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Effect of Coupling Agent, Methylene Diisocyanate, in the Blending of Poly(methyl methacrylate)-Modified Starch and Styrene-Butadiene Rubber

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폴리(메틸 메타크릴레이트)-개질된 전분과 스티렌-부타디엔 고무의 혼합에서 커플링제 메틸렌 디이소시아네이트의 효과

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ABSTRACT : Methylene diisocyanate (MDI) was investigated as a novel interfacial modifier to enhance the performances of poly(methyl methacrylate)-modified starch/styrene-butadiene rubber (PMMA-modified starch/SBR) composites. Owing to the formation urethane linkage on one side and π-π adhesion on the other side, MDI acted as an intermediated linkage role in the PMMA-modified starch/SBR interfaces, which was evidenced by the morphological, mechanical, dynamic mechanical and thermal decomposition studies. As a result, the presence of MDI significantly improved the mechanical properties and thermal stability of PMMA-modified starch/SBR composites. In addition, the effect of starch concentration on the various performances of the resulted MDI/PMMA-modified starch/SBR composites, such as morphology, vulcanization characteristics, mechanical properties, toluene swelling behavior, and thermal stability were investigated and discussed in detail. The obtained MDI/PMMA-modified starch/SBR composites exhibited superior mechanical properties to carbon black/SBR (CB/SBR) composites, demonstrating the potential use of the renewable starch as a substitute for CB in the rubber compounds.

요 약 : 메틸렌 디이소시아네이트(MDI)가 폴리(메틸 메타크릴레이트)-개질된 전분/스티렌-부타디엔 고무(PMMA-modified starch/SBR) 복합체의 물성을 향상시키기 위하여 새로운 개질제로 조사되었다. 한쪽에는 우레탄 결합의 형성으로 인해 다른 한쪽에는 $\pi-\pi$ 접착 때문에 MDI는 PMMA-modified starch/SBR 계면에서 중간 결합 역할을 하는 것이 형태학적, 기계적, 동역학적 그리고 열적 분해 연구에 의하여 증명되었다. 결과적으로, MDI의 존재는 PMMA-modified starch/SBR 복합체의 기계적 물성과 열적 안정성을 괄목할만하게 개선하였다. 게다가, 생성된 MDI/PMMA-modified starch/SBR 복합체의 여러 가지 물성에 대한 전분 함량의 효과가 형태학, 가황 특성, 기계적 물성, 톨루엔 팽윤 거동, 그리고 열적 안정성에서 조사되었고 자세하게 논의되었다. MDI/PMMA-modified starch/SBR 복합체는 carbon black/SBR(CB/SBR) 복합체보다 우수한 물성을 보였고, 고무 배합물에서 CB의 대체물로서 재생 가능한 전분의 유력한 사용을 보여주었다.

Keywords : SBR, starch, methylene diisocyanate, interfaces

Ⅰ. Introduction

To meet the increasing demand for sustainable development, the utilization of various renewable resources such as starch,[1-6] cellulose,[7,8] lignin,[9] chitosan,[10] rice husk,[11] and oil palm ash[12] as reinforcing fillers for rubber compounds have raised considerable interest both in academia and industry. Starch is a natural semi-crystalline biopolymer consisting of a large number of glucose units, which can be derived from various biomasses, including rice, potato, corn, wheat, cassava and so on. If starch is used as reinforcing filler for rubber compounds, it possesses some merits such as light weight, abundantly available, renewable, biodegradable and low cost in comparison with the traditional reinforcing fillers such as carbon black and silica. Additionally, it has been reported that starch filled rubber compounds showed much lower rolling resistance and higher wet resistance compared with carbon black or silica filled rubber compounds, suggesting the development in the fuel efficiency

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of tire treads.[13,14]

The incorporation of natural starch particles generally deteriorated the mechanical properties of rubber compounds, which was mainly due to the huge particle size of starch, poor dispersion state and weak interfacial interaction.[1] In our previous work,[15] in order to overcome these bottlenecks, we developed a novel method called emulsion modification and latex compounding, which is described in detail as below. First, starch was modified by surface grafting of vinyl monomers through emulsion grafting polymerization. This process is called as emulsion modification. It is worthy noting that emulsion polymerization was specially employed to modify starch in order to obtain the smallest modified starch particles (200-400 nm). Afterward, the synthesized modified starch latexes were directly mixed with SBR latex to prepare the modified starch/SBR composites. This process is called as latex compounding. By using this method, modified starch with average particle size of approximate 200-400 nm homogeneously dispersed throughout the SBR matrix, which caused a remarkable improvement in the tensile strength of SBR compounds. Although the smaller particle size and better dispersion were achieved by using this method, the interfacial bonding between modified starch and SBR matrix was still weak, showing up in the slight improvement in the 300% modulus.[16] Therefore, it is very essential to build the strong chemical interfacial bonding between modified starch and SBR matrix.

Isocyanates, containing an isocyanate group (-N=C=O), are generally utilized to react with polyol to produce rigid polyurethane. Its isocyanate group shows highly reactive with the hydroxyl group, resulting in the formation of the strong covalent urethane linkage.[17,18] Therefore, isocyanates are also used as coupling agents, which chemically link between hydrophilic fillers and hydrophobic polymer matrix. In addition, it is worthy noting that the resulted covalent interfacial bonding between hydrophilic fillers and isocyanates is much more effective or stronger than the resulted hydrogen interfacial bonding between hydrophilic fillers and silanes.[18] Therefore, isocyanates are favored. So far, various isocyanates, including methylene diphenyl diisocyanate (MDI),[19-21] toluene diisocyanate (TDI),[22] hexamethylene diisocyanate (HDI),[23] lysine-based diisocyanate (LDI),[23-25] and polymethylene–polyphenyl–isocyanate (PMPI),[26] have been proved as effective coupling agents to enhance the compatibility between filler and polymer matrix.

In this work, MDI was used as a coupling agent to enhance the interfacial bonding between PMMA-modified starch and SBR matrix. The choice of MDI as coupling agent was taken into account on the basis of the following facts: (1) MDI contains two highly active isocyanate groups in the molecule. The isocyanate groups are expected to react with the hydroxyl groups of starch; (2) MDI contains an aromatic group. The aromatic functional group is expected to attach with the aromatic functional group of SBR via π-π interactions; (3) MDI is the most produced diisocyanates in the global market and therefore its price is much lower than other isocyanates. The performances of the resulted MDI/PMMA-modified starch/SBR composites, including morphology, vulcanization characteristics, mechanical properties, toluene swelling behavior, and thermal stability, were investigated and optimized by tailoring the concentration of MDI and starch. Moreover, a comparison investigation was also considered with the starch and the conventional reinforcing filler carbon black.

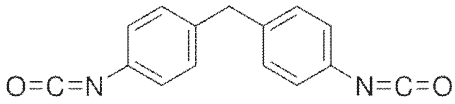

Figure 1. The molecular formula of MDI.

II. Experimental

1. Materials.

Styrene-butadiene rubber latex (SBR 1502) with styrene content 23.5 wt% was manufactured by Korea Kumho Petrochemical Co. (KKPC), South Korea. PMMA-modified starch emulsions with 10, 20, 30 and 40 phr of starch were synthesized via emulsion polymerization using potassium persulfate (KPS) as initiator and dodecylbezenesulfonic acid sodium salt (DBS-Na) as emulsifier, as reported in our previous research.[16] Coupling agent 4,4-methylene diisocyanate (MDI) with high purity (98%) was purchased from Sigma-Aldrich Co.

Figure 1 shows the molecular formula of MDI. Carbon black (CB) Corax N550 (FEF) with nitrogen surface area 42 m^2/g was purchased from Evonik Co. Other chemicals and rubber additives were commercially available and used as received.

2. Preparation process

PMMA-modified starch/SBR composites were prepared by mixing PMMA-modified starch emulsion with SBR latex in a glass container. The mixtures were vigorously stirred at a speed of 1000 rpm in order to obtain the homogeneous dispersion of PMMA-modified starch particles in the SBR latex. And then, the mixtures were shifted to an oven and dried at 70℃ for several days until the weight became constant. MDI and rubber additives were incorporated into PMMA-modified starch/SBR composites on a laboratory two-roll mill. The compounding temperature was controlled at about 50-60℃. In order to make the well dispersion of MDI and avoid pre-vulcanization, MDI was added in the first step and the sulfur accelerators were added in the last step. For the purpose of comparison, the starch/SBR and CB/SBR composites were also pre-

pared using the same method. Table 1 summarizes the compounding formulations and sample codes of all samples. Note that the code Ix indicates the MDI/PMMA-modified starch/SBR composites with x phr of MDI; the code ISx indicates the MDI/PMMA-modified starch/SBR composites with x phr of starch; the code Sx indicates the starch/SBR composites with x phr of starch; the code CBx indicates the CB/SBR composites with x phr of CB. Finally, all the samples were vulcanized under 10 MPa at 150℃ for the optimum cure time t_{90} in a hot-pressing machine, and then the sheets were cut into specimens with a dimension of 25 mm × 6 mm × 2 mm for mechanical tests.

3. Characterization

Cure characteristics were measured at 150℃ by a vulcanization machine (MDR 2020, Myung Ji Tech.). From the cure curves, scorch time (t_{S2}), optimum cure time (t_{90}), minimum torque (M_L), and maximum torque (M_H) could be obtained. Cure rate index (CRI) was employed to evaluate the cure rate of rubber compounds, which was calculated by the following equation[6,15]:

Table 1. Formulations[a] and Codes of the Starch/SBR, MDI/PMMA-Modified Starch/SBR and CB/SBR Composites (Units: phr)

Code	**I0**	**I0.5**	**I1**	**I2**	**I3**
SBR	100	100	100	100	100
Starch	20	20	20	20	20
PMMA[b]	10	10	10	10	10
MDI	0	0.5	1	2	3
Code	**IS0**	**IS10**	**IS20**	**IS30**	**IS40**
SBR	100	100	100	100	100
Starch	0	10	20	30	40
PMMA[b]	0	10	10	10	10
MDI	0	0.5	1	2	3
Code	**S0**	**S10**	**S20**	**S30**	**S40**
SBR	100	100	100	100	100
Starch	0	10	20	30	40
Code	**CB0**	**CB10**	**CB20**	**CB30**	**CB40**
SBR	100	100	100	100	100
CB	0	10	20	30	40

[a] Rubber additives: zinc oxide (3 phr), stearic acid (1 phr), antioxidant 2,2,4-trimethyl-1,2-dihydroquinoline polymer (1 phr), sulfur (2 phr), accelerator n-cyclohexyl-2-benzothiazole sulfonamide (2 phr), accelerator dibenzothiazole disulfide (0.5 phr)
[b] including grafts and homopolymers

$$\mathrm{CRI} = \frac{100}{t_{90} - t_{s2}} \tag{1}$$

The morphology of tensile fractured surfaces was observed by a Field Emission Scanning Electron Microscopy (FE-SEM, JSM-7500, JEOL). Before observation, the specimens were coated with a thin layer of gold. The dispersion state of fillers as well as the roughness of the tensile fractured surface could be observed through FE-SEM micrographs.

Tension tests were conducted following ISO 37 on universal tension machine (UTM, H5KT-0401, Tinius Oisen). The tension speed was set 500 mm/min. From the stress-strain curves, the tensile strength, 300% modulus and elongation could be obtained. Tear tests were conducted following ISO 34-1 on the same UTM. The tear speed was set as 50 mm/min. Hardness shore A was measured by a digital durometer (TH200, Time Group).

Dynamic mechanical properties were investigated by a dynamic mechanical analyzer (DMA8000, Perkin Elmer Instruments) under nitrogen atmosphere. The frequency was kept at 1 Hz and the temperature was increased from -80 to 0 ℃ with a rising temperature rate of 30 ℃/min.

Thermal stability was examined by a thermal gravimetric analysis machine (TGA 4000, PerkinElmer) under the nitrogen atmosphere. The temperature was increased from 30 to 600 ℃ with a heating rate of 20 ℃/min.

Toluene swelling tests were carried out according to the ISO 1817. All the samples were swollen in toluene at room temperature for 24 h. Based on the toluene swelling test, some toluene swelling characteristics, such as the swelling ratio (Q), the molecular weight between crosslinks (M_c), and the degree of crosslinking density (v_c), could be obtained. The swelling ratio (Q) was calculated by the following equation:

$$\mathrm{Q}(\%) = \frac{\mathrm{W} - \mathrm{W}_0}{\mathrm{W}} \times 100 \tag{2}$$

Where W is the weight of swollen rubber compounds and W_0 is the original weight of rubber compounds.

The degree of crosslinking density (v_c) could be also determined by the equilibrium swelling experiment. According to the theory of Flory-Rehner,[27] the molecular weight between crosslinks (M_c) is a function of the volume fraction of rubber in the swollen rubber compounds (V_r), which could be written as following:

$$\mathrm{M_c} = \frac{-\rho_r V_1 (V_r^{\frac{1}{3}} - \frac{V_r}{2})}{\ln(1 - V_r) + V_r + x V_r^2} \tag{3}$$

Where ρ_r is the density of rubber(0.933 g/㎤ for SBR), V_1 is the molar volume of the solvent ($V_{toluene}$ = 106.35 cm^3/mol) and x is the Flory–Huggins polymer solvent interaction parameter. For the SBR/toluene system, x is equal to 0.446.

The volume fraction of SBR rubber in the swollen rubber compounds (V_r) was calculated by the equation:

$$V_r = \frac{(W - FW_o)/\rho_r}{(W - FW_o)/\rho_r + A_o/\rho_r} \quad (4)$$

Where F is the weight fraction of insoluble components in the rubber compounds and A_0 is the weight of absorbed solvent.

Finally, the degree of crosslinking density (v_c) was calculated by the following equation:

$$V_c = \frac{1}{M_c} \quad (5)$$

Ⅲ. Results and Discussion

1. Effect of MDI concentration on the performances of MDI /PMMA-modified starch/SBR composites.

Figure 2 shows the FE-SEM micrographs of the tensile fractured surface of MDI/PMMA-modified starch/SBR composites with 0, 1, 2 and 3 phr of MDI. The composites I0 displayed very smooth tensile fractured surface. With the addition of MDI from 1 to 3 phr, the tensile fractured surface became more and more coarse, which suggested that the incorporation of MDI enhanced the interfacial adhesion. The improved interfacial adhesion could be explained by considering the intermediated linkage role of MDI. On one hand, the isocyanate groups (-NCO) of MDI reacted with the hydroxyl groups (-OH) of starch, resulting in the formation of strong covalent urethane linkages between starch and MDI. The formed urethane linkages have been confirmed using ATR-FTIR spectra.[18] On the other hand, owing to the delocalized π electrons of benzene rings, there would be a strong adhesion between MDI and SBR matrix.[28] As a result, a crosslinked structure was generated with the addition of MDI.

The enhanced interfacial interaction is supposed to improve the mechanical performances and thermal properties of composites. The effect of MDI concentration on the mechanical properties of MDI/PMMA-modified starch/SBR composites was investigated, as depicted in Figure 3. As expected, the incorporation of MDI improved the tensile strength and 300% modulus, while deteriorated the elongation at break. For example, the tensile strength, 300% modulus and elongation of the composites I0 were 9.7 MPa, 2.7 MPa and 940%, respectively. When

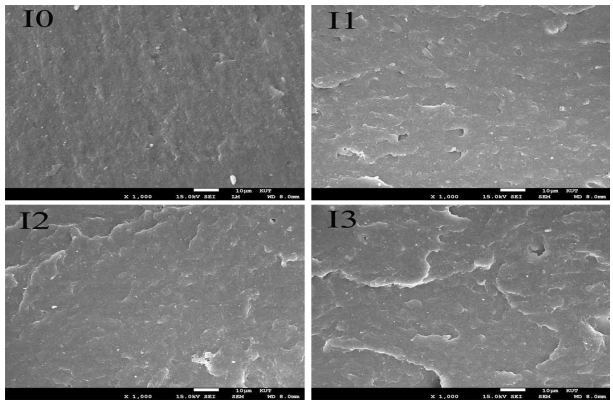

Figure 2. FE-SEM micrographs of MDI/PMMA-modified starch/SBR composites with different MDI concentration. Scale Bar: 10 μm.

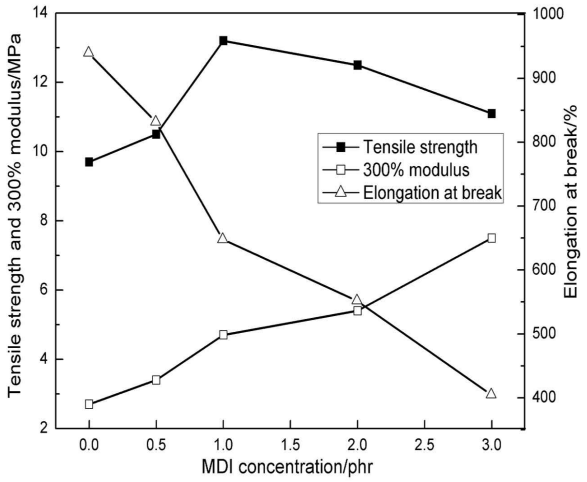

Figure 3. Effect of MDI concentration on the mechanical properties of MDI/PMMA-modified starch/SBR composites.

0.5 phr of MDI was incorporated, the tensile strength and 300% modulus were increased to 10.5 MPa and 3.4 MPa, respectively; whereas the elongation was decreased to 832%. The influence of MDI concentration on the mechanical properties was also significant. As the MDI concentration increased from 0.5 to 3 phr, the 300% modulus was consistently increased from 3.4 to 7.5 MPa, whereas the elongation was consistently decreased from 832% to 405%. The maximum tensile strength was obtained when the concentration of MDI was 1 phr. Beyond 1 phr, the tensile strength decreased marginally, but was still higher than that of the composites I0. This phenomenon has been explained by considering the most effective compatibilization of 1 phr MDI in the interfaces between 20 phr starch and 100 phr of SBR. Similar results have been also observed in other isocyanates coupled biomass/polymer composites, such as MDI/starch/poly(lactic acid)[19] and LDI/bamboo fiber/poly(butylene succinate) composites.[25]

The effect of MDI concentration on the thermal properties of MDI/PMMA-modified starch/SBR composites was studied using DMA and TGA, as summarized in Table 2. It can be

seen that as the concentration of MDI increased, the T_g value successively increased as expected. The incorporation of 0.5, 1, 2 and 3 phr of MDI increased the T_g values to -31.6, -30.7, -30.3 and -27.4℃, which were 2.8, 3.7, 4.1 and 7℃ higher than that of the composites I0, respectively. A similar observation was reported for resorcinol-formaldehyde (RF)/N-β (aminoethyl)-γ-aminopropyl trimethoxy silane (KH792)-modified starch/SBR composites.[2] They observed that compared to the unmodified starch/SBR composites, the T_g value of RF/KH792-modified starch/SBR composites shifts to the higher temperature due to the improved interfacial adhesion. Moreover, the incorporation of MDI led to an increase in the thermal decomposition temperature of the composites, as also shown in Table 2. As the MDI concentration increased, the thermal decomposition temperature for a certain weight loss percent, such as 10%, 30%, 50% and 70% shifted towards a high temperature. For example, the initial decomposition temperature (T10%) of the composites I0 was 294.6℃. The introduction of 0.5, 1, 2 and 3 phr of MDI consistently increased the T10% values to 300.2, 301.5, 302.3 and 304.6 ℃, respectively. The considerable increment in the T_g value as well as the thermal decomposition temperature were ascribed to the strong interfacial bonding between PMMA-modified starch and SBR matrix with the addition of MDI forming the strong covalent urethane bonds on one hand and π – π adhesion on the other hand. The formed PMMA-modified starch/MDI/SBR crosslinking structure significantly enhanced the thermal stability of the composites.[29,30]

Table 2. Effect of MDI Concentration on the Thermal Properties of MDI/PMMA-Modified Starch/SBR Composites

Samples /℃	T_g[a]	Degradation temperature for wt% loss[b]			
		10	30	50	70
I0	-34.4	294.6	427.9	452.0	469.5
I0.5	-31.6	300.2	429.6	456.3	472.7
I1	-30.7	301.5	429.7	455.6	473.0
I2	-30.3	302.3	432.2	456.6	474.0
I3	-27.4	304.6	430.5	456.3	473.7

[a] detected from DMA curves
[b] detected from TGA curves

2. Effect of starch concentration on the performances of MDI/PMMA-modified starch/SBR composites

Figure 4 shows the FE-SEM micrographs of the tensile fractured surface of MDI/PMMA-modified starch/SBR composites with 10, 20, 30 and 40 phr of starch. It can be observed that the dispersion of MDI/PMMA-modified starch in the SBR matrix was quite good. Most of MDI/PMMA-modified starch was deeply embeded into the SBR matrix. As reported in our previous article,[16] without MDI, when starch concentration exceeded 30 phr, the PMMA-modified starch agglomerates with particle size approximate 1-10 μm extensively appeared due to the strong hydrogen bonding between particles. However, in the present research, with the addition of MDI, even when 40 phr of starch were incorporated, there were no agglomerates observed. It has to say that the enhanced interfacial adhesion further promoted the dispersion of PMMA-modified starch

Table 3. Curing Characteristics and Mechanical Properties of MDI/PMMA-Modified Starch/SBR Composites with Different Starch Concentration

Properties/Samples	IS0	IS10	IS20	IS30	IS40
M_L/lb-in	0.9	1.1	3.1	6.7	6.8
M_H/lb-in	9.3	12.3	14.3	22.2	25.5
Delta M/lb-in	8.4	11.2	11.2	15.5	18.7
t_{s2}/min	0.92	1.43	1.55	1.68	1.81
t_{90}/min	7.72	4.75	4.48	4.86	4.63
CRI/min^{-1}	14.7	30.12	34.13	31.45	35.46
Q/%	358	308	259	208	173
M_c/mol·g^{-1}	490	465	456	427	409
V_c×10-3/mol×g^{-1}	2.04	2.15	2.19	2.33	2.44
300 % modulus/MPa	1.2	2.4	4.7	6.3	7.1
Tensile strength/MPa	2.9	7.5	13.2	11.6	10.8
Elongation/%	636	912	648	484	424
Tear strength/KN×m^{-1}	10.2	40.3	50.5	47.6	44.3
Hardness/ Shore A	57.3	63.4	71	73.3	78.1

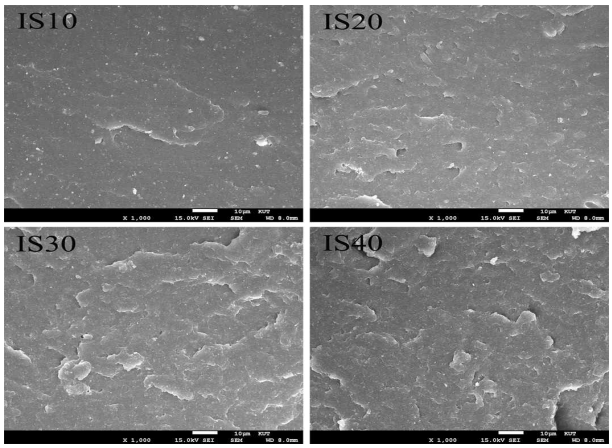

Figure 4. FE-SEM micrographs of MDI/PMMA-modified starch/SBR composites with different starch concentration. Scale Bar: 10 μm.

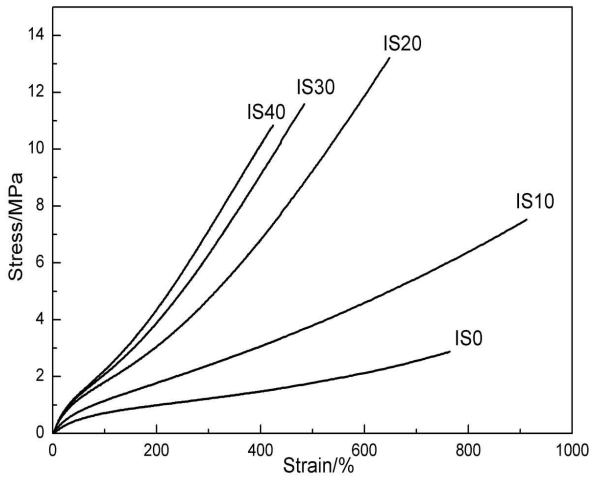

Figure 5. Typical stress-strain curves of the MDI/PMMA-modified starch/SBR composites with different starch concentration. Scale Bar: 10 μm.

even with a high concentration, resulting in a more homogeneous dispersion state.

The effect of starch concentration on the cure characteristics and mechanical properties of MDI/PMMA-modified starch/SBR composites was investigated. As shown in Table 3, the addition of MDI/PMMA-modified starch consistently increased the torque values of SBR compounds, including M_L, M_H and Delta M. Two reasons may be responsible as below. First, as reported in the literature,[31] the Young's modulus of starch was approximately 15 GPa, which was much higher than that of raw SBR (< 10 MPa). The addition of starch restricted the movement of SBR macromolecular chains and therefore increased the torque values of SBR compounds. Second, the incorporated MDI acted as a crosslinking agent between PMMA-modified starch and SBR matrix, which might cause an increase in the crosslinking density of the composites. To confirm our assumption, the crosslinking densities of these composites were calculated, as shown in Table 3.

It can be seen that the crosslinking density was gradually increased from 2.04×10^{-3} to 2.44×10^{-3} mol/g, as the starch concentration increased from 0 to 40 phr. The presence of MDI/PMMA-modified starch also had a significant influence on the cure rate (CRI) of SBR compounds. As shown in Table 3, the CRI value of neat SBR compound was 14.7 min^{-1}. The incorporation of MDI/PMMA-modified starch with 10, 20, 30 and 40 phr of starch significantly increased the CRI values to 30.12, 34.13, 31.45 and 35.46 min^{-1}, respectively. These observations indicated that starch acted as an effective curing accelerator for the SBR compounds. The curing rate of filled rubber vulcanizates might be associated to the filler-rubber matrix adhesion[32] and some filler characteristics[11] such as particle size, surface area, surface reactivity, moisture content and thermal conductivity. Generally, a faster curing rate is obtained when the filler-rubber matrix adhesion is lower or when the filler have a larger particle size, lower surface area, greater moisture content and higher thermal conductivity. In the present study, the observed cure accelerating phenomenon is most probably ascribed to the higher moisture content of starch. It is well known that starch usually exhibits higher humidity or water content because of a large number of hydroxyl groups on the backbone of glucose units.

Figure 5 shows the typical stress-strain curves of neat SBR and MDI/PMMA-modified starch/SBR composites with 10, 20, 30 and 40 phr of starch. The addition of starch conducted to the improvement of the 300% modulus, whereas impaired the elongation. When the composite was incorporated with 20 phr of starch, the stress-strain curve achieved the climax, in which the 300% modulus, tensile strength and elongation were raised to 4.7 MPa, 13.2 MPa and 648%, respectively. Overloading of starch reduced the tensile strength and elongation, which might be attributed to the much higher crosslink density. Wang et al.[33] found that for the DCP/carbon black N330/SBR compounds, when the crosslink density was greater than 0.0018 mol/cm^3, the tensile strength began to decrease sharply. They suggested that for a certain reinforcing system, an appropriate crosslink density existed. Therefore, it is also revealed that for MDI/PMMA-modified starch/SBR composites the optimum crosslink density was determined to be 2.19×10^{-3} mol/g. Further increasing the crosslink density significantly hindered the chain slippage as well as the chain orientation, which were benefit to improving the tensile strength. In addition, a similar trend for tear strength was also observed, as presented in Table 3. The tear strength achieved the maximum value (50.5 KN/m) when the starch concentration was 20 phr. Excess of starch also deteriorated the tear strength. Therefore, based on the results of mechanical properties, it is concluded that the composites containing 20 phr of starch exhibited the optimum mechanical performances, showing

292% increment in 300% modulus, 355% increment in tensile strength, 2% increment in elongation, 395% increment in tear strength and 24% increment in hardness.

Generally, the addition of rigid filler increased the tensile modulus of polymeric composites. This enhancement could be ascribed to the hydrodynamic effect and the adsorption of polymer chains on the filler surface, which increased the crosslink density and decreased the bulk mobility.[34,35] Moreover, for some nanocomposites, such as CNT or clay filled nanocomposites, the aspect ratio of filler and dispersion state also significantly affected the modulus. More specifically, a higher modulus could be obtained when the filler has a larger aspect and a better dispersion state. Until now, several theoretical models have been employed to predict the tensile modulus, and the theoretical results were compared with the experimental results.[34~37] If the theoretical results were much closed to experimental results, a conclusion could be drawn that the dispersion state was homogeneous.

We predicted the tensile modulus of MDI/PMMA-modified starch/SBR composites using Guth-Gold,[38] Modified Guth-Gold,[39] and Halpin-Tsai[40] models.

Guth-Gold model is expressed as the following equation:

$$E = E_0(1 + 2.5\varphi + 14.1f^2\varphi^2) \tag{6}$$

Where E and E_0 are the Young's modulus of filled rubber and unfilled rubber, respectively; and φ is the volume fraction of filler in the compounds. It is worthy noting that Guth-Gold model is only applicable when the filler is spherical shape and the network or interaction arising from the particle aggregation can be neglected.

By considering the influence of the shape of filler on the modulus, Guth introduced a shape factor f into the equation (6), giving the modified Guth-Gold model expression as the following equation:

$$E = E_0(1 + 0.67f\varphi + 1.62f^2\varphi^2) \tag{7}$$

In addition, Halpin-Tsai model are also used to estimate the modulus of polymeric composites, which can be written as the following equation:

$$E = E_0\left(\frac{1 + 2f\varepsilon\varphi}{1 - \varepsilon\varphi}\right) \tag{8}$$

$$\varepsilon = \frac{(E_f / E_0) - 1}{(E_f / E_0) + 2f} \tag{9}$$

Where E_f is the young's modulus of filler. For corn starch, the E_f was estimated to be approximately 15 GPa.[31]

The comparison between the experimentally measured 300% modulus and theoretically predicted modulus using Guth-Gold model, Modified Guth-Gold model and Halpin-Tsai model are shown in Figure 6. It is observed that the theoretically predicted values using the Guth-Gold model were much lower than the experimentally measured values, since the formation of some extent of complex networks from starch agglomerates can't be neglected. For the modified Guth-Gold and Halpin-Tsai models, when the f was applied as 8 and 11, respectively; the theoretically predicted values were closed to the experimentally measured values. It is worth noting that the f of starch obtained by fitting the experimental results was much lower than the shape factors of clay or CNT obtained by fitting the experimental results. For example, Perez et al.[34] used the Modified Guth-Gold model to predict the modulus of CNT/SBR nanocomposites. They found that when the shape factor of CNT was applied as approximate 22, the theoretically predicted values were closed to the experimentally measured values. Renzende et al.[36] also used the Modified Guth-Gold model to predict the modulus of clay/NR nanocomposites. They found that when the f was equal to 48, the predicted results were well fitted with the experimental results. It is well known that starch granules do not have a rod or platelet structure and therefore they exhibit much lower f value than platelet-shaped clay or rod-shaped CNT.

Thermal properties of neat SBR and MDI/PMMA-modified starch/SBR composites with 10, 20, 30 and 40 phr of starch were also studied using DMA and TGA, as summarized in Table 4. It can be seen that the presence of MDI/PMMA-modified starch with 10 phr of starch improved the T_g value of SBR composites from -32.7 to -30.9℃, demonstrating the reinforcing effect of MDI/PMMA-modified starch on the SBR matrix. However, further incorporation of MDI/PMMA-modified starch had little influence on the T_g values. TGA studies indicated that the incorporation of starch accelerated the thermal degradation of SBR composites. As the starch concentration increased the thermal decomposition temperature for a certain weight loss percent, such as 10%, 30%, 50% and 70% shifted towards a low temperature. For example, the initial decomposition temperature ($T_{10\%}$) of the composites IS0 was 415.6℃. The introduction of MDI/PMMA-modified starch with 10, 20, 30 and 40 phr of starch decreased the $T_{10\%}$ values to 333.8, 301.5, 294.4 and 286.5 ℃, respectively. The accelerating effect of starch on thermal decomposition temperature of SBR composites might be due to two reasons. First, starch possessed relative lower thermal decomposition temperature in comparison to SBR. Second, starch might act as a plasticizer for the SBR composites. Similar phenomena have been also observed in the cellulose nanocrystals/nitrile rubber nanocomposites.[8]

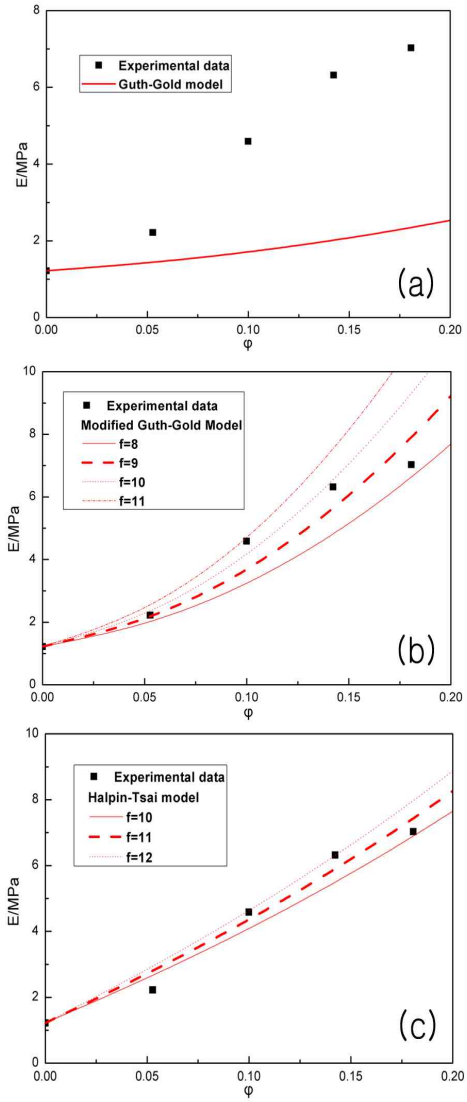

Figure 6. Experimentally measured modulus and theoretically predicted modulus by using (a) Guth-Gold model, (b) Modified Guth-Gold model and (c) Halpin-Tsai model.

Table 4. Effect of Starch Concentration on the Thermal Properties of MDI/PMMA-Modified Starch/SBR Composites

Samples /℃	T_g[a]	Degradation temperature for wt% loss[b]			
		10	30	50	70
IS0	-32.7	415.6	442.3	459.0	472.7
IS10	-30.9	333.8	436.0	458.0	473.4
IS20	-30.7	301.5	429.7	455.6	473.0
IS30	-30.4	294.4	427.2	459.8	481.3
IS40	-30.3	286.5	414.7	455.3	477.7

[a] detected from DMA curves
[b] detected from TGA curves

3. Comparative investigation on the reinforcement of starch, MDI/PMMA-modified starch and carbon black in the SBR composites

By now, the MDI/PMMA-modified starch/SBR composites have been developed. The objective of this research is to utilize of starch as fillers to fully replace the traditional filler carbon black for SBR compounds. Therefore, we comparatively investigated the mechanical properties of the developed MDI/PMMA-modified starch/SBR composites with starch/SBR composites and CB/SBR composites, as shown in Figure 7. It is obvious that relative to the starch/SBR composites, MDI/PMMA-modified starch exhibited superior me chanical properties, including tensile strength, elongation, 300% modulus, and tear strength. The decreased particle size, improved dispersion state, and formation of physical entanglements and chemical bonding between starch and SBR macromolecular chains were responsible for these notable improvements. Compared with CB/SBR composites, MDI/PMMA-modified starch/SBR composites also exhibited superior tensile strength. Although the tensile strengths of MDI/PMMA-modified starch/SBR composites was decreased as the starch exceeded 20 phr, it was still higher than that of CB/SBR composites at the same loading of fillers. As the case of 300% modulus, MDI/PMMA-modified starch/SBR composites showed much higher values in comparison to CB/SBR composites. However, CB/SBR composites possessed better elongation compared to MDI/PMMA-modified starch/SBR composites.

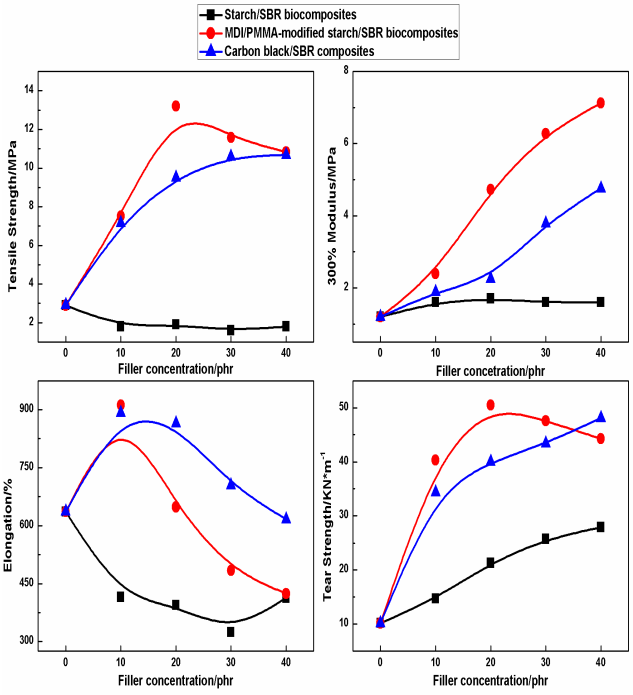

Figure 7. Comparative study on the mechanical properties of starch/SBR, MDI/PMMA-modified starch/SBR composites and carbon black/SBR composites.

Ⅳ. Conclusions

MDI was used as a novel interfacial modifier for PMMA-modified starch/SBR composites. Based on the results, we conclude the following:

1. The presence of MDI enhanced the interfacial bonding between PMMA-modified starch and SBR matrix, which was evidenced by FE-SEM observations, tensile tests, DMA and TGA analyses. The optimum concentration of MDI in the PMMA-modified starch/SBR composites with 20 phr of starch was found be 1 phr.
2. The performances of the resulted MDI/PMMA-modified starch/SBR composites with different starch concentration were investigated. FE-SEM observations showed the homogeneous dispersion state of MDI/PMMA-modified starch throughout the SBR matrix. Cure characteristics indicated the dual roles of MDI/PMMA-modified starch in the SBR compounds, i.e. (1) reinforcing filler and (2) curing accelerating agent. Mechanical tests revealed that when the MDI and starch concentration were 1 and 20 phr, respectively; the optimum mechanical properties were achieved. TGA results demonstrated that the incorporation of starch accelerated the thermal degradation of SBR compounds.
3. In comparison to starch/SBR and CB/SBR composites, MDI /PMMA-modified starch/SBR composites showed superior mechanical properties. Therefore, it is concluded that the developed MDI/PMMA-modified starch could fully apply as the renewable fillers instead of the non-renewable fillers – carbon black to reinforce the rubber compounds.

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