interesting to find that under the same filler content, REC usually did not reach as high a tensile stress as MMT did according to the tables. We claim that this was mainly because of the larger layer size of REC, which hindered its movement so it could not disperse as easily as MMT. Thus, the mechanical properties of REC were not as good as those of MMT, although in contrast at higher filler contents, the larger size was helpful for preventing layer self-aggregation.
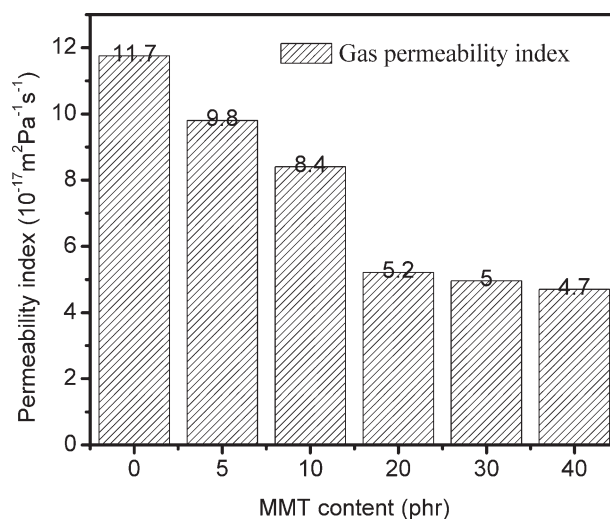
Air Impermeability of MMT/PDII and REC/PDII Composites
Compared with carbon black and silica, nanosize MMT with a huge shape factor modify the rubber's air impermeability effectively by prolonging the gas paths and hindering the diffusion of gas and other small molecules in the matrix. We measured the gas permeability index of layered silicate/PDII composites. Low gas permeability index indicates good air impermeability of the material. As shown in Figure 8, the gas permeability index of the pristine PDII elastomer was $11.7 \times 10^{-17} m^2$ Pa^{-1} s^{-1}; this represented poor gas-barrier properties. However, PDII filled with 20-phr MMT had a permeability index of $5.2 \times 10^{-17} m^2$ Pa^{-1} s^{-1}; this was less than half that of pristine PDII. The gas-barrier properties decreased only slightly with further increases in the MMT content because of the large aspect ratio of MMT. A mass of layers with large aspect ratios tend to aggregate, and this results in poor distribution. As a result, the effect of the filler content on the gas impermeability decreased.

The gas permeability indices of the REC/PDII composites are shown in Figure 9. In contrast to that of MMT/PDII, the gas permeability index of REC/PDII decreased consistently within the range of REC contents studied. The gas permeability index of the composite with 40-phr REC dropped to half of that of pristine PDII. The gas permeability index kept decreasing and

reached 1.7×10^{-17} m^2 Pa^{-1} s^{-1} at an REC content of 80 phr, a reduction of 85.5%, and this indicated excellent gas-barrier properties.

At a given content of layered silicate, such as 10 phr, MMT/PDII showed better air impermeability than REC/PDII because, at such a low content, both the MMT and REC layers could exfoliate and be sufficiently dispersed, but MMT layers with a smaller size and larger aspect ratio were dispersed more uniformly; this resulted in relatively better gas-barrier properties. As the content of layered silicates increased, the distribution of MMT was not as good as that of REC. Thus, at a high content of layered silicates, such as 60–80 phr, the REC/PDII composites presented much better gas-barrier properties than MMT/PDII because the REC layers did not aggregate as easily as the MMT layers. In addition, the thicker layers of REC were less likely to be crushed during the mill process.

Figure 8. Gas permeability values of the MMT/PDII composites.
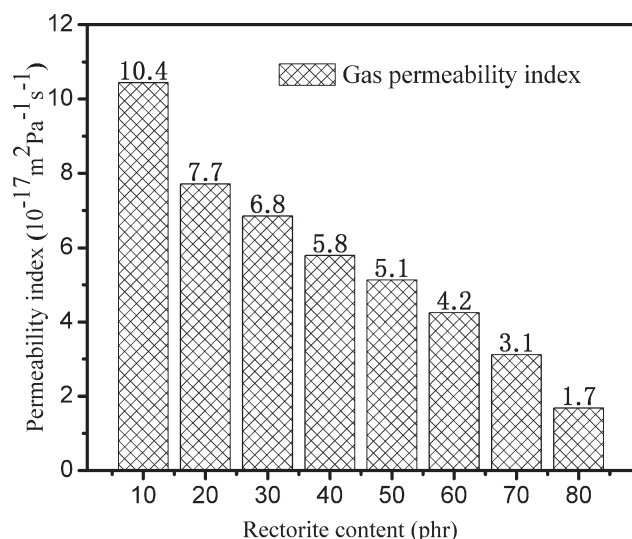
Figure 9. Gas permeability values of the REC/PDII composites.

CONCLUSIONS

To improve the air impermeability of biobased PDII elastomers, we prepared a series of high-air-impermeability natural layered silicate/PDII composites by a cocoagulation method. The MMT- or REC-filled PDII composites were superior, depending on their filler contents. At low filler contents, the MMT/PDII composites had better mechanical and gas-barrier properties, whereas at high filler contents, the REC/PDII composites had better properties. The best airtight sample was the REC/PDII composite with a filler content of 80 phr. The permeability index of this sample was 1.7×10^{-17} m^2 Pa^{-1} s^{-1}, which was 85.5% lower than that of pristine rubber and indicated excellent gas-barrier properties. At lower filler contents, the PDII composites were exfoliated structures, whereas with increasing silicate content, the composites evolved into intercalated structures containing both single layers and multiple layers. This was confirmed by both XRD and TEM. The filler networks were shaped at rich filler contents. As neither PDII nor layered silicates rely on petroleum, layered silicate/PDII composites are surely promising engineering gas-barrier materials for the future.

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