

Polymer Reaction in Polycarbonate with Na_2CO_3

Kunihiko Takeda,¹ Haruo Unno,² Min Zhang¹

¹Nagoya University, Graduate School of Engineering, Department of Materials Functional Engineering, Furoh-cho, Chikusa-ku, Nagoya 464-8603, Japan

²Shibaura Institute of Technology, Department of Materials Science and Technology, 3-9-14 Shibaura, Minato-ku, Tokyo 108-8548, Japan

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ABSTRACT: The recombination of polycarbonate (PC) chains has been researched as one of the studies on self-repairing materials. The specimens, which included sodium carbonate and Tri(2,4-di-*t*-butylphenyl)phosphate, were treated at 120°C in a steam chamber and subsequently at 130°C under nitrogen atmosphere. The molecular weight of the specimen with 0.1 ppm of sodium carbonate increased during the subsequent treatment. The same tendency was observed when sodium carbonate was supplementally added to the specimen. In particular, the molecular weight little changed under severe condition when the concentra-

tion of sodium carbonate was controlled to be 100 to 1000 ppm. The result showed PC could be used as a self-repairing material. The deterioration is expected to be minimized if the recovery rate is the same as the deterioration rate by applying these self-repairing systems. The tensile strength, the transparency, and the reaction schemes are discussed. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 920–926, 2004

Key words: polycarbonate; additives; GPC; IR; mechanical properties

INTRODUCTION

Polymeric materials deteriorate under severe circumstances such as higher temperature, sunlight, and mechanical load. The deterioration reactions are generally irreversible. Many kinds of additives such as antiheat additives, light stabilizers, and oxidation protection agencies have been researched and developed for meeting the strong demand in industry.^{1,2}

On the other hand, the concept of man-made self-repairing materials has been discussed for several decades, and there have been many efforts to prepare advanced materials, system, and equipments that have self-repairing ability.^{3,4} White and Brown and their colleagues published their works on automatically healing and self-repairing polymers. When a crack is generated in resin, the microcapsule that has been blended into it prior to the fabrication is ruptured.⁵ The dicyclopentadiene in the capsule is infiltrated into the matrix, and is polymerized by the ruthenium catalyst that has also been blended into the polymer. Although the structure of the repaired polymer is different from the original one, the toughness can be recovered by 75%. Brown and his coworkers

showed “the epoxy matrix composite which incorporates a microencapsulated healing agent that is released upon crack intrusion.”⁶ The composites of epoxy resin and hollow fiber were reported as self-repairing plastics.^{7,8}

This article reports on the recombination of the polycarbonate (PC) chain and its effect on the tensile strength for a part of our study on self-repairing materials.^{9–12} In particular, the concentration of sodium carbonate on the recovery of molecular weight was focused to develop the self-repairing concept.

EXPERIMENTAL

Preparation of PC and the chemical structure

Two kinds of PCs were used in this experiment. One was prepared with carbonyl halide and hydroxy compound, known as the most popular method. Phosgene, bischloroformate,¹³ and monochloroformate¹⁴ were used as the carbonyl halide. The PC used in this study was manufactured by TEIJIN Ltd. (L1225: weight-average molecular weight (\bar{M}_w) = 27,700, viscosity-average molecular weight (\bar{M}_v) = 22,000).

The other PC was synthesized from a diester carbonate and a hydroxyl compounds by ester exchange method without a catalyst and at 300°C or more. This PC used in this study was made by Asahi Kasei Co. (PC-A, \bar{M}_w = 35,000, \bar{M}_v = 17,000), by the GE Co.

Correspondence to: K. Takeda (nagoyatakeda@numse.nagoya-u.ac.jp).

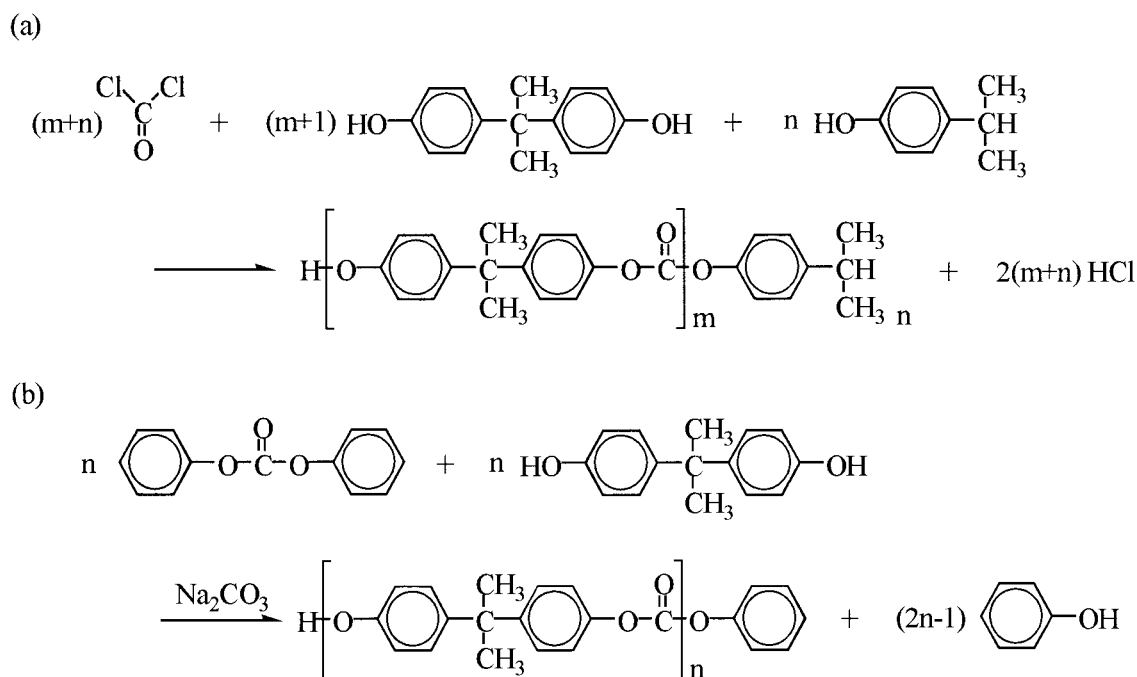


Figure 1 Synthesis method and chemical structure of PC by (a) the phosgene method, and (b) the melt transesterification method.

[(GE141R, $\overline{M}_w = 36,000$, $\overline{M}_v = 23,000$) and (MHL1110: $\overline{M}_w = 36,000$, $\overline{M}_v = 19,500$)].

The reaction schemes and the chemical structures of the two kinds of PCs are illustrated in Figure 1.

Specimens for experiments

The ends of the main chain depended on the preparation method and were recognized as listed in Table I. The additives that had been added prior to the polymerization or for the service time were in the specimens.

To control the concentration of the sodium carbonate, it was removed and readded as listed in Table II.

A twin-screw extruder (S-1 kneader manufactured by Kurimoto Ltd.) and a injection-molding machine manufactured by Modern Machinery (MJEC10) were used to

make dumbbell specimens whose thicknesses were 1.0 mm (for measuring \overline{M}_w) and 3.2 mm (for a tensile test).

Experimental methods

In experimental-1 (Exp.-1), three specimens were put into a steam autoclave (ACV-3167 manufactured by Iwaki Glass Co.) as a deterioration procedure. Subsequently, they were dried in a vacuum drier and used for further reactions and analysis. In experimental-2 (Exp.-2), the tensile strengths as a function of the treatment times of three specimens that had been treated as the same as those in Exp.-1 were measured. In experimental-3 (Exp.-3), the specimens of A and D were prepared, and they were treated under the same circumstance as those of Exp.-1 for 960 h. To observe gel

TABLE I
PC Used in This Study

No.	A	B	C	D
Producing company	ASAHIKASEI	TEIJIN	GE	GE
Grade	PC-A	L1225	GE141R	MHL1110
Polymerization method	Transesterification	Phosgene	Melt Transesterification	Transesterification
Ratio in chain end				
Phenolic	0.30	0.15	0.25	0.30
Phenyl	0.70	—	0.75	0.70
Isopropyl	—	0.85	—	—
Additives	Sodium carbonate	Tri (2, 4-di-t-butylphenyl) phosphate	Tri (2,4-di-t-butylphenyl) phosphate	Stabilizer

TABLE II
Sample Controlled Sodium Carbonate Concentration

No.	Concentration of sodium carbonate
	ppm
A-1	0.1
A-2	1
A-3	10
A-4	100
A-5	1000
A-6	10,000

formation, the transparency was measured by an ultraviolet Spectrophotometer (UV) manufactured by JASCO Co. (V-560DS). The width of the spectral band was 2.0 nm and the wave lengths were 650, 780, and 830 nm. In experimental-4 (Exp.-4), six films were prepared by casting on glass plates and putting into a vacuum drier. After drying, they were put into a chamber at 145°C under nitrogen atmosphere.

The procedures in the experiments and the conditions are summarized in Table III.

The concentration of sodium carbonate was measured by Fluorescent X-ray/mass spectrometry (SPQ-9000, Seiko Instruments Inc.) The molecular weight and the distribution of PC were observed by Gel Permeation Chromatography (GPC) manufactured by Shimadzu Co. (LC-10A) equipped with exclusive columns for gel permeation (GPC-802C, GPC-804C, GPC-8025C). The fractions eluted from GPC were detected by ultraviolet and visible light spectroscopy (SPD-

10A). Prior to the measurement, the gel fraction, which did not solve in chloroform, was separated by a membrane filter. The molecular weight was calibrated by a standard sample of polystyrene (PS) for GPC. This procedure was applied to the measurement of gel amount.

The tensile tester manufactured by Imada Co. (SV-201) was used for measuring the tensile strength in which the tensile rate was 0.5 mm/min. The infrared spectrogram of the casted films (thickness = 5.0 μm) was measured by Fourier transformation Infrared spectrometry, which was manufactured by JASCO Co. (FTIR-230).

RESULTS

Effect of polymer structure and sodium carbonate (Exp.-1)

The effect of chemical structure on the molecular weight was examined in Exp-1 in the first step of the change with the passage of time. The result is plotted in Figure 2. The \overline{M}_w of three specimens decreased by 10–12% after deterioration by hydrolysis. The weight of specimen-A recovered by 4.7% and reached 0.943 after 528 h of treatment. On the other hand, those of specimen-B and -C decreased by the treatment. The end structures of sample-B and -C were not the same, but both of sample-A and -C were phenolic and phenyl ends. Therefore, the end of the PC chain was considered to play an important role in decreasing or increasing the molecular weight.

TABLE III
Experimental Procedures and Conditions

		1	2	3	4
		A,B,C	A	A,D	A-1 - A-6
Shape	—	Dumbbell	Dumbbell	Dumbbell	Film
Length	mm	63	63	63	30
Width	mm	3–13	3–13	3–13	30
Thickness	mm	1.0	3.2	3.2	0.05
Temperature	°C	25	25	—	25
Time	hour	48	48	—	48
Atmosphere	—	Vacuum	Vacuum	—	Vacuum
Pressure	MPa	0.1	0.1	—	0.1
Temperature	°C	120	120	145	145
Time	hour	64	64	960	720
Atmosphere	—	Water Steam	Water Steam	Nitrogen	Nitrogen
Pressure	MPa	0.1	0.1	0.01	0.01
Temperature	°C	130	130	—	—
Time	hour	528	528	—	—
Atmosphere	—	Nitrogen	Nitrogen	—	—
Pressure	MPa	0.01	0.01	—	—
Molecular Weight	—	GPC	—	—	GPC
Chemical Structure	—	—	—	—	IR
Mechanical Property	—	—	Tensile Strength	—	—
Optical Characteristic	—	—	—	UV	—

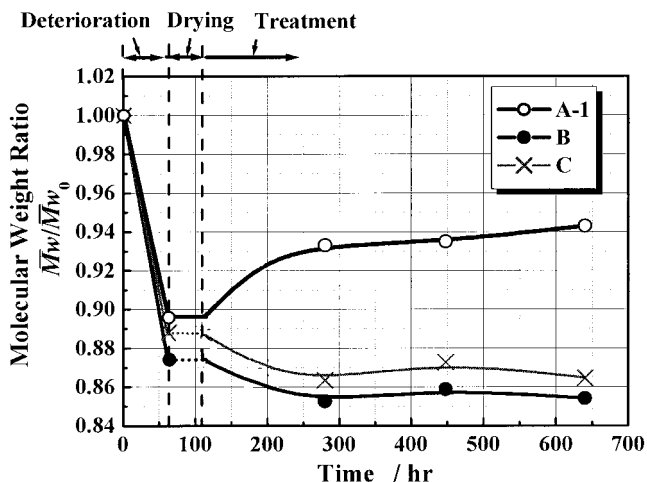


Figure 2 Change of the \bar{M}_w ratio by treatments.

Tensile strength and transparency (Exp.-2 and exp.-3)

To study the performance of the specimens after the treatment, the tensile strength as a mechanical strength and the transparency as a functional characteristics of the treated PC were measured. The tensile strength of the specimens used in Exp.-1 was measured, and the results are plotted in Figure 3. The initial strength was 75 MPa, and it dropped to 68 MPa after hydration. After drying, it recovered to 73.5 MPa, and the recovery rate was about 98%, as shown in Figure 3. The rate was much higher than that of the molecular weight, as shown in Figure 2. The reason is described in the next section.

Generally speaking, gel is recognized in deteriorated polymer by crosslinking or other side reactions. When an amount of gel that can be solved with good solvent is rich and hard, the gel can be recovered by filtration. But it is difficult to recover when the amount

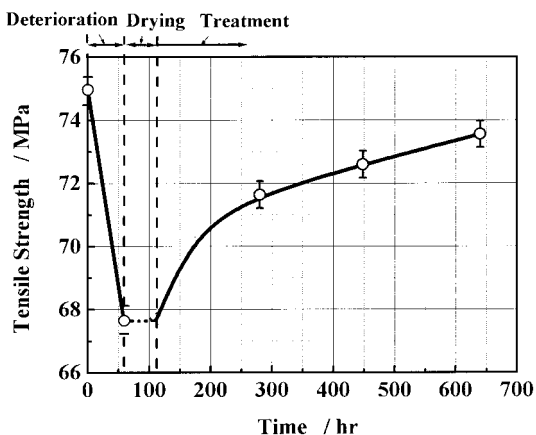


Figure 3 Decrease and increase of tensile strength by treatments.

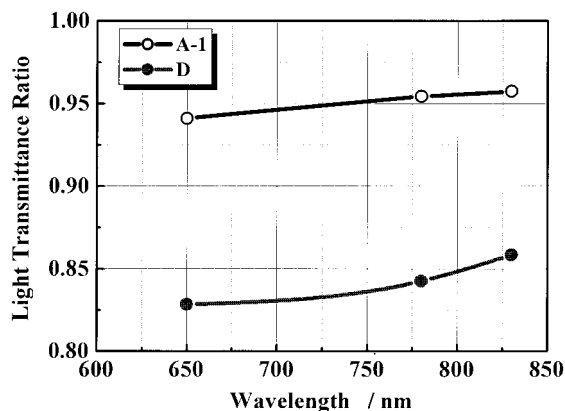


Figure 4 Decrease of light transmittance.

is small or the gel is soft. In that case, the transparency of the polymer is the better index of whether the gel is generated or not.

The transmittance ratios of the specimen A and D were measured and plotted in Figure 4. They were about 0.95 and 0.84 for A and D, respectively. Both specimens were colored to the same degrees. This meant that some irreversible reactions that caused gel formation occurred in specimen D, but an inverse reaction occurred in specimen A, thus contributing to the self-repairing effect.

Dependence of recovery rate of molecular weight on concentration of sodium carbonate (Exp.-4)

The results of Exp.-4, where the concentration of sodium carbonate were 0.1 to 10,000, are shown in Figure 5. The \bar{M}_w of A-1, which included 0.1 ppm of sodium carbonate, decreased 0.88 after 20 days. On the other hand, that of A-4 did not change. The \bar{M}_w were stable when the concentration of sodium carbonate was 100 to 1000; 10,000 ppm of sodium carbonate made the \bar{M}_w drop more rapidly than 0.1 ppm. The

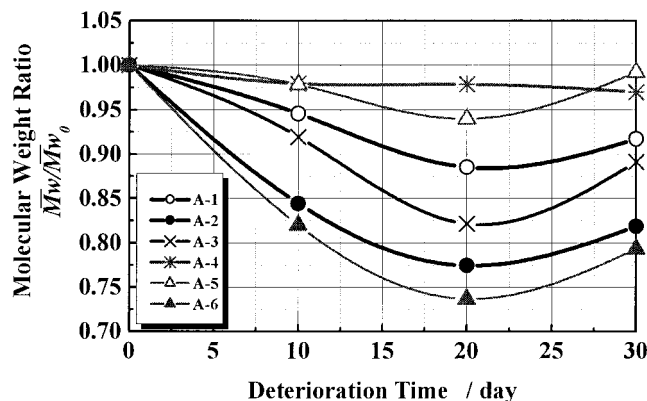


Figure 5 Change of the \bar{M}_w ratio as a function of treatment time.

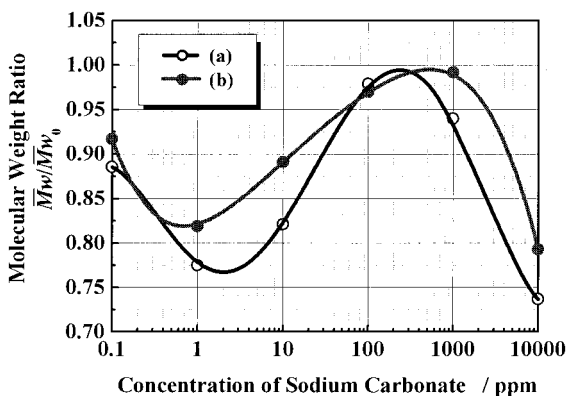


Figure 6 Changing of the \overline{M}_w ratio as a function of concentration of sodium carbonate [deterioration time = (a) 20 days, (b) 30 days].

A-4 specimen was transparent after 30 days and the gel was not recognized.

The shifts of the \overline{M}_w after 20 days and 30 days as a function of the concentration of sodium carbonate are plotted in Figure 6. The two curves were similar. They decreased first and subsequently rose with increasing of the concentration of sodium carbonate in the lower region. They reached about 1.0 between 200–600 ppm, and dropped in the higher region. There were probably at least two reactions in this case. One was the recombination of PC chain by which the \overline{M}_w increased with the adding of sodium carbonate. The other was the scission reactions such as the hydrolysis by sodium carbonate.

The reason why the molecular weight decreased with an increase of the concentration of sodium carbonate at 1 ppm or less was unclear. It was supposed that the decrease was not due to chemical reactions but to a physical cause such as the dispersion of sodium carbonate in PC. When the self-repairing reaction is designed, plural reactions tend to occur like equilibrium reactions at the polymer preparation. The complicated profiles of two curves in Figure 6 seem to be an example.

The infrared spectra of the specimen A-5 are shown in Figure 7. The peaks of 1230, 1370, 1390, and 1480 cm^{-1} were assigned $\nu(\text{C}=\text{O})$, $\delta_s(\text{CH}_3)$, $\delta_{as}(\text{CH}_3)$, $\delta_s(\text{CH}_2)$, and that of 1500, 1600, and 1770 cm^{-1} could be assigned as the stretching vibrations of the aromatic $\text{C}=\text{C}$ and $\nu(\text{C}=\text{O})$. The wave number and the strength did not change. The peak at 2962 cm^{-1} that was assigned as $\nu_{as,s}(\text{CH}_3)$ decreased.^{15,16} It suggested that isopropylidene group changed to another structure, and that the group reacted with another chain and generated crosslinking or degraded into smaller compounds. As the gel was not observed in this experiment, the crosslinking reaction did not occur.

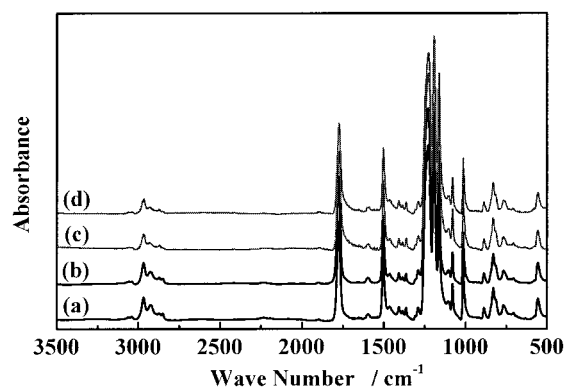


Figure 7 IR spectrum of specimen A-4 [deterioration time = (a) 0 day, (b) 10 days, (c) 20 days, (d) 30 days] (Exp.-2).

DISCUSSION

Thermal and humidity deterioration

The polymer chain, which is composed of hetero atoms such as oxygen, nitrogen, and phosphorous, is hydrolyzed by solvolysis of water and ammonia. When a detail description is required, the conditions, acid or alkaline, should be observed. The additive of proton occurs first, and the addition of water follows in the acidic condition. On the other hand, the OH ion adds a carbonyl carbon and the scission of the ester bond follows under the alkaline. Many articles have reported such hydrolysis,^{17–19} light stability,^{20,21} and thermal degradation in the past.^{22–24}

The other deterioration is thermal degradation. The degradation routes can be divided into two major paths (Figure 8). One is a direct scission of carbonate, and the other is the elimination of a hydrogen atom from isopropylidene group.²⁵

The Fries transfer reaction is famous, as one of the PC degradation paths that is observed under a strong light such as ultraviolet exposure. The thermal degradation and hydrolysis after the Fries transfer reaction have been not elucidated. The subsequent degradation of the structure after the Fries transfer is supposed to be less than the decomposition of the carbonate on the original PC chain.

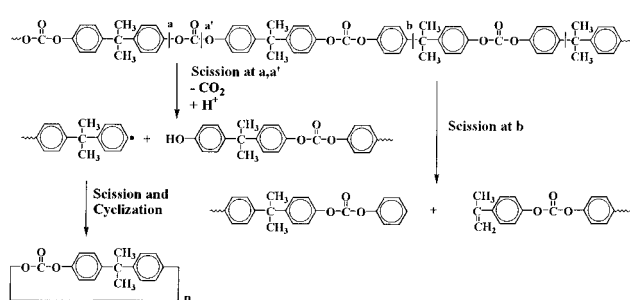


Figure 8 Thermal decomposition of PC in an inert atmosphere.

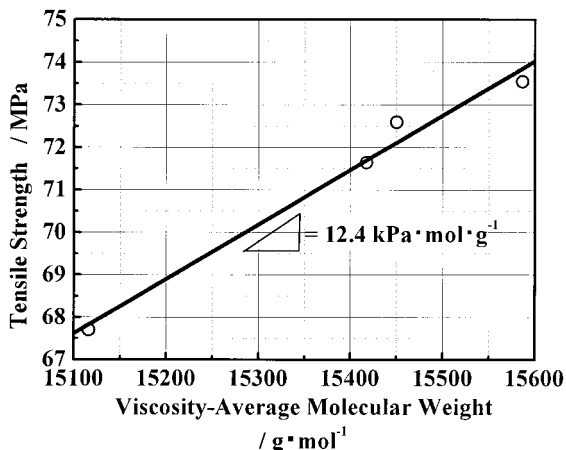


Figure 9 Tensile strength as a function of \bar{M}_v .

The major reaction of the scission chains in this study is considered to be the recombination of a phenyl and a phenolic ends after thermal or hydrolysis degradation from the above description. The results were unexpected, because the molecular weights of the PC would decrease with alkali. The detail reactions are not clear now.

Tensile strength and reaction of recombination

Tensile strength is one of the most important performances for the practical use of PC. If the fluidity is so large that high molecular PC could be easily processed, then the molecular weight must be designed to be much higher. However, the fluidity is severely controlled to shorten the processing and fabrication in the industrial field. The tensile strength of PC as a function of the molecular weight is plotted in Figure 9; 20,000 or more of the \bar{M}_v is required to manufacture excellent molding. The lower the molecular weight, the shorter the molding time, so the molecular weight of PC available in the market is generally low.

For example, the decrease of the molecular weight is remarkable at 50°C or more, and it leads to lose the toughness, which is the most advantage point of the PC.²⁶ The IZOD strength becomes 1/9 after the hydrolysis at 120°C. It is due to the gradient of the relationship between the tensile strength and the molecular weight. The gradient strongly depends on the \bar{M}_v in the lower region. The gradients are about 7 to 13 kPa · mol · g⁻¹ in the various regions as shown in Figure 10.

The tensile strength was observed to recover, as shown in Figure 3, whose recovery rate (98%) was higher than that of the \bar{M}_w (94%; Fig. 2). It was due to the nonlinear relation between molecular weight and tensile strength, as shown in Figure 10. The relation in Exp.-1 is plotted in Figure 9, and the gradient was 12 kPa · mol · g⁻¹.

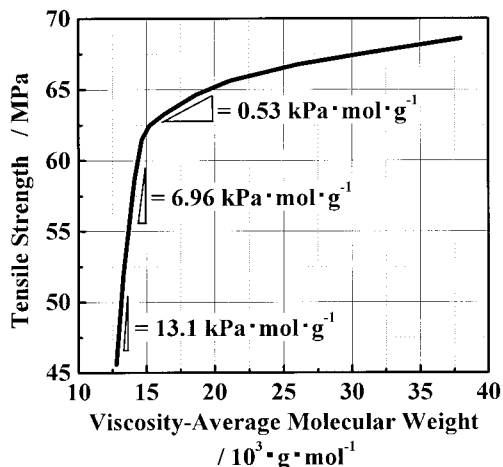


Figure 10 Dependence of \bar{M}_v on tensile strength of PC.

All of the reactions to restore the molecular weight was considered and depicted in Figure 11. As the molecular weight of PC whose ends were phenolic and phenyl groups was restored, the phenolic end generated by hydrolysis reacted with a phenyl end with sodium carbonate. A sodium phenoxide was probably eliminated from the chain because the slight smell of phenol was observed. The hydrolysis was simultaneously accelerated with sodium carbonate.

PC as a self-repairing material

The light stabilizer directly reacts with light before the light damages the materials. Therefore, the light stabilizer itself gradually deteriorates by changing its chemical structure and losing its function. Namely, the effect as a stabilizer decreases in proportion to the period of the use. The protection method using the additives that react with a deterioration factor is called

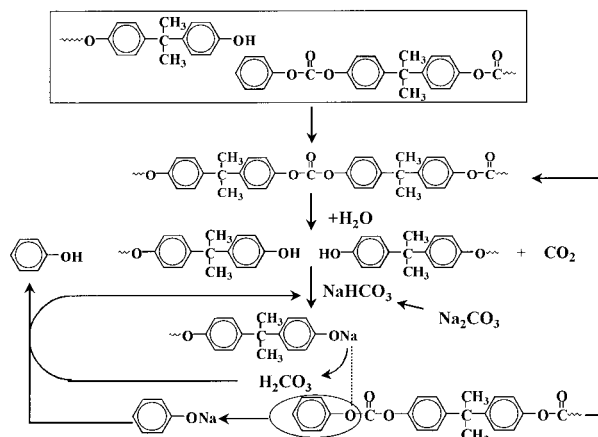


Figure 11 Deterioration and recovery reactions.

as "passive protection" in our group. A lot of research for the preparation of stronger materials has been conducted because the use of the additives is not desirable for industrial application of plastics to sophisticated goods in terms of safety and the effect on the environment.

On the other hand, a living body can be said to be composed of polymeric materials in a sense. The materials used there are generally weaker than those made by mankind because a living body can use restricted materials that react with many chemicals at room temperature. The life span, however, is longer than that of man-made materials. For example, the life span of human beings is about 80 years, and there are some trees that live for 1000 years or more. The reason why a living body has longer life than man-made goods is considered to be because the former can protect its body with a biological protection system such as metabolism. It is one of the excellent protection mechanism found in a living body, and can be called "self-repairing." The self-repairing reaction is called as "active protection," as opposed to the "passive protection" mentioned above. The authors have reported one of the examples in which the continuous self-repairing reaction can be observed in polyphenylene-ether (PPE), which includes a hydrogen donor and self-repairing agents.²⁷ The self-repairing reaction similar to the metabolic reaction in a living body was observed in the case of PPE.

Similar materials have been already developed, and are called "intelligent materials." However, they have mechanisms that react against the stimulus under different circumstances. The concept of "stimulus-answer" is different from that of "passive and active." The production of melamine in melanocyte under the skin is the typical example of passive protection and stimulus-answer, and the repaired system of thymine dimmer with several enzymes is that of the active protection and no-stimulus response. Both have the same purpose to protect DNA from ultraviolet light.

The data obtained in this study were not sufficient for the construction of the self-repairing or active protection materials. But we consider that PC is one of the most prominent polymers that shows the repairing phenomena.

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