


## 실리카와 전분/셀룰로오스 혼성체가 보강된 스티렌-부타디엔 고무 복합체의 물성에 대한 연구

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## Mechanical Performance and Oil Resistance Behavior of Modified Starch/Cellulose with Silica by Adsorption Method Filled into SBR Rubber Latex

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**초록:** 스티렌-부타디엔 고무 Latex 1502에 세가지 충전제(실리카, 실리카와 전분 혼성체, 실리카와 셀룰로오스 혼성체)를 콜로이드 흡착법으로 혼합하여 고무복합체를 제조하였다. 주사전자현미경을 통해서 가교 구조를 확인하였으며, 고무복합체의 비중, 경도, 인장강도, 저장탄성률, 동학역적 성능 및 내유성을 조사하였다. 실험의 결과에서 실리카와 전분/셀룰로오스 혼성체가 고무와 상호 침투 네트워크(Interpenetrating network)를 형성하여 좋은 보강 성능을 보였다. 그 중에서도 실리카와 셀룰로오스 10 phr 혼성체가 SBR 복합체에 가장 좋은 보강 효과를 보였다.

**Abstract:** Styrene-butadiene Rubber (SBR) composites were manufactured by colloidal adsorption method with three kinds of reinforcing agents (silica, starch-silica gel hybrid and cellulose-silica gel hybrid) and SBR 1502 latex. The cross-link structure of compounds was observed with field-emission scanning electron microscope (FE-SEM). The density, hardness value, tensile strength, storage modulus, dynamic mechanical property, and oil resistance had been characterized. From the results of all tests, starch/cellulose-silica hybrid could make good reinforcement effect due to the interpenetrating network between hybrid and rubber matrix had been formed. The best filler was cellulose-silica hybrid 10 phr, which showed the best reinforcement effect with SBR compound.

**Keywords:** cellulose, starch, styrene-butadiene rubber, silica, oil resistance.

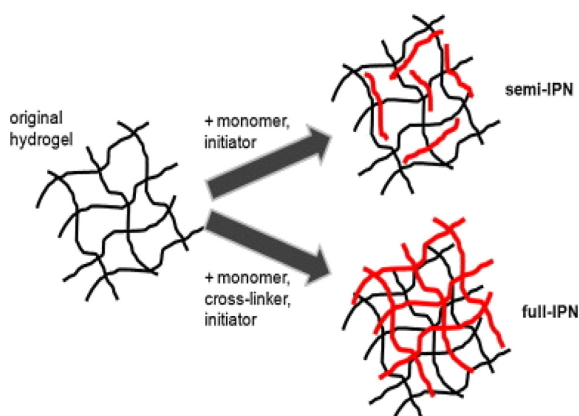
### Introduction

As the surge in the oil price and global warming occurring from carbon dioxide emissions, the application of natural resources in the polymer matrix has attracted enormous interest from both academic and industrial researchers in recent years. The application of renewable resources instead of non-renewable resources in the polymer matrix not only largely reduces the cost of products, but also is good for our environment.<sup>1</sup> Among lots of the renewable resources, starch and

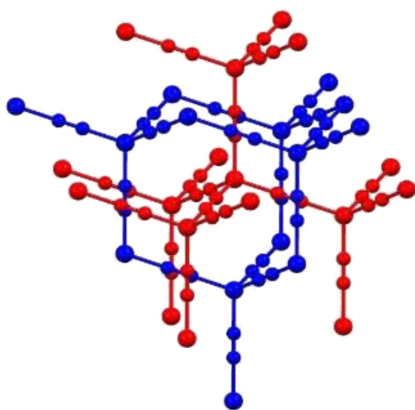
cellulose are cheapest and most abundant natural resources on the earth, which can be derived from corn, wheat, potato, rice and wood etc.<sup>2</sup> Therefore, starch and cellulose have been widely investigated for the potential application in various fields, such as coating, adhesives, flocculants, superabsorbent polymers, biodegradable polymers and packing films.<sup>3</sup>

Recently, the development of starch/cellulose as reinforcing filler in the rubber compounds has received increasing attention. But as common natural polymer, one of the major bottlenecks for starch/cellulose used as reinforcing filler in the rubber compounds is their large particle sizes. Another one of the major bottlenecks is their hydrophilic surface,<sup>4</sup> which lead to poor interfacial adhesion with the hydrophobic rubber matrix, especially for the non-polar rubber, such as SBR and

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**Figure 1.** Principle of interpenetrating polymer network.



**Figure 2.** Structure diagram of interpenetrating polymer network.

NR. Therefore, various surface modification methods, such as grafting of poly(butyl-acrylate), esterification with xanthate,<sup>5</sup> crosslinking with resorcinol-formaldehyde and isocyanate have been reported to enhance the interfacial bonding.<sup>6</sup>

Almost physical crosslinking methods depend on non-covalent bond, such as hydrogen bond, van der Waals force and other intermolecular force.<sup>7</sup> Recently, some researchers use network structure or cyclic structure hydrogel as the physical crosslink agent, which could provide more hydrogen bonds to form the physical crosslinking network. And this method offers a much wider range of properties than conventional crosslinked elastomers because the domains that act as crosslinks are reversible. And interpenetrating polymer network (IPN)<sup>8</sup> is shown in Figures 1 and 2. It is a polymer comprising two or more networks which are at least partially interlaced on a polymer scale but not covalently bonded to each other. In interpenetrating polymer network, when the physical crosslinking and chemical crosslinking occur simultaneously in a polymer material, it is speculated that the material may have

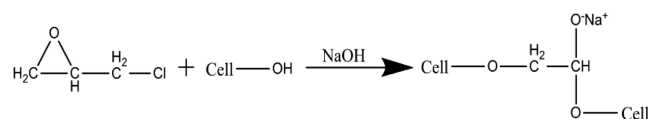
better mechanical properties, such as modulus, hardness and crosslinking density.<sup>9</sup>

In this research, the starch/cellulose had been modified into gel-state, and then mixed with silica to get the gel-hybrid which could institute the interpenetrating network polymer with SBR latex by gel adsorption method, and then get the vulcanizates during the curing processes. Finally, the mechanical properties with various methods were characterized, such as DMA, tensile stress, oil resistance, and others.

## Experimental

**Materials.** Styrene-butadiene rubber latex 1502 (effective mass 61±1%, styrene 23.5%) was obtained from Korea Kumho Petrochemical Company (KKPC), Korea; cellulose powder (microcrystalline) was obtained from DaeJung Company, Korea; starch (corn) was provided by Duksan Pure Chemical Company, Korea; sodium hydroxide (NaOH), extra pure (above 95%); sulfur, powder, extra pure (above 99%), were purchased from Dae Jung Company, Korea; methanol, extra pure (99.5%); zinc oxide, extra pure (99%); stearic acid, extra pure (95%); dodecyl-benzene-sulfonic acid, sodium salt, (DBS-Na) (50%), ethanol, extra pure (above 98%) were purchased from Samchun Pure Chemical Company, Korea; sodium hydroxide, extra pure (above 95%), was purchased from Dae Jung Company, Korea; urea, extra pure (above 99%); epichlorohydrin, extra pure (99.5%); *N*-cyclohexyl-2-benzothiazolylsulfenamide, extra pure (above 95%); 2,2'-dibenzothiazolyl disulfide, extra pure (above 95%), were purchased from Tokyo Chemical Industry Company, Japan.

**Steps of Cellulose Hybrid-SBR Composite Synthesis.** Cellulose was poured into a NaOH/urea solution with a ratio of 6 wt%/4 wt% in water, and dropped the epichlorohydrin<sup>10</sup> (used as crosslinking agent) into the system, which was showed in Scheme 1, here cellulose was defined as Cell-OH, stirred and heat at 50 °C to get the cellulose gel state. Then added silica powder into the reaction system to get the cellulose hybrid, and after that, poured the SBR latex into this system with DBS-Na (dodecyl-benzene-sulfonic acid, sodium salt) which used as surfactant. Stirred slowly for about 20 min



**Scheme 1.** Synthesis principle of cellulose gel.

**Table 1. Formulations of Test Sample Compounds**

	Compositions								
	SBR (phr)	Stearic acid (phr)	CBS <sup>a</sup> (phr)	DD <sup>b</sup> (phr)	Zinc oxide (phr)	Silica (phr)	Cell. hybrid (phr)	Starch hybrid (phr)	Sulfur (phr) <sup>c</sup>
Neat	100	2	2	0.5	3	0	0	0	1.75
Star.hybrid 5	100	2	2	0.5	3	0	0	5	1.75
Star.hybrid 10	100	2	2	0.5	3	0	0	10	1.75
Cell.hybrid 5	100	2	2	0.5	3	0	5	0	1.75
Cell.hybrid 10	100	2	2	0.5	3	0	10	0	1.75
Silica 5	100	2	2	0.5	3	5	0	0	1.75

<sup>a</sup>*N*-Cyclohexyl-2-benzothiazole-sulfonamide. <sup>b</sup>2,2-Dibenzothiazolyl disulfide. <sup>c</sup>phr; part per hundreds of rubber.

and cooled down at room temperature. Finally, the cellulose hybrid SBR composite had been synthesized.

**Compounding Process.** The composites were dried in an oven at 70 °C until the weight kept constantly. The compounding process was conducted on a two-roll mixing mill. And the formulation of conventional elastomeric additives was shown in Table 1. Note the sulfur and accelerators were mixed in the final step to avoid the prevulcanization. Finally, the compounds were vulcanized under 10 MPa for  $t_{90}$  at 150 °C in a heat pressing machine (auto hydraulic press type, ocean science). The thickness of the specimens was about 1 mm. For the purpose of comparison, we also prepared neat SBR, SBR filled with 5 phr silica.

**Characterization.** The curing characterization was test by an RPA-V1 (U-CAN, Taiwan), the morphology of the samples after the tensile test was carried out on a FE-SEM (JSM-7500F, JEOL Ltd. Japan). Density of samples had been measured by density test machine according to ASTM D792-13. Shore A hardness of the specimens was obtained with shore durometer type a according to ASTM D22-40. Tensile strength of samples was performed on a Tinius Olsen H5KT-0401 testing machine at a speed of 500 mm min<sup>-1</sup> according to ASTM D412 with the average of three measurements. Specimens on

standard dumb-bell shape were cut from the vulcanizate sheet with dimensions 25 mm×6 mm×1 mm (length×width×thickness). Dynamic mechanical properties of the vulcanizates were investigated by a DMA 8000 (Perkin Elmer Instruments) from -80 to 0 °C with a frequency of 1 Hz and a rising temperature rate of 3 °C/min under nitrogen atmosphere according to ASTM D7028-2007e1. Oil resistance were tested by a rubber aging chamber (with lab in Korea), put the samples into tubes filled with test oil, and set these tubes into rubber aging chamber and heat at 135 °C for 168 h. After that, the hardness values and tensile strength results of samples were characterized.

## Results and Discussion

Curing test results of compounds with additives were listed in Table 2.

From this table, the torque values of all the samples had been increased, due to the strength of fillers, which strongly restricted the deformation and consequently increased the mechanical properties of SBR composites.

The curing rate index (CRI) was applied to indicate the vulcanization rate. The CRI values of silica-SBR was decreased compare to the neat SBR, because when SBR compounded

**Table 2. Curing Characteristic Results**

	Maximum torque, $M_H$ (dNm)	Minimum torque, $M_L$ (dNm)	$\Delta M$ (dNm)	Scorch time, $t_{s2}$ (min)	Cure time, $t_{90}$ (min)	Cure rate index (CRI min <sup>-1</sup> )
Neat	6.4	0.5	5.9	6.71	13.05	15.77
Starch hybrid 5	10.2	0.8	9.4	2.28	5.41	31.95
Starch hybrid 10	9.9	0.9	9.0	3.12	5.27	46.51
Cellulose hybrid 5	10.4	0.9	9.5	2.11	6.43	23.15
Cellulose hybrid 10	10.6	0.8	9.8	2.41	6.92	22.17
Silica 5	9.5	0.9	8.6	4.51	15.07	9.47

with silica powder, the filler aggregation affected chain mobility,<sup>11</sup> which will reduce the vulcanization rate.

But as other compounds filled with cellulose hybrid filler and starch hybrid filler, because the more compact crosslinking structure between rubber and gel-silica hybrid, the dislocation effect may not reduce the chain mobility due to the adsorption effect of gel-hybrid, which would short the distance of rubber chains.

Thus, the CRI of compounds filled with gel-hybrid fillers has larger values than neat SBR compound. Also, the compounds filled with gel-hybrids had larger  $M_H$  and  $\Delta M$  than neat SBR, due to the effect of adsorption and physical crosslinking, which can make the matrix structure more compact and stable.<sup>12</sup> From this table, it can be found that with the ratio of filling increasing, the  $M_H$  and  $\Delta M$  of starch hybrid compounds had been decreased, but the CRI value had been increased rapidly. As for cellulose hybrid compounds, the  $M_H$  and  $\Delta M$  values had been increased with the filling ratio increased, but the CRI value had been decreased. The possible reason of this phenomenon is: The adsorption force<sup>13</sup> of starch gel is smaller than cellulose gel, and cellulose gel has much more network state structure which will form obstacles between the rubber chain, so the rubber molecule chain mobility of starch hybrid compounds may be better than cellulose hybrid compounds, so the curing rate of starch hybrid compounds also will be faster than cellulose hybrid compounds, the more filling ratio of starch hybrid, the faster the vulcanization rate; the more cellulose hybrid filling ratio, the slower vulcanization rate.

And the crosslinking structure of cellulose gel is more compact than starch gel, so the  $M_H$  and  $\Delta M$  of cellulose hybrid compounds increased with the filling ratio increased, but as the starch hybrid, the  $M_H$  and  $\Delta M$  value had been decreased with the filling ratio increasing, the possible reason of that may be the starch gel inflated in water, but when the composites drying in vacuum, it would destroy the crosslinking structure, so the more filling ratio starch hybrid filler, the less  $M_H$  and  $\Delta M$  value.

The results of samples' density were shown in Figure 3. From the figure, it can be found the density values of other compounds were larger than the neat compound. The more density, the more compact matrix structure, maybe the more crosslinking density.

The results of hardness test were shown in Figure 4. From these results, it can be observed that the hardness value of compounds was increased after filling process. The reason of this result may be the fillers could provide more crosslinking

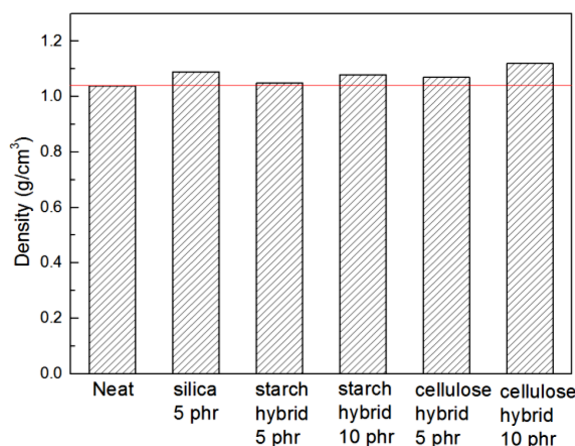


Figure 3. Density test results of compounds.

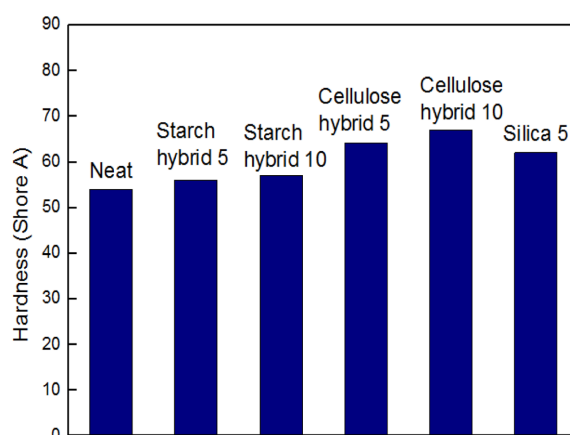


Figure 4. Hardness test results of compounds.

when filled into SBR rubber material, and make the matrix compact. When they dispersed into rubber matrix, the matrix had become a whole uniform state, so the hardness value had been increased.

Figure 5 showed the FE-SEM micrographs. From graph Figure 5(a) and 5(b), it can be found that the structures of cellulose hybrid and starch hybrid in SBR compounds, and the structure of cellulose hybrid compound looked like a whole. But as Figure 5(b) showed, it can be found the structure of starch hybrid compound looked relatively loose. And large, individual blocks of gel could be seen in the Figure 5(b). It could prove that after drying process, the network structure of starch gel had been partially destroyed, but as cellulose gel, it didn't seem to get influence due to the drying process. The possible reason of that may be the network structure of cellulose gel is stronger than starch gel, and after drying, the cellulose hybrid composite can maintain a more completed network structure. Figure 5(c) and Figure 5(d) showed the

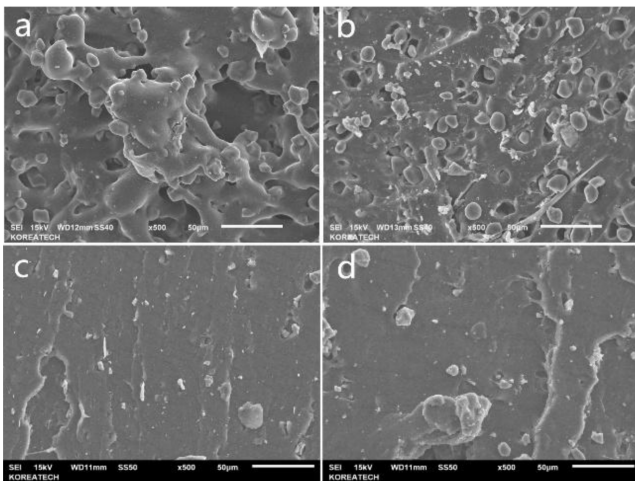
graph of cellulose hybrid compound and starch hybrid compound. From these graph, it can be found that the structure of cellulose hybrid compound looked more compact than starch hybrid compound. And the particle size of cellulose hybrid is also smaller than starch hybrid. The smaller filler particle size may provide better mechanical properties of rubber compounds.

Tensile strength results were shown in Table 3. It can be found gel-hybrid could provide great tensile reinforcement to SBR latex, and cellulose hybrid 10 phr could provide best reinforcing effect. The reason of this phenomena may be due to cellulose hybrid not only has compact network structure which would provide physical crosslinking for rubber chain, but also has so many -OH groups, they would provide more hydrogen bonds between cellulose hybrid and vulcanizing agent sulfur which provide single sulfur bonds for chemical crosslinking of

rubber matrix. It was shown in Figure 5. So it could make better combination with SBR matrix.

The results of dynamic mechanical analysis (DMA) were shown in Figure 6 and Figure 7. From these figures, it can be found the storage modulus of cellulose hybrid compound is larger than starch hybrid compound, which means cellulose hybrid would make the SBR matrix more compact, and the  $\tan\delta_{\max}$  of cellulose hybrid compound is also lower than starch hybrid compound. The value of  $\tan\delta_{\max}$  could be considered as an efficient parameter to evaluate the interfacial interaction between two phase. The interaction parameter  $B$  between polymer matrix and filler phase was calculated by using the following eq. (1):<sup>14</sup>

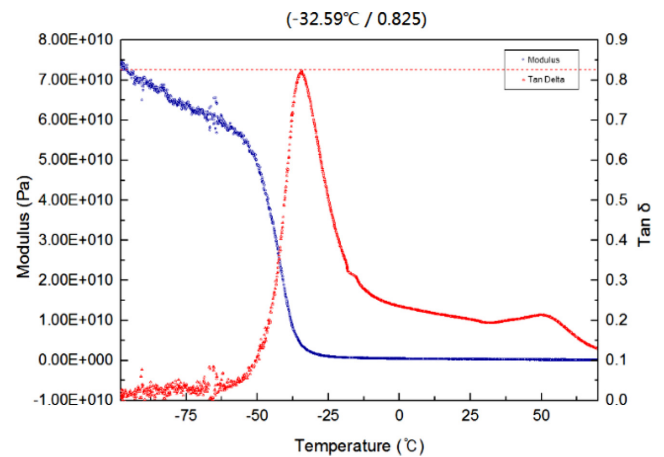
$$B = \frac{1}{V_f} \left( 1 - \frac{\tan\delta_{\text{filled}}}{\tan\delta_{\text{unfilled}}} \right) \quad (1)$$



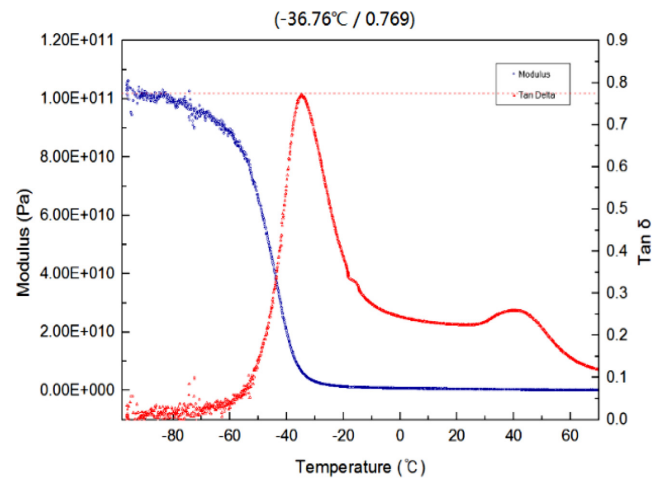
**Figure 5.** FE-SEM micrographs of (a) compound filled with cellulose hybrid before vulcanization; (b) compound filled with starch hybrid before vulcanization; (c) compound filled with cellulose hybrid after vulcanization; (d) compound filled with starch hybrid after vulcanization.

**Table 3. Tensile Strength Results of Compounds**

Compounds	Tensile strength (MPa)	Strain (%)	100% Modulus (MPa)
Cellulose hybrid 10	7.65	509	5.15
Cellulose hybrid 5	6.89	521	4.27
Starch hybrid 10	5.27	575	2.94
Starch hybrid 5	4.33	592	2.29
Silica 5	4.09	688	2.06
Neat	2.13	696	1.14



**Figure 6.** DMA results of starch hybrid compound.



**Figure 7.** DMA results of cellulose hybrid compound.

**Table 4. Oil Resistance Results of Compounds**

Compounds	$\Delta$ Tensile strength%	$\Delta$ Strain%	$\Delta$ Volume%	$\Delta$ Hardness shore A%
Cellulose hybrid 10	-7.9	-8.5	-4.95	+4.05
Cellulose hybrid 5	-12.7	-14.3	-6.65	+3.21
Starch hybrid 10	-19.5	-19.8	-10.27	+0.19
Starch hybrid 5	-24.6	-23.9	-13.75	-2.15

Where  $\tan\delta_{\text{filled}}$  and  $\tan\delta_{\text{unfilled}}$  are the loss factor of filled and unfilled polymer matrix, respectively;  $V_f$  is the volume fraction of filler. Greater value of  $B$  means greater interfacial strength. We noticed that the interaction parameter  $B$  is inversely dependent on the value of  $\tan\delta_{\text{filled}}$ . Therefore, lower value of  $\tan\delta_{\text{filled}}$  means stronger interfacial strength for the filled rubber compounds. So cellulose hybrid compound has strong interfacial strength than starch hybrid compound.<sup>15</sup>

## Conclusions

Starch hybrid and cellulose hybrid were synthesized by gel-adsorption method, then compounded with SBR rubber latex to make interpenetrating polymer network method by both physical crosslinking and chemical crosslinking. The results of curing characteristic showed the  $\Delta M$  value of cellulose hybrid 10 phr compound is the largest in the test, which meant cellulose hybrid 10 phr filler had superior reinforcing effect of increasing stiffness and crosslinking rate. The density and hardness results showed cellulose hybrid 10 phr compound had the most compact matrix structure. And FE-SEM graphs showed the states of compounds before and after vulcanization filled with different fillers (cellulose hybrid and starch hybrid), it can be seen that cellulose hybrid can form more compact matrix structure with rubber material, just like a whole network, but as starch hybrid compound, it showed individual gel blocks in the matrix. So cellulose hybrid would improve better mechanical properties during the graphs. The results of tensile strength, DMA, and abrasion resistance showed cellulose hybrid 10 phr could provide the best mechanical properties reinforcement of SBR rubber. And the result of oil resistance test showed gel-hybrid could improve the oil resistance of

SBR rubber, and cellulose hybrid 10 phr showed the best reinforcement effect, which would extend the service life of some rubber products like rubber roller and conveyor belt.<sup>16-18</sup> Above all, cellulose hybrid will become a potential filler for rubber industry in the future.

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