International Journal of Adhesion & Adhesives 68 (2016) 326–332

Contents lists available at ScienceDirect

International Journal of Adhesion & Adhesives

journal homepage: www.elsevier.com/locate/ijadhadh

# Characterization and application of propylene grafted hydrogenated dicyclopentadiene hydrocarbon resin

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## ARTICLE INFO

*Article history:*
Accepted 31 March 2016
Available online 19 April 2016

*Keywords:*
Hydrocarbon resin (HCR)
Propylene
Dicyclopentadiene (DCPD)
Rolling ball tack
Loop tack
180° Peel adhesion strength
Shear adhesion strength

## ABSTRACT

Hydrocarbon resins, which are defined as low molecular weight, amorphous, and thermoplastic polymers, are widely used as tackifiers for various types of adhesives, as processing aids in rubber compounds, and as modifiers for paint and ink products, and for use in plastics polymers such as isotactic polypropylene. Recently, the quantities of the hydrocarbon resin' raw materials which are the side products from naphtha cracking process have decreased because of light-feed cracking such as gas cracking, so new raw materials for hydrocarbon resin production are essential. To be satisfied with the previously mentioned factors, the substitution of hydrocarbon resin raw materials with renewable resources is a worthy consideration. Moreover, new hydrocarbon resin having high adhesion performance, low specific gravity, and good compatibility with various polymers has been requested in various adhesives.

To meet those requests, in this study, propylene instead of side product from naphtha cracking as main raw material of hydrocarbon resin were partially used. The propylene serves as a new, sustainable raw material and was successfully grafted onto dicyclopentadiene. The reaction of the propylene with dicyclopentadiene was confirmed because, according to NMR and FT-IR analyses, a pendant methylpropylene group exists in the structure of the propylene-grafted, hydrogenated dicyclopentadiene hydrocarbon resin. To establish an optimal production condition regarding the propylene-grafted, hydrogenated dicyclopentadiene hydrocarbon resin, numerous experiments were conducted according to the mole ratio of the raw materials and the polymerization temperature. The propylene-grafted, hydrogenated dicyclopentadiene hydrocarbon resin that was manufactured according to optimal conditions results in a lower specific gravity and a high molecular weight, whereby the advantages of the adhesion properties of an SIS-based pressure-sensitive-adhesive are exploited. When the propylene-grafted, hydrogenated dicyclopentadiene hydrocarbon resin was formulated with the SIS-based pressure-sensitive-adhesive, both the heat stability and the shear-adhesion strength are sound.

## 1. Introduction

Hydrocarbon resins (HCRs), which are low molecular weight, amorphous, thermoplastic polymers, have been widely used as tackifiers for various types of adhesives, as processing aids in rubber compounds, and as modifiers for paint and ink products, and as the basis of plastics polymers such as isotactic polypropylene. Commonly, pressure sensitive adhesive tapes contain a HCR and a base polymer, such as natural rubber, synthetic rubber or a block copolymer. In such applications HCRs act as diluents so as to aid the tape production process, as well as improve the peel strength of the resulting adhesive [1]. Many researchers [1–9] have investigated the mechanisms responsible for tack development resulting from the addition of HCRs. These resins have historically been produced by the polymerization of various feed stocks, typically olefin, diolefin, aliphatic, aromatic, or mixtures thereof. Typical polymerization systems include cationic and thermal polymerization. Cationic polymerization typically uses a Friedel–Crafts catalyst to polymerize aliphatic and aromatic monomers. Typical aliphatic monomers are C5 paraffines, olefins, and diolefins. To control the molecular weight of the HCR, tricyclodecene

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http://dx.doi.org/10.1016/j.ijadhadh.2016.04.002
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has been traditionally used. The thermal polymerization of hydrocarbon resin typically results from a Diels–Alder reaction of cyclopentadiene or dicyclopentadiene (DCPD) and optionally C5 conjugated dienes or C9 monomers without catalyst. However, HCRs produced by thermal polymerization have a high degree of unsaturation which can promote color-related issues. Thus, hydrogenation under high temperature and pressure conditions is often deemed necessary.

The current diaper megatrend is the development of a thin, light, odorless, and sustainable diaper; to meet these requirements, it is necessary to follow the trend regarding the adhesive that is applied to a diaper whereby a low-density, low-odor, and sustainable adhesive needs to be developed. Based on these tendencies, the modification of new, sustainable raw materials for a low odor, low specific gravity, and effective adhesion property is required for the development of a newly designed HCR. Moreover, the quantities of HCR raw materials, which are the side products from naphtha cracking process, have recently decreased because of light-feed cracking such as gas cracking [10]; to overcome this problem, new, sustainable raw materials must be found.

In this study, propylene serves as a new, sustainable raw material and was successfully grafted onto DCPD. The reaction of the propylene with DCPD was confirmed because, according to NMR and FT-IR analyses, a pendant methyl-propylene group exists in the structure of the propylene-grafted, hydrogenated DCPD HCR. To establish an optimal production condition regarding the propylene-grafted, hydrogenated DCPD HCR, numerous experiments were conducted according to the mole ratio of the raw materials and the polymerization temperature. The propylene-grafted, hydrogenated DCPD HCR that was manufactured according to optimal conditions results in a lower specific gravity and a high molecular weight, whereby the advantages of the adhesion properties of an SIS-based pressure sensitive adhesive (PSA) are exploited. When the propylene-grafted, hydrogenated DCPD HCR was formulated with the SIS-based PSA, both the heat stability and the shear-adhesion strength are sound.

## 2. Experimental

### 2.1. Materials

Propylene, DCPD, and toluene were obtained from Sigma Aldrich (99% Purity). $AlCl_3$ as catalyst and t-butyl chloride (t-BuCl) as co-catalyst were also obtained from Sigma Aldrich (99% Purity). Tricyclodecene (TCDE) was employed as a chain transfer agent and was obtained from Kolon Industries, Inc. Various HCRs such as hydrogenated DCPD HCR (SU-100S, SU-400, and SU-500 from Kolon Industries Inc. in Korea) were used in the hot melt pressure-sensitive-adhesive application. SIS(Styrene-Isoprene-Styrene Block Copolymer, Kraton D-1160) from Shell in USA was used and paraffinic process oil from Michang in Korea was used in same application.

### 2.2. Propylene-grafted hydrogenated DCPD HCR ($H_2$-C3-DCPD) preparation

The HCR employed in this investigation was produced using cationic catalyst systems in a solution phase copolymerization process. Propylene and toluene were mixed with DCPD monomer in a 1 l autoclave. The mixture was polymerized in the presence of $AlCl_3$ and t-butyl chloride as catalysts for 2 h. Following the polymerization step, the acid catalyst in the polymerized product was neutralized by mixing with hot water and stirring at 1000 rpm for 1 h. The polymerized product was separated from the water/polymer mixture by holding for 1 h at 60 °C without stirring. A metal catalyst was used for the hydrogenation of the initial product. 5 wt% of the catalyst was added to the polymerized product followed by hydrogenation for 1.5 h at 80 kgf/cm$^2$ and 230 °C. Finally, any non-reacted monomer was removed by an evaporation step at 250 °C.

### 2.3. Resin characterization

The molecular weights and molecular weight distributions of the HCRs were determined by gel permeation chromatography using a Waters GPC (Column: HR-1, HR-2, HR-3, HR-4). The solvent used was tetrahydrofuran (THF). A refractive index detector was used. Polystyrenes with a range of molecular weight values were used as the calibration material.

The softening point of HCRs were determined by use of an Automatic Softening Point Tester (Meitech Com.) with a speed of 5 °C/min based upon ASTM E28. A 50 wt% solution of HCR in toluene was employed to assess the color characteristics of the resins (based on Gardner # and HAZEN # values) which were assessed using a colorimeter to ASTM D 1544.

The specific gravity of the HCRs were determined by use of an electronic densimeter SD-200L to ASTM D 71.

C3 grafting to DCPD was determined by 600 MHz NMR (Nuclear magnetic resonance) from Bruker Company.

FT-IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrophotometer in transmittance mode, with 4 cm$^{-1}$ resolution and with 40 accumulations. The frequency range from 400 to 600 cm$^{-1}$ was covered. KBr (150 mg) pellets were prepared on a quartz mortar with approximately 4.5 mg (*ca.* 3%) of sample. The sample was then transferred to a metal container and pressed at 784 MPa for one minute to provide pellets of 0.55 mm width.

An HCR formulation based upon an HCR/SIS/Process Oil combination of 57/25/18 wt% was used to prepare a hot melt pressure sensitive adhesive (HMPSA) by stirring at 180 °C for 3 h. To measure rolling ball tack, 180° peel adhesion, and shear adhesion strength of the adhesive, the HMPSA was coated onto a PET film substrate to produce a coating thickness of approximately 20 µm.

A ChemInstruments TT-100 rolling ball tack tester, which meets the standards set by the Pressure Sensitive Tape Council's Method No. 6 [11] (Pressure Sensitive Tape Council-6) and ASTM (ASTM D3121), was used for assessing the tack of the HMPSAs. The HMPSA was coated onto a PET film. Following coating the film was dried for 2 min at 130 °C in an oven. An initial value of rolling ball tack after drying was measured.

180° Peel adhesion test method (Pressure Sensitive Tape Council-1, peel adhesion for single coated tapes at 180° angle) was used to measure the adhesion strength of HMPSA. The HMPSA was coated on the PET film with a thickness of 25 µm. The film was then cut into a strip with a width of 25 mm and was placed on a stainless steel panel (SUS304, ChemInstruments Com. in USA) which was then used as the substrate. This assembly served as the test specimen which was pressed using a 2 kg iron roller to develop good contact between the adhesive and the stainless steel panel. The iron roller was moved backward and forward once, which was defined as one press cycle. Test specimens were subjected to two press cycles. The prepared specimens were held for 20–40 min. before being subjected to peel adhesion tests. The 180° peel adhesion was measured at a peel rate of 300 mm/min. at room temperature using a Universal Test Machine Model H5KT (Hounsfield). The initial value of 180° peel adhesion was measured.

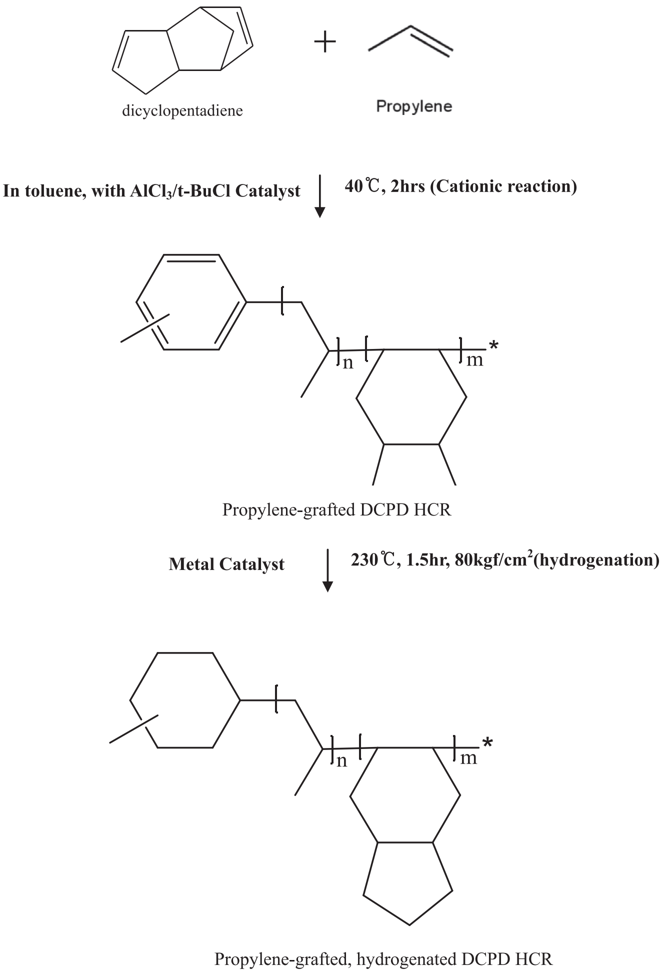
The shear-adhesion (holding power) strength test, Pressure Sensitive Tape Council-7 or ASTM D3654 [11] , was used to measure the cohesive strength of HMPSA. The HMPSA was coated onto PET film with a thickness of 25 µm. The film was cut into a strip with a width of 25 mm and was placed on a stainless steel panel (SUS304, ChemInstruments Com. in USA) and used as the substrate. This assembly served as ~~a~~ the test specimen which was pressed using a 2 kg iron roller to develop good contact between the adhesive and the stainless steel panel. The iron roller was moved backward and forward once, which was defined as one press cycle. Test specimens were subjected to two press cycles. The prepared specimens were held for 20–40 min. before being subjected to cohesion tests. Finally, the prepared specimens were placed in the shear adhesion rack with extending tape hanging downward and 1 kg weight was secured to the free end with an appropriate hook. The time for total separation to occur was measured for shear adhesion strength at 45 °C.

The rheological properties of HMPSA were measured on a TA instruments AR 2000. Specimens with a thickness of 2 mm and diameter of 8 mm were prepared and measured at a shear rate of 1 Hz. The testing temperatures employed were in the range of −50 to 120 °C with a heating rate of 7 °C/min.

## 3. Results and discussion

Propylene as sustainable new raw material was grafted to DCPD monomer, which is a commonly used for manufacturing a HCR, to make new HCR. As shown in Scheme 1, the propylene-grafted, hydrogenated DCPD HCR was synthesized by cationic reaction with Lewis acid catalyst such as $AlCl_3$.

Fig. 1 shows C3 grafting to DCPD by NMR analysis. Signals were very complicated in the $^1H$ NMR spectra of the samples obtained in the cationic DCPC/TCDE/propylene copolymerization in toluene.



**Scheme 1.** Elementary manufacturing steps for propylene-grafted, hydrogenated DCPD HCR (cationic reaction).

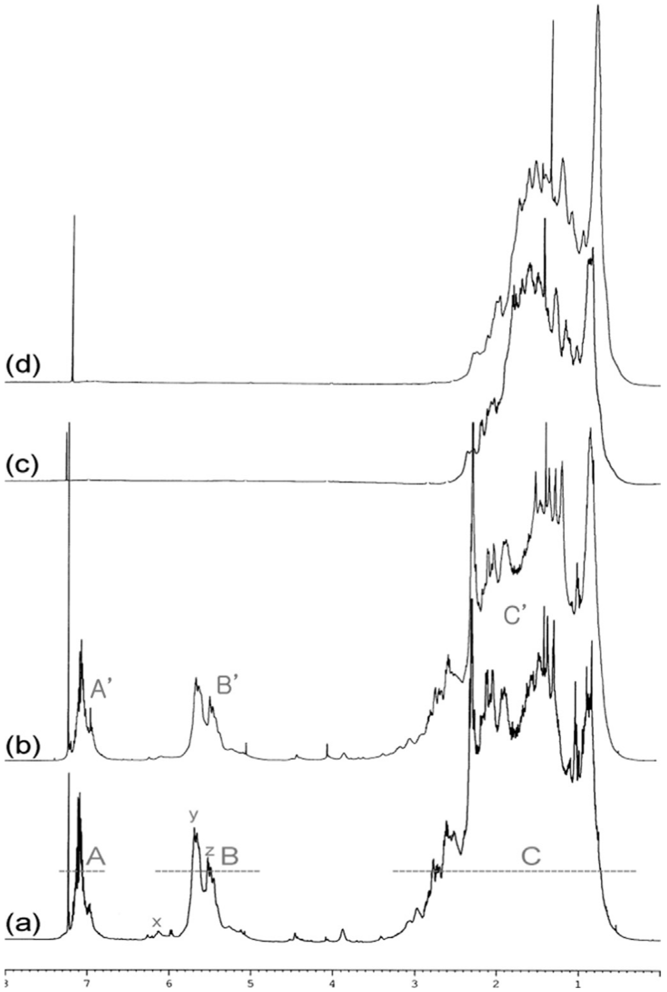


**Fig. 1.** $^1H$ NMR spectra of the HCR by cationic polymerization of DCPD/TCDE (mole ratio: 1/1) in toluene in the absence of propylene (a) and in the presence of propylene (b). [(c) and (d), after hydrogenation, respectively].

Signals at the aromatic region (~7 ppm) were clearly attributed to incorporation of toluene at a chain end (VIII-units). Toluene was involved in the polymerization as a chain transfer reagent. DCPD can be incorporated into polymer chain in various fashions (Chart 1). DCPD has two kinds of double bonds: norbornene-type and cyclopentene-type. The norbornene-type double bond is more reactive than the cyclopentene-type and propagation occurs mostly through the norbornene-type leaving cyclopentene-type double bonds which were observed as two broad signals at 5.6 and 5.4 ppm in the $^1H$ NMR spectrum. The latter (marked as '*z*') was attributed to normal 1,2-enchainment (I-units) and the former (marked as '*y*') was to abnormal enchainment due to carbocation rearrangement (II-units). Small signals above 6 ppm (marked as '*x*') were assigned to norbornene-type double bonds (III-units). In the cationic polymerization of DCPD alone, the signal intensity at the aliphatic region (0.5–3.3 ppm, C region in Fig. 1) was significantly higher than the calculated value based on the chain structure composed of unit-I, II and III. Hence, another type of enchainment should be proposed, by which both double bonds in DCPD were involved in propagation, not leaving any pendant double bond. Peng proposed formation of transannular unit (V-unit) [12]. The transannular unit (V-units) was fairly high, 30 mol%, while I-units and II-units were 25 and 45 mol%, respectively, in the polymer sample obtained in the cationic polymerization of DCPD alone at the similar conditions of our studies. In our studies, we additionally fed tricyclodecene(TCDE), which resulted in

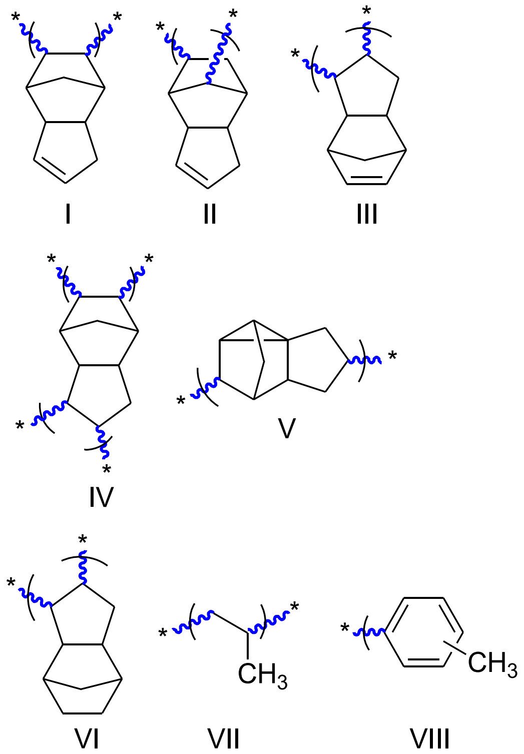


**Chart 1.** Repeat units and chain end in the HCR formed by cationic polymerization of DCPC/TCDE/propylene copolymerization in toluene.

significantly different polymer properties. TCDE was involved in the polymerization as a chain transfer agent such as toluene. When accepting the participation of TCDE in propagation, there might be some chance for both double bonds in DCPD to participate in propagation not leaving any double bond (VI-units).

Analysis of integration values of A, B, and C regions in the $^1$H NMR spectrum of the sample obtained in the cationic polymerization of DCPD/TCDE in toluene in the absence of propylene (Fig. 1(a)) indicated that mole ratios of toluene chain end (VIII-units, A/4), sum of I, II, and III-units (B/2), and sum of IV, V, and VI-units [{C-10(B/2)–3(A/4)}/13] were 1:4.2:6.5. In the $^1$H NMR spectrum of the sample, which was obtained at the same conditions except additional feed of propylene (Fig. 1(b)), almost the same pattern of signals were observed except the increase of signals below 1.0 ppm, which indicated incorporation of some propylene. The methyl ($CH_3$) signal in incorporated propylene units should be observed around 0.9 ppm. Under the assumption that the ratio between the mole ratio of sum of I, II, and III-units and sum of IV, V, and VI-units is identical both in the absence and in the presence of propylene, we could calculate the incorporated propylene amount. The mole ratios of toluene chain end (VIII-units), sum of I, II, and III-units, sum of IV, V, and VI-units, and propylene units (VII-units) were A′/4:B′/2:B′*{C-10(B/2)–3(A/4)}/13B:[C′ – 10(B′/2) – 3(A′/4) – 13B′*{C-10(B/2)–3(A/4)}/13B]/6. By dividing B′/2 by A′/4, the reference value of VIII-units was set to 1 to get proportional ratio with Fig. 1(a). By hydrogenation, all the signal observed at the aromatic region (~7 ppm) and double bond region (5–6 ppm) was disappeared (Fig. 1(c) and (d)). Observation of significantly higher signal below 1.0 ppm for the sample prepared by feeding propylene was also in accordance with incorporation of propylene.

As shown in Fig. 2, the propylene-grafted, hydrogenated DCPD HCR was also assigned by FT-IR. It was known that the propylene was successfully grafted to DCPD because the intensity of the bending peak at 1370 $cm^{-1}$, from pendant methyl group of propylene was also increased as the C3/DCPD mole ratio was increased.

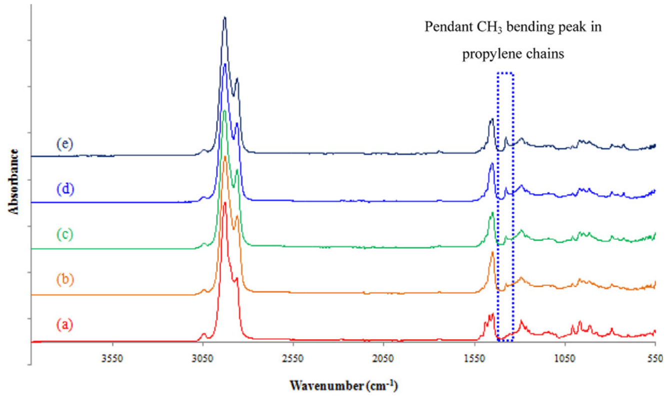


**Fig. 2.** FT-IR according to C3/DCPD mole ratio (a) only DCPD, (b) C3/DCPD mole ratio = 1, (c) C3/DCPD mole ratio = 2, (d) C3/DCPD mole ratio = 3, and (e) C3/DCPD mole ratio = 4.

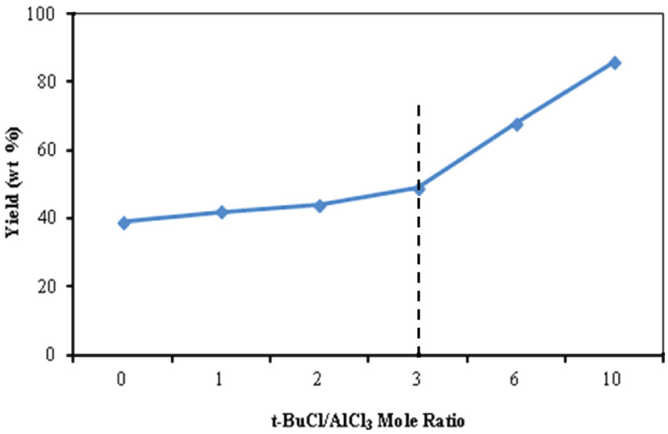


**Fig. 3.** Production yield according to t-BuCl/$AlCl_3$ mole ratio (C3/DCPD mole ratio: 2, TCDE/DCPD mole ratio: 0.57, $AlCl_3$/(DCPD + C3) mole ratio: 0.0125, polymerization temp.: 25 °C, polymerization time: 1 h).

**Table 1**
Production yield according to t-BuCl/$AlCl_3$ mole ratio.

| t-BuCl/$AlCl_3$ mole ratio | 0 | 1 | 2 | 3 | 6 | 10 |
|---|---|---|---|---|---|---|
| Yield (wt%) | 39 | 42 | 44 | 49 | 68 | 86 |

To find the optimal synthesis conditions, a variety of experiments were attempted. Fig. 3 and Table 1 show a production yield according to the t-BuCl/$AlCl_3$ mole ratio. If the t-BuCl content as a co-catalyst was increased, the production yield was also increased. By considering the manufacturing cost, a t-BuCl/$AlCl_3$-mole ratio of 3 was considered the optimal condition because the cost of the t-BuCl is higher than that of $AlCl_3$. As shown in Fig. 4 and Table 2, while the increase of the polymerization temperature increased the production yield and the polydispersity of HCR. whereas the C3/DCPD grafting ratio was not affected polymerization-temperature range of 30–60 °C. A lower HCR polydispersity leads to a more effective adhesive performance; moreover, a higher production yield results in greater productivity. From the test result, the optimal polymerization temperature is 40 °C. Fig. 5 and Table 3 show the C3/DCPD grafting ratio and the production yield in relation to the C3/DCPD mole ratio. By considering production yield, a C3/DCPD mole ratio of 3 was determined as the optimal mole ratio. As shown in Fig. 6 and Table 4, the specific HCR gravity was at its lowest for a C3/DCPD mole ratio of 3 at polymerization

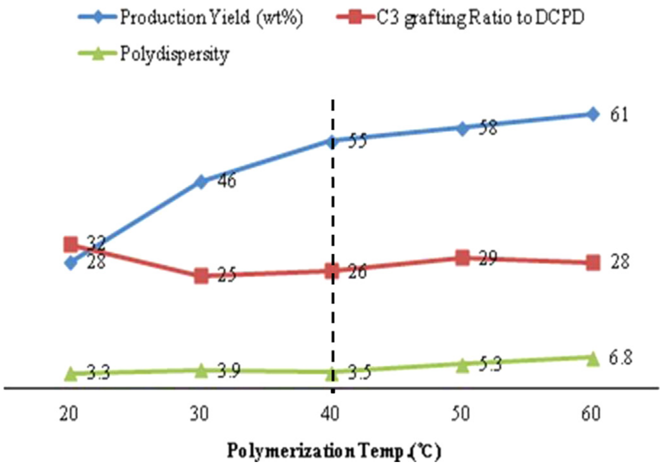


**Fig. 4.** C3 grafting ratio to DCPD, production yield, and polydispersity according to polymerization temperature (t-BuCl/$AlCl_3$ mole ratio: 3, $AlCl_3$/(DCPD+C3) mole ratio: 0.0125, C3/DCPD mole ratio: 2, TCDE/DCPD mole ratio: 0.57, polymerization time: 2 h).

**Table 2**
C3 grafting ratio to DCPD, production yield, and polydispersity according to polymerization temperature.

| | | | | | |
|---|---|---|---|---|---|
| Polymerization temperature(°C) | 20 | 30 | 40 | 50 | 60 |
| Production yield (wt%) | 28 | 46 | 55 | 58 | 61 |
| C3 grafting ratio to DCPD | 32 | 25 | 26 | 29 | 28 |
| Polydispersity | 3.3 | 3.9 | 3.5 | 5.3 | 6.8 |

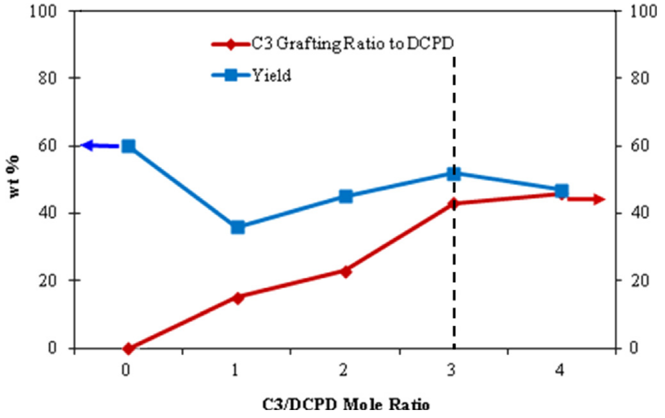


**Fig. 5.** C3 grafting ratio to DCPD and production yield according to C3/DCPD mole ratio (t-BuCl/$AlCl_3$ mole ratio: 3, $AlCl_3$/(DCPD+C3) mole ratio: 0.0125, TCDE/DCPD mole ratio: 0.57, polymerization temp.: 40 °C, polymerization time: 2 h).

**Table 3**
C3 grafting ratio to DCPD and production yield according to C3/DCPD mole ratio.

| | | | | | |
|---|---|---|---|---|---|
| C3/DCPD mole ratio | 0 | 1 | 2 | 3 | 4 |
| C3 grafting ratio to DCPD | 0 | 15 | 23 | 43 | 46 |
| Yield (wt%) | 60 | 36 | 45 | 52 | 47 |

temperature of 40 °C, meaning that a higher C3/DCPD grafting ratio results in a lower specific gravity. Generally, a narrow polydispersity of HCR fosters a more effective adhesive performance; thus, as shown in Fig. 7 and Table 5, the TCDE/DCPD mole ratio was determined to reduce the polydispersity of HCR—where TCDE was mainly used as a chain-transfer agent for the polymerization of C5 HCR—and, in consideration of the production yield, a TCDE/DCPD mole ratio of 1 was determined as the optimal mole ratio.

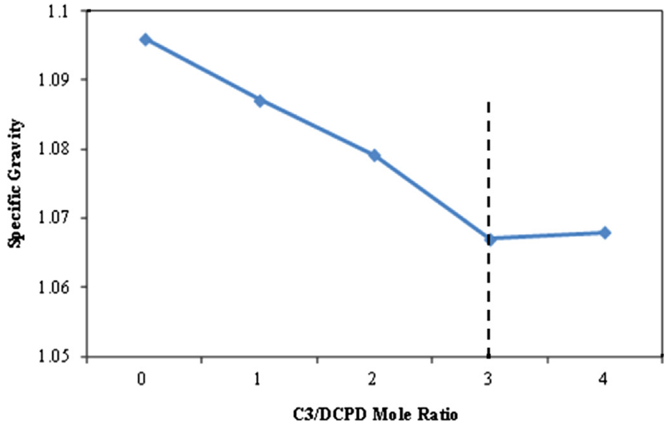


**Fig. 6.** Specific gravity of HCR according to C3/DCPD mole ratio (t-BuCl/$AlCl_3$ mole ratio: 3, $AlCl_3$/(DCPD+C3) mole ratio: 0.0125, TCDE/DCPD mole ratio: 0.57, polymerization temp.: 40 °C, polymerization time: 2 h).

**Table 4**
Specific gravity of HCR according to C3/DCPD mole ratio.

| | | | | | |
|---|---|---|---|---|---|
| C3/DCPD mole ratio | 0 | 1 | 2 | 3 | 4 |
| Specific gravity of HCR | 1.096 | 1.0871 | 1.0792 | 1.067 | 1.068 |

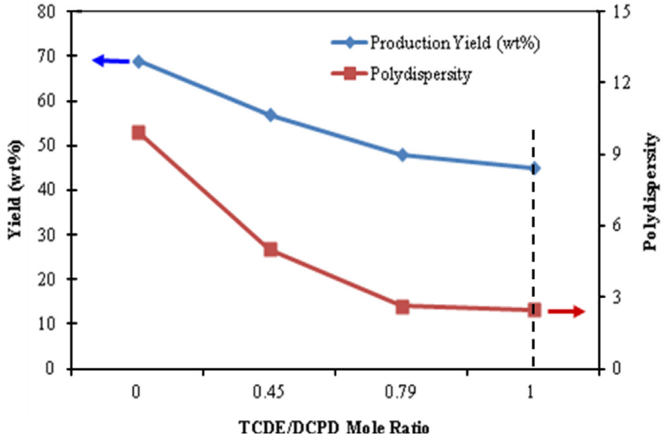


**Fig. 7.** Production yield and polydispersity of HCR according to TCDE/DCPD mole ratio (t-BuCl/$AlCl_3$ mole ratio: 3, $AlCl_3$/(DCPD+C3) mole ratio: 0.0125, C3/DCPD mole ratio: 2, polymerization temp.: 40 °C, polymerization time: 2 h).

**Table 5**
Production yield and polydispersity of HCR according to TCDE/DCPD mole ratio.

| | | | | |
|---|---|---|---|---|
| TCDE/DCPD mole ratio | 0 | 0.45 | 0.79 | 1 |
| Production yield (wt%) | 69 | 57 | 48 | 45 |
| Polydispersity | 9.96 | 5.03 | 2.63 | 2.49 |

**Table 6**
Optimal manufacturing condition of propylene-grafted, hydrogenated DCPD HCR.

| | |
|---|---|
| Monomer mole ratio | DCPD:TCDE:Propylene=1:1: 3 |
| Catalyst mole ratio | t-BuCl:$AlCl_3$=3:1 |
| Catalyst and monomer mole ratio | $AlCl_3$:(DCPD+Propylene)=0.0125:1 |
| Polymerization temperature (°C) | 40 |

Table 6 shows the optimal manufacturing conditions for propylene-grafted, hydrogenated DCPD HCR based on the above tests. Table 7 shows a comparison of the physical properties of the

**Table 7**
Physical HCR properties.

| HCR | Softening point (°C) | Color (HAZEN #) | Specific gravity | Molecular weight (Mw) | Poly-dispersity |
|---|---|---|---|---|---|
| SU-100S (hydrogenated DCPD) | 100 | 30 | 1.08 | 500 | 2.2 |
| SU-400 (C9-grafted hydrogenated DCPD) | 100 | 30 | 1.08 | 600 | 2.3 |
| SU-500 (fully hydrogenated DCPD) | 100 | 20 | 1.07 | 450 | 2.1 |
| $H_2$-C3-HCR (propylene-grafted, hydrogenated DCPD) | 100 | 30 | 1.02 | 1800 | 2.4 |
| Method | ASTM E28 | ASTM D1544 | ASTM D71 | GPC | |

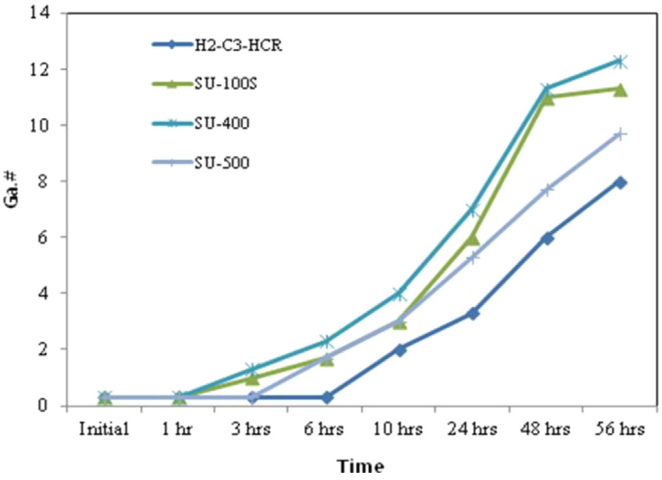


**Fig. 8.** Heat stability of used HCRs at 200 °C oven.

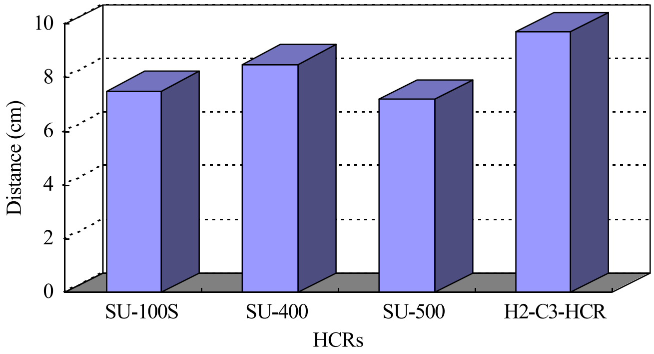


**Fig. 9.** Rolling ball tack of hot melt pressure sensitive adhesive (formulation: HCR/SIS/Process Oil =57/25/18 wt%).

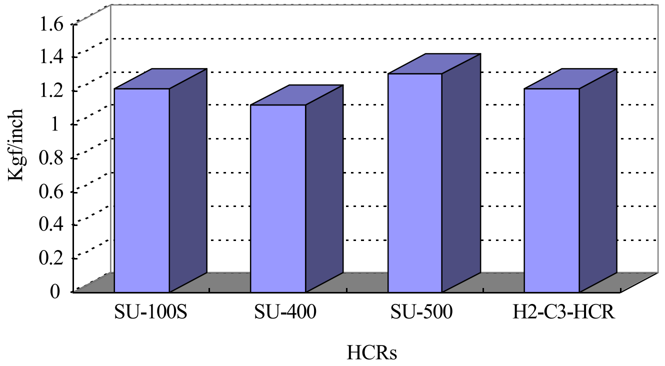


**Fig. 10.** 180° Peel adhesion of hot melt pressure sensitive adhesive (formulation: HCR/SIS/Process Oil =57/25/18 wt%).

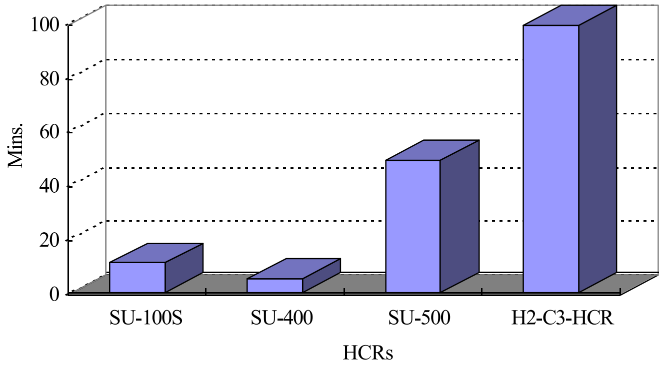


**Fig. 11.** Shear adhesion strength of hot melt pressure sensitive adhesive (formulation: HCR/SIS/Process Oil =57/25/18 wt%).

propylene-grafted, hydrogenated DCPD HCR that was manufactured under the optimal conditions and a conventional hydrogenated DCPD HCR; using this comparison as a basis, the lower specific gravity and higher molecular weight of the propylene-grafted, hydrogenated DCPD HCR means that it may be suitable for a lower density and stronger adhesion properties regarding the adhesive. Fig. 8 shows the heat-stability comparison of the propylene-grafted, hydrogenated DCPD HCR that was manufactured under the optimal conditions and the conventional hydrogenated DCPD HCR at 200 °C, whereby a lower Ga.# results in a greater heat stability; according to the results, the heat stability of the propylene-grafted, hydrogenated DCPD HCR is superior because of a high molecular-weight effect.

The propylene-grafted, hydrogenated DCPD HCR was manufactured under the optimized polymerization conditions and evaluated according to a HMPSA application for a comparison with a conventional hydrogenated DCPD HCR, as shown in Table 7. Fig. 9 shows the rolling-ball-tack property of the HMPSA as a function of HCR type and the result indicates that the rolling-ball tack depends on the molecular weight. The low molecular weight of a HCR such as SU-500 provides a more effective tack property than those of the other types; however, the tack properties of the adhesive comprising the propylene-grafted, hydrogenated DCPD HCR are lower due to a high molecular weight. Fig. 10 shows the 180° peel-adhesion strength on the substrate of a stainless used steel (SUS); according to the result, the peel-adhesion strength of the adhesive comprising the propylene-grafted, hydrogenated DCPD HCR is similar to those of the others. Fig. 11 shows the shear-adhesion strength on the SUS substrate; here, the shear-adhesion strength is dependent on the molecular weight of the HCR and a moderate compatibility between the HCR and the SIS. According to the results, the molecular weight of the propylene-grafted, hydrogenated DCPD HCR is high, its compatibility with the SIS is moderate, and the corresponding shear-adhesion strength is superior to those of the others.

Fig. 12 shows the rheological properties of the HMPSA including glass-transition temperature ($T_g$), storage modulus ($G'$), and damping ($\tan\delta = G''/G'$), which are used for the prediction of practical-use temperatures, impact properties, energy dissipation, stiffness, and many other performance properties. Homogeneous

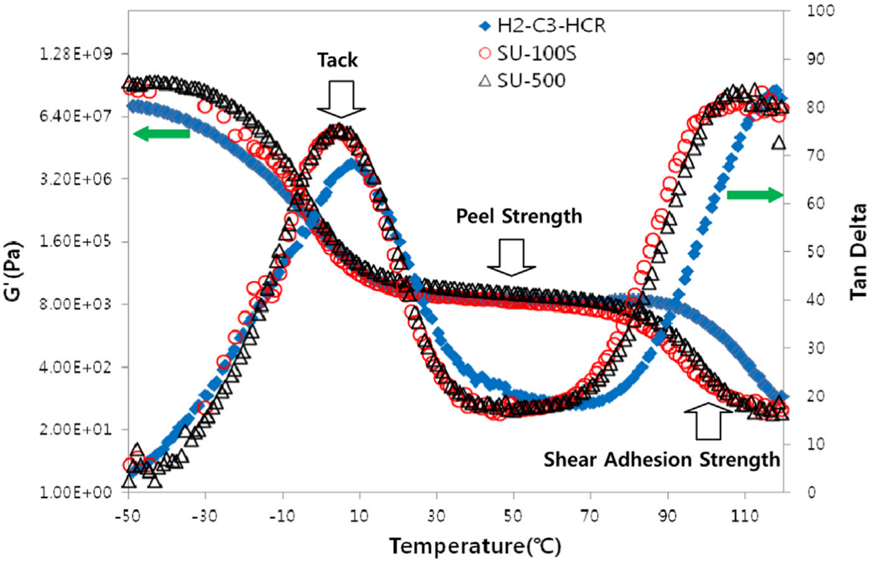


**Fig. 12.** Rheological properties of HMPSA (formulation: HCR/SIS/Process Oil =57/25/18 wt%).

blends exhibit only one $T_g$ in tan $\delta$ (tan delta); thus, the evaluation of $T_g$ provides information regarding compatibility and inter-phase effects. As shown in Fig. 12, it is quite obvious that the HCRs and SIS system employed were compatible with the base resin because there was only one $T_g$ peak within 0–10 °C temperature range; furthermore, the lowest tan $\delta$ value in the $T_g$ represents the least effective tack property because the value of the loss modulus ($G''$) that provides a key tack-property effect was also the lowest. Using the result shown in Fig. 9, it can be predicted that the rolling-ball-tack property of the adhesive comprising the propylene-grafted, hydrogenated DCPD HCR is the lowest. The storage moduli ($G'$) that are also plotted in Fig. 12 were virtually identical to the ambient temperature, so it can be predicted that the corresponding 180° peel-adhesion strength, like those indicated previously in Fig. 10, will be similar and virtually independent of formulation; regarding the shear-adhesion strength, as the $G'$ is the highest at the high temperatures that define the melt-flow region, it can be predicted that like Fig. 11 it is the highest.

## 4. Conclusions

The propylene-grafted, hydrogenated DCPD HCR was successfully synthesized with optimized condition as follows. The feed mole ratio of DCPD/TCDE/Propylene was 1/1/3 and the mole ratio of t-BuCl/$AlCl_3$ catalyst was 3/1. The mole ratio of catalyst ($AlCl_3$)/monomer (DCPD+Propylene) was 0.0125/1. The polymerization time and temperature were 2 h and 40 °C respectively. It was assigned by FT-IR and NMR that the propylene was successfully grafted to DCPD.

Regarding basic properties and application characteristics, it has lower specific gravity and higher molecular weight than conventional hydrogenated DCPD HCR and it has the best heat stability and shear adhesion strength in SIS based PSA because of its high molecular weight but its rolling ball tack property was the worst.

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