

Mechanical Properties of Block Poly(propylene carbonate-cyclohexyl carbonate) Investigated by Nanoindentation and DMA Methodologies

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ABSTRACT: To extend the practical application of poly(propylene carbonate) (PPC), the chemical methods were used to improve its mechanical properties. In this connection, random copolymer poly(propylene-cyclohexyl carbonate) (PPCHC) and di-block copolymers poly(propylene carbonate-cyclohexyl carbonate) (PPC-PCHC) were synthesized. Dynamic mechanical analysis (DMA), nanoindentation and nanoscratch test were applied to evaluate their mechanical properties. The storage's modulus, Young's modulus (E) and hardness (H) obtained from DMA and nanoindentation tests showed that the introduction of the third monomer cyclohexene oxide (CHO) can greatly improve the mechanical properties of PPC, and that the block copolymer PPC-PCHC had better mechanical properties than the random copolymer PPCHC. The annealing treated PPC-PCHCs exhibited deteriorated mechanical properties as compared with untreated PPC-PCHC. From the results of scratch tests, the plastic deformation of PPC-PCHC was smaller than those of PPC and PPCHC. Meanwhile, the plastic deformations of the heat-treated PPC-PCHCs were smaller than the untreated PPC-PCHC because of the possible rearrangement of the molecular chains of PPC-PCHC. The scratch hardness (H_s) of the block copolymer PPC-PCHC is larger than random polymer PPCHC and PPC, but lower than the values of heat-treated samples indicating that the surfaces' hardness of block polymers increase after heat treatment. These different measurement methodologies provide a more precise assessment and understanding for the synthesized block polymers. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Biopolymers are increasingly attractive because of their environmental issues. Nevertheless, their relatively poor mechanical properties limit their practical applications. In this sense, the assessment of their mechanical behaviors is practically necessary and important. Many new methodologies have been used for this purpose. For example, the scratch test, as a simplification of the complex abrasion process has been used for identifying the main parameters in the wear resistance of material surfaces.¹ During a scratch process, the viscoelastic and viscoplastic behaviors have been related to dynamic mechanical properties. The distinction between ductile and brittle behavior in scratch process leads to the definition of some specific tests and parameters. Ductile deformation during a scratch is often evaluated through the contact pressure, the residual depth of the groove, and the height of the pile-up.^{2–7}

The microindentation hardness technique has had widespread application in polymer research.⁸ The technique has been

increasingly used in the characterization of homopolymers, polymer blends, and copolymers. One attractive feature of this technique is its ability for the micromechanical characterization of the polymeric materials. The influence of different molecular parameters (molecular weight, branching degree etc.) on the crystalline morphology in semicrystalline polymers and the microphase separated morphology in block copolymers has been examined in preceding studies using the technique.⁹ Young's modulus and hardness analyzing by nanoindentation permit a direct visualization of the morphology and its influence on the micromechanical deformation processes under the action of an applied load. The micromechanical properties of different amorphous,⁹ rubber-toughened,¹⁰ particle-filled polymers,¹¹ and block copolymers¹² can be characterized in detail with help of these techniques.

As we all known, carbon dioxide is currently regarded as a major greenhouse gas.^{13–16} The utilization of CO₂ became a hot topic of intensive study for the sake of environmental concerns

Table I. Basic Properties of the Resultant Samples

Samples	$M_n/M_w/PI^a$	Composition (molar fraction %) ^b			
		f_{CO_2}	f_{PC}	f_{CHC}	f_{PE}
PPC	217K/378K/1.7	47.3	47.3	-	5.4
PPCHC	198K/418K/2.1	47.1	43.1	4.0	4.8
PPC-PCHC-0h					
PPC-PCHC-2h ^c	253K/461K/1.8	48.8	43.0	5.8	2.4
PPC-PCHC-14h ^c					
PPC-PCHC-24h ^c					

^aMolecular weight was determined by GPC using PS calibration, ^bDetermined by ¹H NMR spectroscopy, ^cAnnealed at 130°C for 2, 14, and 24 h, respectively.

and use of this potential carbon resource. Using the supported zinc glutarate (ZnGA) as catalyst to synthesize poly(propylene carbonate) (PPC) from CO₂ and propylene oxide (PO) has been reported by our research group. PPC has found usages in many applications, such as ceramic binders, evaporation mold, and adhesives.^{17–19} However, the relatively poor thermal and mechanical properties of PPC are still the bottleneck of its practical application. The work about the modification and applications of PPCs has been paid much attention and recognition by researchers. To improve the relatively poor properties, a third monomer CHO was introduced into the copolymerization of CO₂ and PO.^{20–24} However, one glass transition which is higher than that of PPC but not higher than 45°C was observed in most of the terpolymers indicating they are random copolymers. Inspired by the structure of styrenic block copolymers and the types of polymers are typically synthesized by sequential monomer addition or macroinitiation,²⁵ random copolymer poly(propylene-cyclohexyl carbonate) (PPCHC) and di-block copolymers poly(propylene carbonate-cyclohexyl carbonate) (PPC-PCHC) were synthesized using CO₂ with PO and CHO. The main chemical strategy is that CHO possesses a rigid six-membered ring. The cyclohexyl groups can restrict the rotation of the molecular chain, leading to an improvement of mechanical properties, but not crosslinking. The resultant ternary block copolymers exhibit better thermal stability and higher mechanical properties when compared with PPC.

To assess the mechanical properties of these synthesized polymers, we report here with the application of nanoindentation in the investigation of the Young's modulus (E) and hardness (H). Subsequently, we compared the experiment results with those obtained from DMA tests. We then studied the surface properties of a bulk polymer scratched by a conical indenter with a

rounded extremity. For the block copolymers, we also wanted to know if the heat treatment had some influences on their mechanical properties. In this work, nanoindentation and scratch test were first used to characterize the micromechanical properties of block polycarbonate based on carbon dioxide.

EXPERIMENTAL

Materials

Carbon dioxide of a purity of 99.99% was used without further treatment. PO of a purity of 99.5% and CHO of a purity of 95.0% were refluxed over CaH₂ for 4 and 24 h, respectively and then distilled under dry nitrogen gas. Prior to use they were stored over 4-Å molecular sieves. Other solvents and reagents such as ethanol, chloroform were of analytical grade and used without further purification.

Supported multi-component zinc dicarboxylate catalyst was prepared according to previous work.²⁴ The catalyst was white powder with Zn content of 11.6 wt %.

General Procedure for Terpolymerization of CHO, PO, and CO₂

The block copolymerization was carried out in a 500 mL stainless steel autoclave equipped with a mechanical stirrer. Multi-component catalyst (Zn2G) was introduced into the autoclave and the autoclave with catalyst inside was dried for 24 h under vacuum at 80°C and cooled down to room temperature before the reaction mixture was injected into it. Then the purified PO was immediately added into the autoclave. The autoclave was pressurized to 5.2 MPa via a CO₂ cylinder and heated at 70°C for 20 h. Following the evacuation of CO₂ and unreacted PO, CHO was introduced into the autoclave in an inert atmosphere. The autoclave was repressurized with 5.2 MPa of CO₂ and the reaction was performed at 80°C for another 20 h. Then the pressure in the autoclave was reduced to atmosphere to terminate the block copolymerization.

The random terpolymerization of CO₂, PO, and CHO was also performed in a 500 mL autoclave equipped with a mechanical stirrer. First, dry supported multicomponent zinc dicarboxylate catalyst was introduced into the autoclave as quickly as possible. The autoclave was then capped with its head, and the entire assembly was connected to the reaction system equipped with a vacuum line. The autoclave with catalyst inside was further dried for 6 h under vacuum at 80°C. Upon cooling down, CHO and PO were added to the autoclave. Subsequently, the autoclave was pressurized to 5.2 MPa via a CO₂ cylinder. The terpolymerization was performed under stirring for 40 h. Thereafter, when the reaction finished, the autoclave was cooled to room temperature and the pressure was released.

Table II. The Required Inputs of the Nanoindentation

Poissons ratio	Surface approach velocity (nm s ⁻¹)	Depth limit (nm)	Strain rate target (1 s ⁻¹)	Allowable drift rate (nm s ⁻¹)	Harmonic displacement target (nm)	Approach distance to store (nm)	Frequency target (Hz)
0.35	10	2000	0.05	0.05	2	1000	45

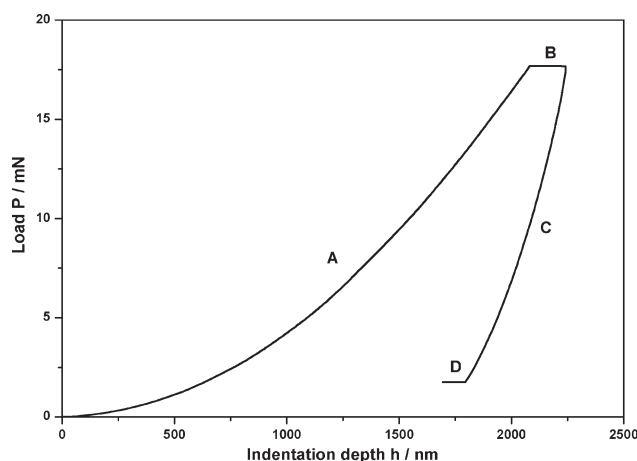


Figure 1. Example of load-displacement curve.

The resulting block and random copolymers were respectively dissolved in a proper volume of chloroform and 15 mL dilute HCl (5 wt %) was added to extract the catalyst residual from the product solution. The organic layer was then washed with distilled water for three times. The viscous solution was concentrated to a proper concentration by using a rotary evaporator. Finally, it was precipitated by being poured into vigorously stirred ethanol. The as-made copolymer (Table I) was filtered and dried under vacuum at a temperature of 120°C until a constant weight was obtained.

Measurements

Dynamic Mechanical Analysis. Dynamic mechanical properties of the samples (Cylinder shape, Radius: 5 mm) were measured by a dynamic mechanical analyzer (DMA) SDT861^e (Mettler, ToLeDo company) under nitrogen atmosphere at a heating rate of 2°C min⁻¹ from -30 to 150°C. The tests were done under the frequency of 0.3, 0.5, 1.0, 3.0, 5.0, 10.0 Hz.

Nanoindentation. The tests were performed on a Nano-Indenter II according to the methods developed by Loubet et al.,²⁶ Oliver and Pharr²⁷ and Lucas et al.²⁸ In this experiment, a diamond Berkovich-type indenter tip was forced into the matrix being studied under continuous conditions.⁹ The indentation depth was linked to the contact area between the indenter and the material under test. This procedure allows the mechanical properties of the sample to be investigated and can provide data to calculate the hardness *H* and Young's modulus *E*.^{1,2,8,9} The calculation is made by making an indentation with a well-controlled force *P* while continuously monitoring and measuring the displacement *h* of the indenter. The required inputs of the nanoindentation are shown in Table II. Poisson's ratio is defined as the ratio of the contraction strain normal to the applied load divided by the extension strain in the direction of the applied load. For a perfectly incompressible material, the Poisson's ratio would be exactly 0.5. Most practical engineering materials have Poisson's ratio between 0.0 and 0.5. Poisson's ratio of the material obtained from the technical literature, which is about 0.35 for the polymers.²⁹

Figure 1 shows an example of the load-displacement curve versus the indentation depth *h*. The nonlinearity is mainly due to the change of the contact area during the indenter penetration

Table III. The Required Inputs of Scratch Test

Scratch length (μm)	Surface approach velocity (nm s ⁻¹)	Scratch velocity (μm s ⁻¹)	Scratch orientation (0 to scratch down) (deg)	Delta X for finding surface (μm)	Delta Y for finding surface (μm)	Maximum scratch load (mN)
200	100	10	180	-50	-50	40
Allowable drift rate (nm s ⁻¹)	Profiling acquisition rate (Hz)	Approach distance to store (nm)	Starting scratch load (mN)	Cross profile length (μm)	Perform cross profile	Scratch acquisition rate (Hz)
2	5	2000	0	100	1	5
Surface approach distance (nm)	Profiling velocity (μm s ⁻¹)	Surface approach sensitivity (%)	Crossprofile location (input scratch load) (mN)	Load applied during profiling (μN)		
3000	10	20	10	100		

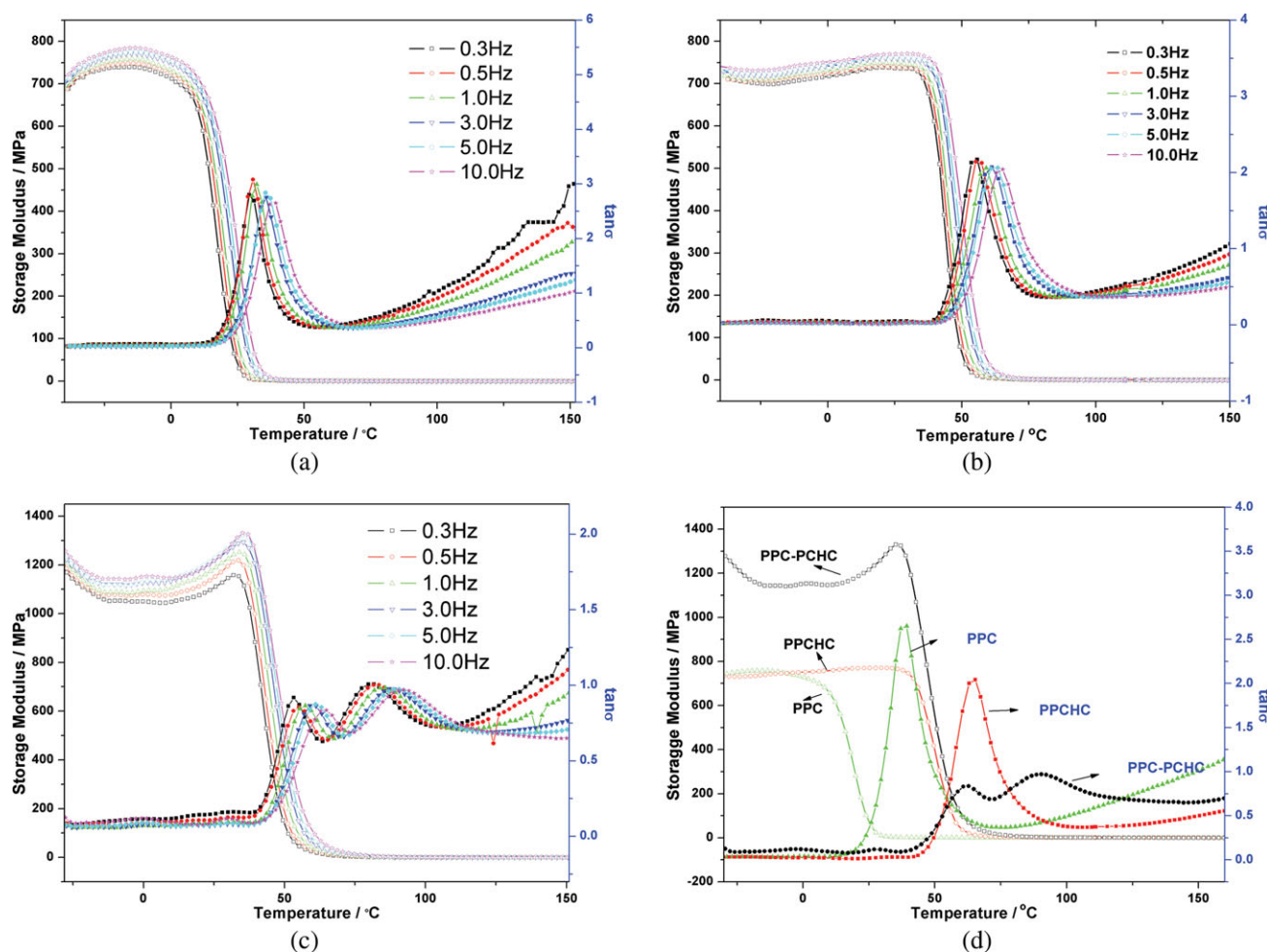


Figure 2. DMA results of (a) PPC, (b) PPCHC, (c) PPC-PCHC, (d) Compare DMA results under the frequency of 10 Hz. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

which is related to the viscoelastic properties of the sample. Each indentation experiment consisted of four segments. The first segment was the approach segment with an indenter surface approach rate of 10 nm/s. Once the indenter contacted the surface it was loaded at constant rate of 2 $\mu\text{N/s}$ to an indentation depth of 1800 nm (A). Subsequently, a hold segment (B) of 30 s was inserted. This hold segment, inserted immediately after the loading segment, is not an essential part of an indentation experiment but offers an opportunity to monitor possible creep of mechanical stabilization.

In the following unloading segment (C), 90% of the load was programmed to be removed at an unloading rate of 1.6 $\mu\text{N/s}$, after which a second hold segment of 30 s (D) was imposed. This hold segment, inserted after a partial unloading segment, provided opportunity to correct for the thermal drift of the apparatus during the indentation process.

A remote video control system was installed to facilitate the programming of the individual indentation positions. The specimen was subsequently transferred to the indenter by means of a computer-controlled high precision X–Y stage with $\pm 50 \mu\text{m}$.

Scratch Testing. A typical scratch experiment was performed in three stages: an original profile, a scratch segment, and a resid-

ual profile. The indenter actual penetration depth under the sample surface was estimated by comparing the indenter displacement normal to the surface during the scratching with the altitude of the original surface morphology obtained by profiling the surface under a very small load at a location where the scratch was to be performed. Roughness and slope of the surface were taken into account in the calculation of the indenter penetration. And the required inputs are as shown on Table III.

Additional morphological information can be determined by profiling across the scratch. The knowledge of load and penetration depth are involved in the abrasion process, a measurement of residual scratch depth p , width d , and pile-up height h_p , allows the estimation of the polymers' plastic deformation behavior.

Based on the width values and strain values, scratch hardness (H_s) could be calculated using the following equation:

$$H_s = q \frac{4F_N}{\pi d^2}$$

where F_N is the normal load (N), d is the recovered scratch width (m), and q is a coefficient which is a function of the

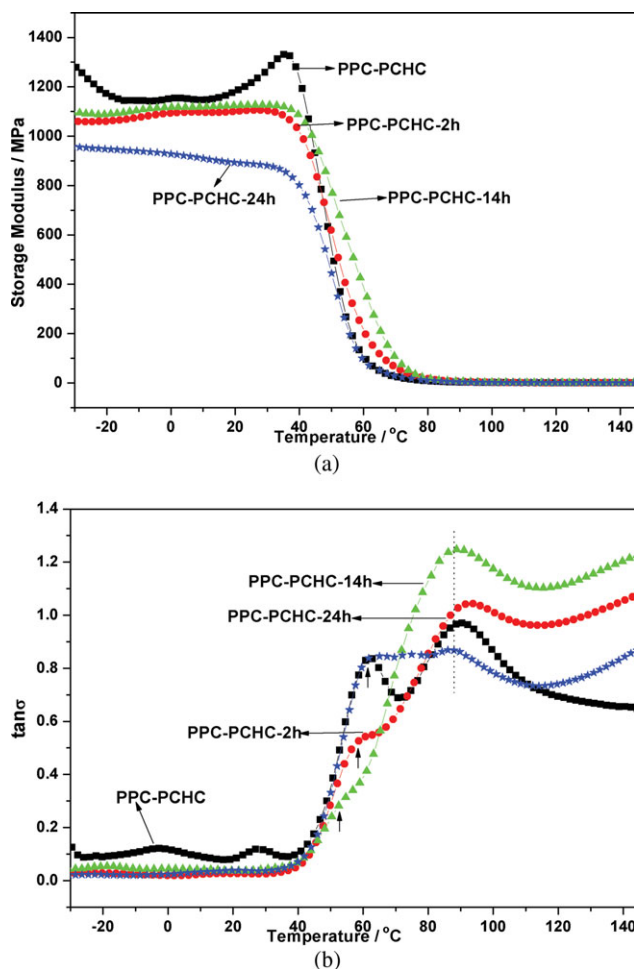


Figure 3. DMA results of the annealed block species at 10 Hz (a) storage modulus, (b) $\tan \delta$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

elastic/plastic behavior of the softer material ($q = 1$ for very elastic contact without fracture and $q = 2$ when there is high amount of plastic deformation). Here, we assume q equal to 2.0.³⁰

RESULTS AND DISCUSSION

DMA Test

The dynamic mechanical properties of the resultant copolymers were shown in Figure 2. From Figure 2(a–c), we can see that with increasing frequency, the storage modulus and $\tan \delta$ are all right shifting. Figure 2(d) shows the differences in dynamic mechanical properties among PPC, PPCHC, and PPC-PCHC. The storage modulus of PPC-PCHC is higher than the random copolymer PPCHC and both of them are higher than pure PPC. This is due to the steric hindrance of CHO inhibits the chains' movement and then improves the mechanical properties of polymers. The $\tan \delta$ spectra of PPC-PCHC appears two peaks, one is at about 60°C and another is at about 80°C, confirming the block copolymer structure. The $\tan \delta$ spectra of PPC and PPCHC are about 40 and 65°C, which are lower than PPC-PCHC, meaning the thermal property inferior to PPC-PCHC.

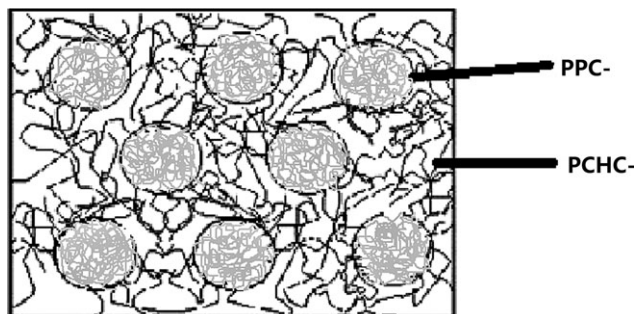


Figure 4. Proposed model of PPC-PCHC after heat annealed.

The storage modulus of the block copolymers annealed for 2, 14, and 24 h are slightly different from the untreated PPC-PCHC [Figure 3(a,b)]. The $\tan \delta$ spectra of the annealed samples also exhibit two peaks, however, the peak representing PPC segment becomes unapparent with increasing the annealing time. Presumably, PCHC segments tend to rearrange and limit the movement of PPC segment at a temperature higher than 130°C. This phenomenon of the limited movement of PPC

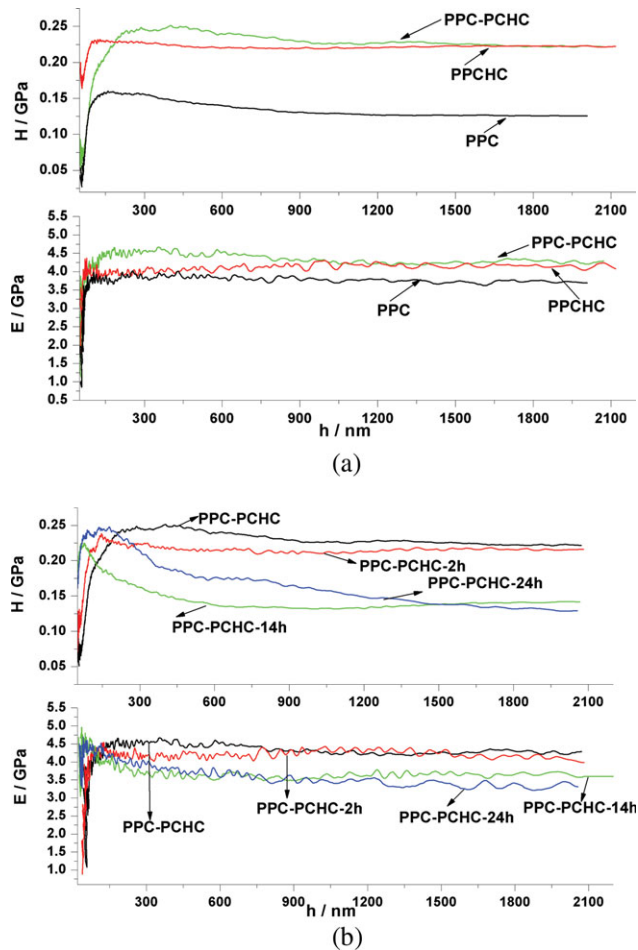


Figure 5. Hardness H and Young's modulus E versus the indentation depth h (a) PPC, PPCHC, PPC-PCHC (b) the annealed block species. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. The Results of the Hardness H and Young's Modulus E

Samples	Hardness, H -indentation (GPa)	Young modulus, E (GPa)
PPC	0.155	3.779
PPCHC	0.221	4.028
PPC-PCHC1-0 h	0.235	4.379
PPC-PCHC1-2 h	0.225	4.278
PPC-PCHC1-14 h	0.128	3.955
PPC-PCHC1-24 h	0.125	2.253

segments appeared more and more apparent with increasing annealing time as shown in Figure 4.

Nanoindentation Characterization

To investigate the micromechanical properties of polymers and study the influence of the heat treatment on block copolymers, nanoindentation, and scratch tests were respectively studied. Figure 5(a,b) shows the evolution of E and H versus the indentation depth of different samples. At small depths, the hardness apparently increases and asymptotically approaches a constant value at a depth of 50 nm. The initial increase is associated with elastic deformation of the polycarbonates and is caused by the tip defect. The values for Young's modulus (E) were calculated from the contact stiffness. All hardness and Young's modulus were obtained from the constant value and are summarized in Table IV.

From Figure 5(a,b) and Table IV, we can see that the hardness (H) and the Young's modulus (E) of the block copolymer PPC-PPCHC (0.235, 4.379 GPa) is higher than those of random copolymer PPCHC (0.221, 4.028 GPa), and whereas, those of PPCHC is higher than those of PPC (0.155, 3.779 GPa). However, the hardness and Young's modulus values of DGEBA-MTHPA are about 0.37 and 5.1 GPa³¹ and about 0.30 and 5.39 GPa for PMMA.³² The Young's modulus shows the same trend as those of storage's modulus measured by DMA. For the block copolymer samples subjected to annealing treatment, the H and E values of the block copolymers decrease with increasing the annealing time, which from 0.235 to 0.125 GPa and from 4.379 to 2.253 GPa respectively. According to Figure 5(b), the E and H of PPC-PCHC-14 h, PPC-PCHC-24 h increase at the initial

depth and then decrease dramatically when the depth is deeper, which means that the specimen's surface is harder than internal structure. This is owing to that the block copolymers contains about 2 wt % propylene carbonate produced during the polymer synthesis. It is very difficult to remove because of its extremely high boiling temperature of about 300°C. The thin surface layer is relatively easier to be dried compared to inside section.

Scratch Measurements

As discussed above, the block polymers have different micromechanical properties on its surface and at its inside. Therefore, we carried out scratch tests to study the surface properties and plastic deformation behaviors of these new polymers (Table V). In this penetration depth range, the indenter geometry can be considered as a perfect Berkovich indenter, meaning that the tip rounding. Figures 6 and 7 illustrate the evolution of the penetration depth and residual morphology of the scratch. The common residual scratch morphology exhibits a groove with two pile-up pads formed by the plastic flow around the indenter during the experiment. Because the grooves are not sharp, the amount of elastic deformation taking underneath the indenter is important for our samples. The residual morphology expresses the plastic deformation taking place during the scratch. From the groove's total depth, it is apparent that the plastic deformation of PPC-PCHC (793.1 nm) is smaller than that of PPC (1035.5 nm) and random PPCHC (942.7 nm). For the annealed PPC-PCHCs, the plastic deformations are smaller than that of untreated PPC-PCHC, which decrease from 793.1 to 696.6 nm. This demonstrates that the microphase separation contributes to the decrease of the plastic deformation of the terpolymers. In scratch testing as well as in indentation testing, the key to accurate analysis is to appropriately estimate the contact area during the experiment. The groove topology gives access to the contact width which will help in the estimation of the actual contact area. From the values of scratch hardness (H_s), the block copolymer PPC-PCHC (0.186 GPa) is larger than random polymer PPCHC (0.174 GPa) and PPC (0.161 GPa), but lower than the values of heat treated samples. So it can be concluded that the surfaces' hardness of block polymers increase after heat treatment, which have the same trend with the hardness of nanoindentation.

Table V. Scratch Test Results

Samples	Scratch width (μm)	Total height of groove (nm)	Residual scratch depth (nm)	Pile up (height nm^{-1})	H_s (GPa)
PPC	12.6	1035.5	690.3	345.2	0.161
PPCHC	12.1	942.7	732.3	210.4	0.174
PPC-PCHC1-0 h	11.7	793.1	657.4	135.7	0.186
PPC-PCHC1-2 h	10.8	786.5	592.3	194.2	0.219
PPC-PCHC1-14 h	11.2	696.6	534.9	161.7	0.203
PPC-PCHC1-24 h	10.6	787.8	573.0	214.8	0.227

CONCLUSIONS

The DMA, nanoindentation, and nanoscratch techniques can be employed to characterize the micromechanical properties of CO₂ based biodegradable copolymer PPC, random copolymer PPCHC and block copolymer PPC-PCHC. The nanoindentation

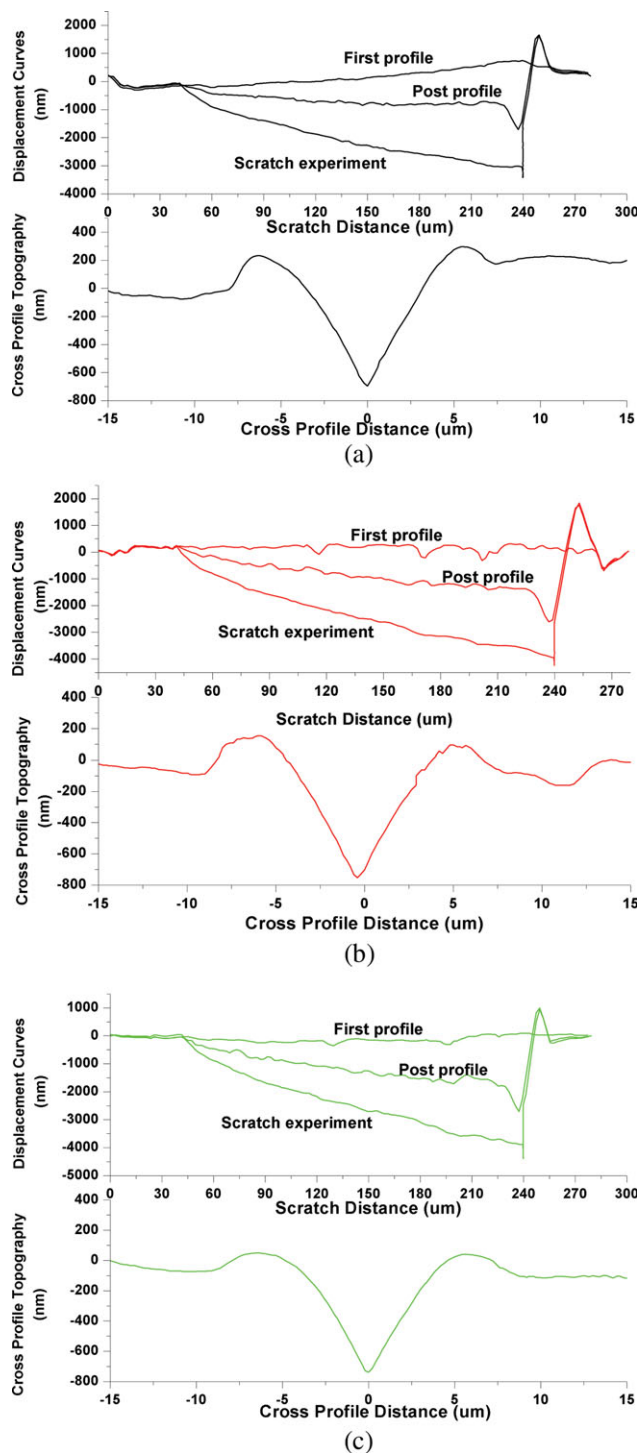


Figure 6. Scratch results of (a) PPC, (b) PPCHC, (c) PPC-PCHC. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

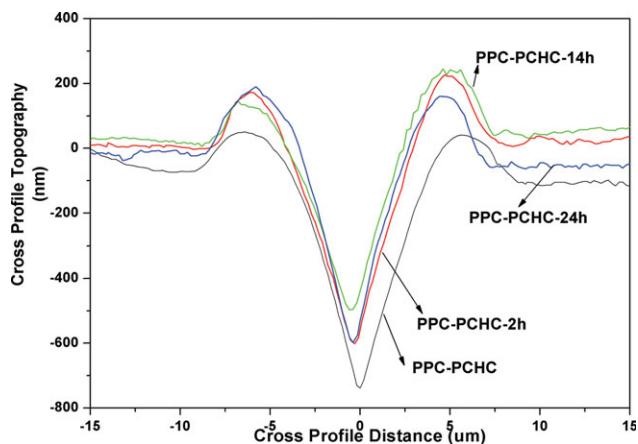


Figure 7. Scratch results of the annealed species. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

technique provides a new insight for high spatial resolution mechanical properties of polymers. The Hardness and Young's modulus data obtained from the nanoindentation tests indicated that the introduction of the third monomer CHO can greatly improve the mechanical properties of PPC, and that the block copolymer PPC-PCHC had better mechanical properties than the random copolymer PPCHC. The same conclusion can also be drawn by comparing the storage's modulus of the three polymers measured by DMA. So block copolymerization is better than random copolymerization for improving the mechanical properties of polycarbonate based on carbon dioxide. Both nanoindentation tests and DMA tests results showed that the annealing treatment may deteriorate the mechanical properties of PPC-PCHC. The nanoscratch results showed that the plastic deformation of PPC-PCHC was smaller than that PPC and random PPCHC, and the plastic deformation of PPC-PCHCs decreased with increasing annealing time. From the values of scratch hardness (H_s), the block copolymer PPC-PCHC is larger than random polymer PPCHC and PPC, but lower than the values of heat treated samples. So it can be concluded that the surfaces' hardness of block polymers increase after heat treatment, which have the same trend with the hardness of nanoindentation. In summary, this is a good experience for us to study the micromechanical properties of the polycarbonate based on carbon dioxide, which shows PPC and its terpolymers have the potential for more wide application. The above results manifested the effectiveness of nanoindentation and nanoscratch methods for micromechanical property evaluation for the synthesized new polymers.

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