

Effect of 5-ethylidene-2-norbomene or cyclopentene comonomers on the micro-structures, mechanical and dynamic mechanical properties of polydicyclopentadiene

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ABSTRACT

A copolymerization reaction was carried out by adding different contents of 5-ethylidene-2-norbomene or cyclopentene to dicyclopentadiene (DCPD) using an optimized polymerization process. The effects of different amounts of the comonomers on the conversion, mechanical properties and thermal stability of the polymer products were investigated and compared. The results showed that the addition of 5-ethylidene-2-norbomene accelerated the reaction rate and had little effect on the overall conversion rate of the reaction, while the addition of cyclopentene decreased the reaction rate and conversion rate. The tensile modulus, tensile strength, flexural modulus and flexural strength of the copolymer showed a trend of increasing and then decreasing with the increase of the comonomers content, reaching a peak at 5wt% of 5-ethylidene-2-norbomene or 3wt% of cyclopentene. At this peak condition, its impact strength could be improved by 50% compared to DCPD homopolymer. Below this peak condition, the T_g and thermal stability of the copolymer did not change significantly. **Polyolefins J (2022) 9: 139-149**

Keywords: Polydicyclopentadiene; 5-ethylidene-2-norbornene; cyclopentene; copolymerization reaction.

INTRODUCTION

Due to its excellent mechanical and thermodynamic properties, polydicyclopentadiene (PDCPD) is widely used in automobile parts, sports equipment, and furniture shells [1,2,3]. However, with the development of industry, pure PDCPD materials have been unable to meet the application of some special fields, such as racing cars, aircraft shells, etc. [4]. Therefore, the modification of PDCPD has attracted great attention

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in recent years, including the improvement of polymer properties by adding a comonomers and copolymerizing with DCPD [5].

The addition of monomeric small molecules or macromolecular polymers other than DCPD to copolymerize with the original system simplifies the polymerization process and improves mechanical properties. Leach [6] used 1,4,5,8-dimethano-1,4,4a,5,8,8a-





octahydronaphthalene (DMON) and DCPD copoly merization under the action of a two-component catalyst. The study showed that with the addition of a small amount of the comonomers, the impact strength was significantly improved, the tensile property increased from 5% to 47%, and the impact strength was also higher than that of DCPD homopolymer. Mathers et al. [7] used Grubbs 2nd generation catalysts for ROMP of DCPD and monoterpenes to produce polymers with good solubility. The molecular weight and glass transition temperature of the polymers were analyzed to decrease with the addition of the comonomers and monomers in the following order: d-limonene > limonene oxide > β -pinene. Wilson et al. [8] copolymerized DCPD with dimethylnorbornene ester (DNE) with Grubbs catalyst, and the copolymer poly(DCPD/ DNE) was subjected to lap-shear experiments and tapered double cantilever beam (TDCB) fracture test. The characterization revealed that the adhesion of the modified copolymer to the epoxy resin base was significantly better than that of the homopolymer of DCPD, but the mechanical properties did not change significantly compared with PDCPD.

The choice of catalyst affects the degree of crosslinking and microstructure of the copolymer, which in turn affects its thermal and mechanical properties [9]. Since ruthenium-based catalysts are highly tolerant of functional groups and insensitive to oxygen and proton groups, so Grubbs catalyst is usually chosen as the catalyst for the DCPD injection molding process, and attempts are made to use 5-ethylidene-2-norbomene (ENB) and cyclopentene (CPE) as the comonomers involved in the copolymerization reaction [10-12]. ENB and CPE are both obtained from DCPD through Diels-Alder reaction [13,14], and the copolymerization reaction of these two monomers with DCPD can make the DCPD more fully utilized. In addition, ENB and CPE have a lower freezing point and can serve to reduce the coagulation of DCPD, which facilitates industrial operation.

Yang et al. [15] prepared DCPD and ENB composite materials with the Grubbs 1st generation and 2nd generation catalysts, respectively, and he studied the curing kinetics and thermo-mechanical properties of the polymerization reaction under the action of the two catalysts by DSC. It was found that the addition of ENB and 2nd generation catalysts significantly accelerated the curing process of DCPD and improved the fracture strain and toughness compared to the 1st generation catalysts. Tyler [1] used Grubbs 1st generation catalyst to prepare the crossing-linked copolymer of DCPD with ENB and HDMN and found that the copolymer had better toughness. Kessler et al. [16-18] studied the ROMP kinetics of DCPD with ENB in the presence of Grubbs catalyst and found that the addition of ENB accelerated the polymerization reaction, and that the onset of polymerization was highly dependent on the type of monomer and the concentration of catalyst. Cao et al. [19] examined the copolymerization reaction of DCPD with styrene (St) and CPE and found that for different copolymerization systems, the addition of St accelerated the copolymerization reaction and shortened the gelation time. However, the addition of CPE had little effect on its polymerization rate, but the excess affected the glass transition temperature.

In this paper, using the optimized polymerization process, different contents of ENB/CPE were added to DCPD for copolymerization reaction. The effects of different amounts of the comonomers on the conversion rate, mechanical properties and thermal properties of polymer products were studied and compared. Finally, the optimal amount of the comonomers was determined to develop PDCPD modified products with excellent comprehensive performance.

EXPERIMENTAL

Materials

All ROMP synthesis procedures were conducted in an anhydrous and anaerobic environment via Schlenk line techniques. Dicyclopentadiene (DCPD,95%), 5-ethylidene-2-norbornene (ENB,98%) and cyclopentene (CPE,98%) were purchased from JK Chemical (Shanghai, China), and Aladdin (Shanghai, China), respectively. The above three monomers were distilled through CaH₂ in a nitrogen atmosphere. Grubbs 2^{nd} generation catalyst was purchased from Macklin Chemical (Shanghai, China) and used as received. CH₂Cl₂ was purchased from Aladdin, was dried over excess CaH₂ and distilled in the nitrogen atmosphere for 8 hours or more. Toluene was purchased from Titan Chemistry (Shanghai, China) and was also used as received to evaluate the swelling behavior of the prepared polymer.

Preparation of copolymers

The polymerization was carried out in an 8mL reagent bottle under atmospheric pressure. Six different loadings of ENB (0,5,10,25,50,100 wt%) were added proportionally to 2 g purified DCPD. The Grubbs 2^{nd} catalyst was weighed with the molar ratio of monomer/catalyst of 10,000:1 in the glove-box, injected 1mL CH₂Cl₂ and shaken well, and then added into the DCPD/ENB blend solution for full stirring at 60°C, and gel time was recorded.

Five different loadings of CPE (0,1,3,5,10wt%) were added proportionally to 2 g purified DCPD. Other operations are the same as ENB.

Preparation of copolymer with RIM

The comonomers (ENB or CPE) were added to the Schleck bottle containing DCPD according to a certain mass ratio, and the mixed monomer solution was placed in a low-temperature reaction bath and stirred well. A certain amount of catalyst powder was weighed from the glove box (10,000:1 ratio of catalyst to monomer) and dissolved in dichloromethane solution to form a 30 mg/mL catalyst solution, then the catalyst solution was injected into the monomer mixture solution with a syringe, mixed and stirred thoroughly. After that, the mixture was quickly injected into a homemade nickel alloy one-piece four-cavity mold, which had been pumped three times and preheated to 60°C, and then sealed with nitrogen gas. After 1 h of reaction, the mold temperature was raised to 140°C for post-curing treatment for 1 h. After the mold cooled, the copolymer product was removed from the mold.

Conversion rate

The copolymer may contain unreacted monomers and small molecular impurities, so the sample needs to be pumped into a vacuum drying oven at 80°C to remove these residual molecules. The conversion rate of polymer products was calculated using Equation 1:

$$CR = \frac{m_2}{m_1} \times 100\% \tag{1}$$

where CR is the conversion rate, m_1 is the sample

weight before vacuum drying and m_2 is the sample weight after vacuum drying.

Swelling measurements

The copolymer has a highly cross-linking mesh structure that is insoluble in any solvent and can only swell. The thin slices with thickness of 2 mm and mass of about 100mg were prepared and vacuum-dried for 12h at 60°C before swelling. Samples were immersed in a 100 mL brown bottle filled with toluene for 4 days to reach the swelling balance.

The swelling rate (S) can be obtained according to Equation 2:

$$S = \frac{m_2 - m_1}{m_1} \times 100\%$$
 (2)

FTIR analysis

A Fourier infrared spectrometer (VERTEX70) produced by Bruker, Germany, was used for infrared spectrum analysis of the samples. High-purity DCPD was solid at room temperature, and all solid samples were tested by the KBr tablet pressing method after being ground into powder.

Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis of the samples was performed by a DMA1 thermo-mechanical analyzer from METTLER TOLEDO. Single cantilever mode was adopted, and the sample size was 35×10×4 mm³. A loading frequency of 1 Hz, heating rate of 3°C/min, and temperature range of 30-200°C were applied.

Mechanical properties

Test specimen was prepared according to GB/T2567-2008. Tensile and bending properties were characterized and tested by a CMT4204 microcomputer electronic universal testing machine produced by MTS, and notched impact strength was tested by a pendulum impact testing machine produced by the same company. At least 5 tests were performed in each group.

Thermogravimetric analysis

TGA of each copolymer sample was measured using a TA Q500 dynamic thermo-mechanical analyzer at a heating rate of 20°C min⁻¹ from 25°C to 600°C under nitrogen atmosphere, and the mass loss and decomposition

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rate versus temperature were recorded.

RESULTS AND DISCUSSION

Effect of comonomers on polymerization

Figure 1 shows gel time, conversion rate, swelling ratio of copolymerization systems with different ENB(a) or CPE(b) contents. It can be seen from Figure 1(a) that as the amount of ENB is added, the gel time of the copolymerization reaction is gradually shortened. The ring tension of norbornene on ENB is larger than that of norbornene on DCPD. When ENB is involved in the copolymerization reaction, the proportion of ENB on the molecular chain increases, leading to an increase in ring tension, and therefore the reactivity increases, the polymerization speed is accelerated, and the gel time becomes shorter. This is because ENB contains a norbornene ring structure. When DCPD is copolymerized with ENB, the proportion of norbornene rings with greater ring tension increases, the reaction activity becomes better and the polymerization rate becomes faster, so the corresponding gel time decreases.

However, as seen from Figure 1(b), with the increase of CPE content, the gelation time of copolymerization reaction gradually elongated, which was opposite to the tendency of ENB. This was because the ring tension of cyclopentene was only 2.9 kcal/mol, which had little influence on the norbornene ring (83.6 kcal/mol) on dicyclopentadiene, so cyclopentene was relatively stable and its reaction activity was lower than that of dicyclopentadiene.

Additionally, with the addition of ENB, the conversion rate of copolymerization reaction is at a very high level, more than 99%, while the conversion rate of copolymerization decreased with the increase of CPE content, although the conversion rate remained above 98%. Because the releasing heat produced by ROMP reaction enables ENB and CPE to fully undergo further



Figure 1. Gel time, conversion rate and swelling ratio of copolymerization systems with different ENB(a)/CPE(b) contents.

cross-linking reactions in the post-curing process and the comonomers are almost reacted.

Effect of comonomers on the structures

Figure 2 shows the FT-IR spectra of DCPD, poly(DCPD), poly(DCPD/ENB) and poly(DCPD/CPE) copolymers. It can be seen that the FT-IR spectra of DCPD/ENB and DCPD/CPE copolymers are very similar to that of DCPD homo-polymer. All of the polymers have an absorption peak at 3005 cm⁻¹, indicating the C-H stretched vibration in linear olefins. As well, a new absorption peak occurs at 1650 cm⁻¹, indicating the C=C bond of the linear olefins, when the absorption peaks of C=C in DCPD, ENB and CPE ring at 1571 cm⁻¹ disappeared. Therefore, it can be easily inferred that after the copolymerization, the norbornene ring in DCPD and ENB was opened to form the linear olefin.

It can be seen from Figure 1(a) that the swelling ratio of the copolymer has a rising trend with the increment of comonomers, presenting a decrease in cross-linking density. The cross-linking density of poly(DCPD/ ENB) increased slightly when the ENB content was lower (5 wt%), probably because at lower ENB content (less than 5 wt%), less ENB was involved in the reaction in the main chain, and the generated poly(ENB) linear structure was interspersed in the main network structure, forming a semi-interpenetrating network structure, which macroscopically showed that the cross-linking degree of poly(DCPD/ENB) was increased. However,



Figure 2. FT-IR spectra of DCPD, PDCPD, DCPD and ENB copolymer, and DCPD and CPE copolymer.

as the ENB content continued to increase, the Grubbs catalyst reacted preferentially with the norbornene ring in DCPD and ENB, and the amount of catalyst involved in opening the cyclopentene ring in dicyclopentadiene decreased accordingly, so the cross-linking reaction involved decreased and the cross-linking degree of poly(DCPD/ENB) decreased as well. From Figures 1(b), with the increase of CPE content, the content of CPE involved in the main chain is increasing. Meanwhile, the content of cyclopentene rings involved in the cross-linking reaction in DCPD decreases, and the proportion of linear chains on the main chain increases, so the cross-linking degree of poly(DCPD/CPE) is relatively dropped.

Effect of comonomers on the dynamic mechanical properties

The energy storage modulus (E') and loss factor (Tan δ) of copolymers with different ENB/CPE contents are shown in Figure 3. The energy storage modulus in the glassy state (E' at 30°C) and the rubbery state (E' at T_g + 30°C) were extracted from the E'-t curves (Figurs. 3(a) and 3(c)) and the approximate cross-linking density (v_e) was calculated according to the rubber theory. The temperature corresponding to the peak point where the loss factor (Tan δ) changes with temperature is the glass transition temperature (T_g), which is extracted from Figures. 3(b) and 3(d). Finally, the DMA data were collated in Table 1, where the cross-linking density (ve) was calculated according to Equation 3.

$$V_{e} = \frac{E'_{at Tg} + 30^{\circ}C}{3RT_{g}}$$
(3)

where R is the gas constant, and T_g is the glass transition temperature(K).

The energy storage modulus of all copolymerized samples decreased gradually with the increase of temperature. With the increase of ENB content, the energy storage modulus and cross-linking density of the copolymer in both glassy and rubbery states increased and then decreased, and reached a peak at 5 wt% of ENB content. When the ENB content is < 5 wt%, it is consistent with the reason for the increase of the solubility, which is macroscopically manifested as an increase of the cross-linking degree. When the ENB content is $\geq 5 \text{ wt}\%$, the ENB involved in the main





Figure 3. Energy storage modulus (E') and loss factor (Tan δ) of copolymers with different ENB(a-b)/CPE(c-d) contents.

chain increases rapidly and the cross-linking degree decreases significantly. However, with the increase of CPE content, the energy storage modulus and crosslinking density of copolymer in the glassy state and rubbery state showed an overall downward trend.

Table 1.Summary of DMA for poly(DCPD), poly(DCPD/ENB) and poly(DCPD/CPE).

m _{dCPD} /m _{enb/CPE}	T _g (°C)	E′ at 30°C	E′ at T _g +30°C	v _e (mol/m³)
100/0	147.6	1627.5	29.2	2535.8
95/5(ENB)	149.3	1650.5	34.1	2961.3
90/10(ENB)	145.3	1623.4	25.8	2240.5
75/25(ENB)	142.7	1601.6	11.6	1007.4
50/50(ENB)	132.6	1499.1	10.6	920.5
0/100(ENB)	108.0	1469.3	6.0	585.1
99/1(CPE)	144.2	1616.3	24.13	2146.25
97/3(CPE)	145.7	1623.4	25.32	2252.09
95/5(CPE)	140.2	1610.8	17.67	1330.21
90/10(CPE)	129.8	1600.4	12.03	950.29

With the increase of CPE content, the energy storage modulus and cross-linking density of copolymer in the glassy state and rubbery state showed an overall downward trend. In particular, when the content of CPE is $\geq 5 \text{ wt\%}$, the energy storage modulus of poly (DCPD/ CPE) rubber decreases from 28.51 MPa to 17.67 MPa, the corresponding cross-linking density also decreases from 2535.83 mol/m³ to 1330.21 mol/m³. It may be because the addition of CPE will affect the reactivity of the whole copolymerization reaction. More CPE is involved in the main chain of DCPD with the increase of CPE content, the proportion of linear chains on the main chain increases, and macroscopically it shows a rapid decrease in cross-linking density.

The T_g of poly (DCPD/ENB) and cross-linking density have the same change trend, and also reach the peak when ENB content is 5 wt%. This is because the cross-linking density is the largest at this time, and the movement of the chain segment is the most difficult, and more energy is needed to make the chain segment move, so T_g is the largest. The T_g of poly (DCPD/CPE) decreases with the increase of CPE content because as the cross-linking density decreases, the chain segment motility becomes better, and the lower the energy required for the polymer chain segments to start moving, the lower the temperature can trigger the chain segment motion, thus the T_g becomes lower. In addition, there was only one peak in the loss factor and temperature curve of copolymers under different comonomers contents, which indicated that copolymer was homogeneous in the microstructure.

Effect of comonomers on the mechanical properties

The tensile properties of copolymers of DCPD at different comonomers contents are shown in Figure 4. From Figure 4(a) and 4(c), it can be seen that the tensile modulus and tensile strength of copolymers show a

trend of rising and then falling with the increase of ENB/CPE contents. The tensile modulus and tensile strength of DCPD copolymer products were optimal at 5 wt% of ENB or 3 wt% of CPE, respectively. This is since when the comonomers content was added at a low amount, part of the ENB/CPE did not participate in the main chain reaction, but formed a linear structure interspersed in the network structure of the PDCPD, making the mechanical properties of the copolymer superior. However, when the comonomers' contents continue to increase, the tensile modulus and tensile strength of copolymers decrease because the crosslinking density of the copolymers decreases. At this time, cross-linking density is the most important factor affecting the tensile properties of the copolymers, so the tensile properties of the copolymers are gradually deteriorating. For instance, when the ENB content was 25 wt%, the tensile modulus of poly(DCPD/ ENB) dropped from 1860 MPa to 1750 MPa, and when the CPE content was 5 wt%, the tensile modulus



Figure 4. Stress-strain curves of cured DCPD/ENB(a-b) and DCPD/CPE(c-d) blends with the 2nd generation Grubbs' catalysts.

of poly(DCPD/CPE) dropped from 1860 MPa to 1700 MPa. As can be seen from Figure 4(b) and 4(d), the elongation-at-break of the copolymer increased with the increase of the content of the comonomers. For example, the elongation-at-break of the copolymers increased from 50.5% to 78.3% at 25 wt% of ENB and up to 70.7% at 5 wt% of CPE. This is because with the decrease of cross-linking density, the forces between molecular chains become weaker, so the molecular chain movement becomes more active, and the elongation-at-break of the copolymer will increase.

Like tensile properties, the bending modulus and bending strength of the copolymers are similar to their tensile properties as the comonomers content increases, showing an overall trend of increasing and then decreasing (Figure 5). When the content of the comonomers exceeds a certain amount, the cross-linking





density of the copolymer decreases rapidly, and the bending strength and modulus of the copolymer also decrease sharply.

The impact strength data of DCPD copolymer with different contents of the comonomers are shown in Figure 6. As can be seen from the figure, the notched impact strength of the copolymers increases with the increase of the content of ENB and CPE. The reason is that when the comonomers content is low, the crosslinking density of the copolymer is larger, and it is difficult to move with it under the action of external force, showing brittle fracture, so the impact strength of the copolymer is relatively small. However, with the increase of ENB and CPE content, the cross-linking density of copolymer decreased, the activity space of the chain segment was larger, and the brittleness improved. At an ENB content of 5 wt%, the impact strength of the copolymer increased from 31 kJ/m² to 46.8 kJ/m², an increase of about 50%, but the impact strength increased slowly when the ENB content was greater than 5 wt%. When the CPE content was less than 3 wt%, the impact strength of poly(DCPD/CPE) increased sharply from 30.7 kJ/m² to 45.7 kJ/m², but when the CPE content was more than 3 wt%, the impact strength increased slowly. The reason is that the addition of cyclopentene will make the viscosity of the copolymerization system larger, which is unfavorable to the discharge of solvent and air bubbles in the system, so the impact toughness is affected.

In general, when the content of ENB is 5 wt% or CPE is 3 wt%, the copolymer has the best comprehensive



Figure 6. Impact strength data of DCPD copolymer with different contents of ENB and CPE.

mechanical properties. Compared to poly(DCPD), the copolymer has increased tensile and bending strength, and the increase rate of the notched impact toughness is more than 50%.

Effect of comonomers on the thermal properties

The TGA and DTG spectra of poly(DCPD), poly(DCPD/ENB) and poly(DCPD/CPE) are shown in Figure 7. The degradation temperatures $Td_{5\%}$, $Td_{10\%}$, and $Td_{50\%}$ corresponding to the weight loss rates at 5%, 10%, and 50%, and the degradation temperature Td_{max} corresponding to the maximum weight loss rate are obtained from Figure 7. It can be seen that the copolymers of DCPD have the same trend of heat loss curves as the homopolymers as the comonomers content increases, and the decomposition temperature of the special comonomers of homopolymer



Figure 7. TGA and DTG spectra of poly(DCPD), poly(DCPD/ ENB) (a), and poly(DCPD/CPE) (b).

was not seen from the figure, indicating that most of the comonomers were involved in the copolymerization reaction. All polymers have no weight loss before 250°C, but there is a slight loss between 250 and 400°C, which may be due to the oligomer formed by unreacted DCPD monomers and small and medium-sized molecules in the system, as well as the degradation of oligomers generated by "chain backbite reaction" in the copolymer system. Subsequently, there is a large weight loss plateau on the thermal weight loss curves of all copolymers at 400-500°C, and all copolymers degrade rapidly in this range.

The thermal degradation temperatures of the copolymers both decreased with the increase of the comonomers content. In detail, when the ENB content was 5 wt%, the thermal stability and carbon residue rate of poly(DCPD/ENB) changed little, and when the comonomers content continued to increase, Td_{max} and carbon residue rate decreased significantly. However, when the ENB content reached 25 wt%, the Td_{max} of the copolymer decreased from 480.5°C to 428.3°C, and the residual carbon rate decreased from 19.9% to 10.7%, which is because the cross-linking density became significantly smaller and the thermal stability would decrease.

When the comonomer is CPE, the best thermal stability is obtained at 3wt% CPE content, and the degradation temperature trend of the copolymer is consistent with that of poly(DCPD/ENB). When the CPE content is 3%, the Td_{max} of the copolymer is obtained at 489.5°C, which is slightly higher than the Td_{max} of the DCPD homopolymer (480.5°C), because the cross-linked structure is more uniform and the thermomechanical properties are better at this time. When the CPE content is 5 wt%, the Td_{max} of the copolymer drops to 462.8°C, which is because the cross-linking density becomes smaller and the thermal stability is more significantly reduced.

CONCLUSIONS

The copolymerization reaction of DCPD with ENB or CPE was performed to investigate the effects of the addition of the comonomers on the reactivity of the copolymerization system, the swelling properties,



static and dynamic mechanical properties and thermal properties of the copolymers. The addition of ENB can make the reaction rate faster and does not affect the overall conversion rate of the reaction very much, while the addition of CPE decreases the reaction rate and conversion rate. The tensile modulus, tensile strength, bending modulus and bending strength of the copolymer showed increasing and then decreasing trends with the increase of the comonomers content, with a peak at 5 wt% of ENB or 3 wt% of CPE. Therefore, the optimum addition of ENB was determined to be 5 wt%, at which time the impact strength increased from 31 kJ/m² to 46.8 kJ/m², an increase of about 50%. The T_{σ} and thermal stability of poly(DCPD/ENB) did not change much when the ENB content was lower than 5 wt%. However, the optimum CPE addition of 3 wt% resulted in better tensile and flexural properties, while the impact strength increased from 31 kJ/m² to 45.7 kJ/m², which is about 50% higher. Both T_{σ} and thermal stability of poly(DCPD/CPE) did not vary significantly at CPE content below 3 wt%.

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CONFLICTS OF INTEREST

The authors declare that they have no conflicts of interest.

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