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Mechanisms of Hydrogen Evolution and Stabilization of UV-Cured Urethane Acrylate Resin for Coating of Optical Fiber

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ABSTRACT

The mechanism of hydrogen evolution from UV-cured urethane acrylate resin for coating optical fiber was studied using electron spin resonance (ESR) and infrared spectroscopy (IR). The origin of the evolution of hydrogen was presumed to be the thermal oxidation of polyalkyleneglycol chains formed by the photo-degradation of the urethane bond in the resin. The evolution of hydrogen was inhibited by addition of a hindered amine light stabilizer or of a sulfur-containing antioxidant. The stabilization mechanisms of these inhibitors were also studied.

INTRODUCTION

It has been pointed out that hydrogen from the coating materials causes a significant increase in the attenuation of optical fibers in the wavelength region of a near infrared laser beam.[1]

The optical loss derived from hydrogen evolution from coating materials was regarded as being due to absorption of the laser light by Si—OH bonds formed by the reaction of hydrogen with quartz fiber.[2] Recently, instead of thermally curable silicone resin, UV-curable urethane acrylate resin has been widely used as the coating material of optical fibers. However, hydrogen evolution from urethane acrylates has also been reported.[3]

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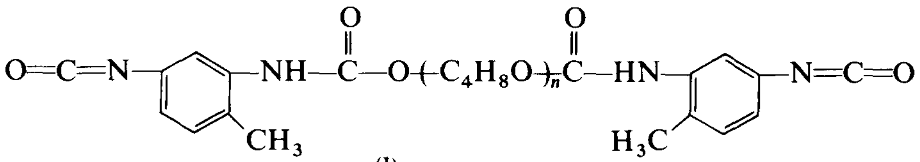
To ensure long life of optical fiber, an accelerated test for hydrogen evolution from the coating materials at elevated temperature has been carried out by the manufacturers of both optical fibers and UV-curable resins. In this present work, the origin and the mechanism of hydrogen evolution from the urethane acrylate resin during the acceleration test were investigated and the effectiveness and the mechanism of inhibition were also studied.

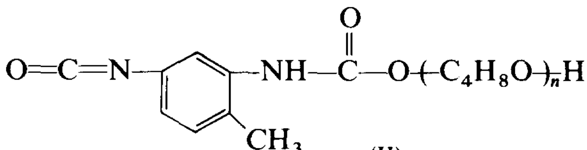
EXPERIMENTAL

Materials

The prepolymer was prepared by a standard synthetic method,[4] from polytetramethyleneglycol (PTMG), toluenediisocyanate (TDI) and 2-hydroxyethylacrylate (HEA). Model compounds with partial structure of the urethane acrylate resin, TDI-PTMG-TDI (I), TDI-PTMG (II) and TDI-HEA (III), were also synthesized from the calculated amount of TDI, PTMG and HEA.



(I)



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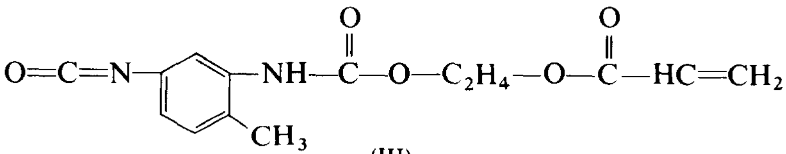

(III)

A commercial grade of reactive monomer, of the acrylic ester type, was used without purification. A sulfur-containing photo-sensitive initiator (commercial grade) was used without purification. The weight composition of the UV curable resin was as follows: prepolymer (50), reactive monomer (50), photo-sensitive initiator (3). The resin was cured by irradiation with a metal-halide lamp (1 J/cm^2), of the resin coated on a glass plate (thickness, 250 ± 50 μ). The hindered amine light stabilizer, bis(2,2,6,6-tetramethyl-4-piperidinyl)-sebacate (770) (Ciba-Geigy Ltd) and the sulfur-containing antioxidant, dilauryl-3,3-thiodipropionate (TPL) (manufactured by this company) were used without purification.

Quantitative analysis of hydrogen

The sample (1 g) was placed in a headspace bottle (Gasukuro Kougyou Ltd, inner volume, 100 ml) and heated at 150°C for 3 h. After the bottle was cooled to ambient temperature, 1 ml of the gas in the bottle was injected into a Shimazu GC-9A gas chromatograph equipped with a thermal conductivity detector. A molecular sieve 13X column (3 mm i.d., 6 m long, 80–100 mesh) was used with argon (40 ml/min) as carrier gas. The oven was operated isothermally at 40°C. The hydrogen concentration was determined by an external reference method.

Photo-degradation of prepolymer and thermal oxidation of PTMG

Prepolymer was held between crystal plates 20 cm from a light source, an Ushio super high pressure mercury lamp, and was irradiated at ambient temperature. Changes in the IR spectra were recorded using a JASCO model A-3 instrument. The PTMG was heated in air at 120°C and the IR spectra recorded at 2-hourly intervals (25 μm film thickness).

Measurement of electron spin resonance (ESR)

ESR spectra were measured on a JEOL FE-2XG X-band ESR spectrometer after irradiation of the samples with an Ushio super high pressure mercury lamp at -150°C. The spectra of the resin films were measured by fixing the films around the sample tube.

Measurement of chemiluminescence

The UV-cured resin (10 mm^2) was temperature programmed under flowing air (20°C/min from ambient temperature to 120°C and held for 30 min) and the chemiluminescence intensity at each temperature was recorded on a chemiluminescence photometer (Tohoku Densi Sangyou Model CX-7-TC).

RESULTS AND DISCUSSION

Origin of hydrogen evolved

Table 1 shows the amounts of hydrogen evolved from various samples heated at 150°C for 3 h. The following facts may be deduced:

TABLE 1
The Amounts of Evolved Hydrogen

Sample name	*Amount of hydrogen evolved* (*μl/g*)[a]
Urethane acrylate	
with irradiation[b]	121
without irradiation	<1
Reactive monomer	
with irradiation[b]	23
without irradiation	<1
Photo-sensitive initiator	<1
PTMG	650
HEA	<1
TDI-PTMG-TDI	<1
TDI-PTMG	190
TDI-HEA	<1

[a] Heating condition: 150°C, 3 h.

[b] Irradiation condition: metal-halide lamp, exposure 1 J/cm^2.

(a) Very little hydrogen is generated from the reactive monomer and the photo-sensitive initiator. The origin of the hydrogen is mainly from the urethane acrylate prepolymer.

(b) Irradiated urethane acrylate prepolymer evolves more hydrogen than unirradiated material, indicating that the light is involved in the mechanism of hydrogen evolution.

(c) While the amount of hydrogen evolved from HEA, TDI-HEA (III) or TDI-PTMG-TDI (I) is very small, from PTMG and TDI-PTMG (II) it is very large.

These results lead to the conclusion that hydrogen evolution from the UV-cured resin originates from thermal oxidation of the polyalkyleneglycol chain formed by the photo-scission of the urethane bond.

Photo-degradation of urethane acrylate

It is well known that polyurethanes are easily degraded by sunlight, especially when aromatic isocyanates have been used in their preparation.[5] The photo-sensitive properties of the urethane acrylates are believed to be similar to those of polyurethanes.

The photo-degradation process of the urethane acrylate was followed by the change in the IR spectrum during irradiation by a mercury lamp. The time dependence of the change in the absorbance at 1520 cm^{-1}, a band specific to the amine group, is shown in Fig. 1.

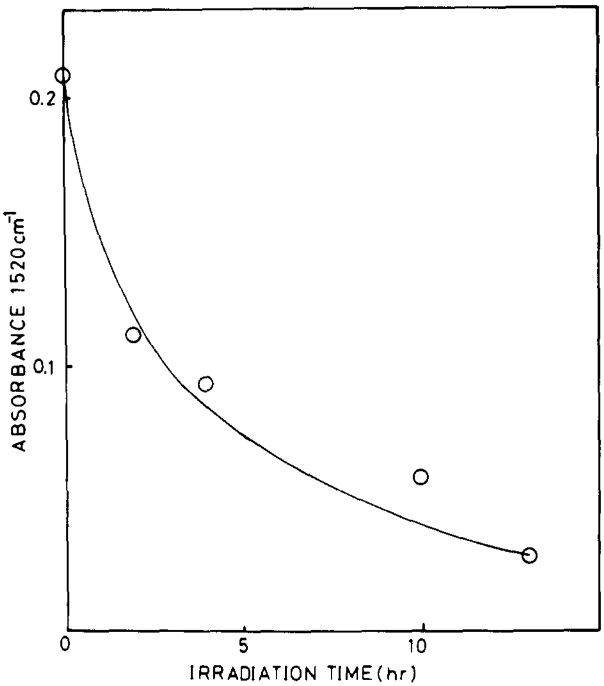

Fig. 1. Time dependence of the change in the IR absorbance of the urethane acrylate at 1520 cm^{-1}. The absorbances were measured from a tangent baseline.

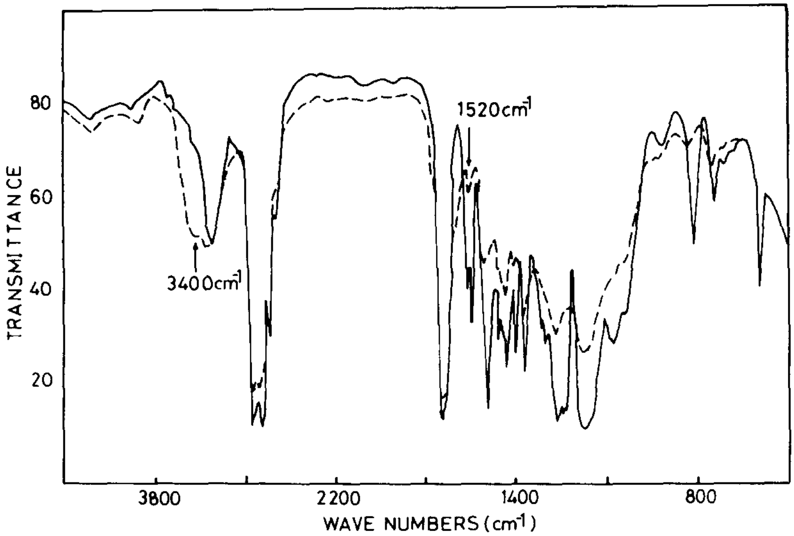

Fig. 2. The IR spectrum of urethane acrylate, before (——) and after (- - -) irradiation (10 h).

As expected, urethane acrylate was rapidly degraded by light. Figure 2 shows its IR spectrum before and after irradiation. After irradiation, a band specific to the hydroxyl group appeared at 3400 cm^{-1}.

Thermal oxidation of the alkyleneglycol chain

The PTMG was chosen as a model compound to examine the thermal oxidation of alkyleneglycol. Figure 3 shows the change with time of the IR absorption of the carbonyl group at 1720cm^{-1}, and the amount of hydrogen evolved from PTMG at 120°C. Both the absorbance of the carbonyl group and the amount of hydrogen evolved increase with heating time, which indicates that the hydrogen generated arises from thermal oxidation of PTMG. These results are very much in agreement with the data in Table 1. Thus, it seems reasonable to conclude that the mechanism of hydrogen generation from UV-cured resin is as follows. The urethane bond in the urethane acrylate is partially degraded by UV light during the curing process of the resin to form a polyalkyleneglycol chain, which evolves hydrogen as a result of thermal oxidation.

Stabilization effect of additives

Two stabilizers with different functions were separately added to the resin, namely, light stabilizer 770 and antioxidant TPL. Films of the cured resin containing these additives were kept under sunlight for 1 week.

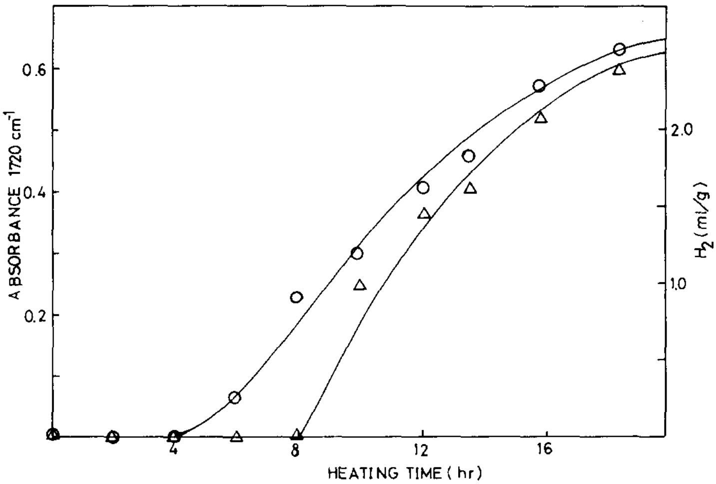

Fig. 3. Change with time of the IR absorbance at 1720 cm^{-1} and the amount of hydrogen evolved from PTMG. ○, IR absorbance; △, amount of hydrogen evolved. The absorbances were measured from a tangent baseline.

TABLE 2
The Amounts of Hydrogen Evolved from Films Containing Various Amounts of Additives[a]

Type and concentration of additives	*Amounts of hydrogen evolved* (μl/g)[b]
No additive	125·0
Hindered amine light stabilizer, 770	
0·1%	56·7
0·5%	17·9
1·0%	6·5
Sulfur-containing additive, TPL	
0·1%	85·2
0·5%	16·1
1·0%	5·6

[a] Irradiation condition: sunlight for 1 week.
[b] Heating condition: 150°C, 3 h.

Table 2 shows the volume of hydrogen evolved from samples containing various amounts of additives. Only the addition of 0·5% of both 770 and TPL was effective in inhibiting the generation of hydrogen (Table 2). These results were similar to those reported by Chan *et al.* and Okagawa *et al.*[6,7]

Mechanisms of stabilization by additives

To clarify the individual functions of the additives, ESR was applied to the detection of the radicals formed by photo-scission of urethane bonds and chemiluminescence measurements to evaluate the degree of thermal oxidation (amount of hydroperoxide involved).

The ESR spectra, measured at −150°C after irradiation by a mercury lamp, are shown in Fig. 4. There was no difference between the spectra of the additive-free sample and that containing TPL, while the spectrum of the sample containing 770 is identical to that of a simulated nitroxyl radical spectrum.[8] This means that TPL played no role in the inhibition of photodegradation of the urethane bond.

The change in the ESR spectrum of the additive-free sample with temperature is shown in Fig. 5. The spectral pattern changes as the temperature is raised, which means that various radicals are formed by light irradiation. This ESR spectral behavior is similar to that of polyurethane resin reported by Osawa and Nagashima.[9] The ESR spectrum when 770 was

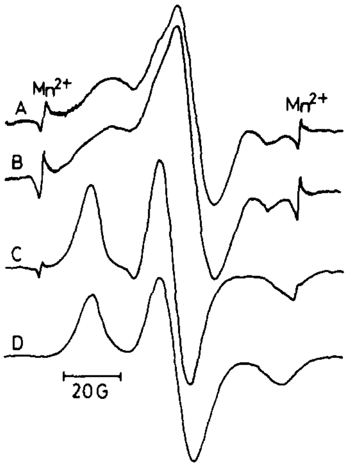

Fig. 4. The ESR spectra of films of cured resin containing additives. A, additive-free; B, 1% of TPL; C, 1% of 770; D, simulated spectrum of nitroxyl radical, simulation parameters Ax = 7·6G, Ay = 6·0G, Az = 31·8G, gx = 2·0088, gy = 2·0062, gz = 2·0027.

contained in the sample was assigned to a nitroxyl radical of 770, oriented in a disorderly fashion in the solid.

Peaks observed in the spectrum of the additive-free sample were not found in this spectrum, indicating that the nitroxyl radical of 770 acted as a radical scavenger in the UV-cured resin as it generally does in other types of resin.[10,11]

In order to evaluate the degree of thermal oxidation, the change in chemiluminescence intensity with temperature of the above samples was

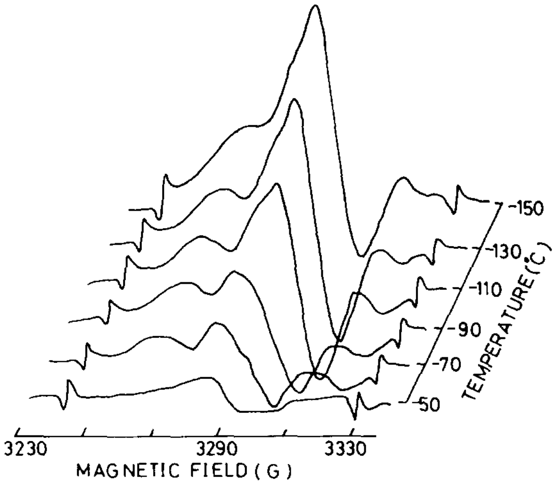

Fig. 5. Change with temperature of the ESR spectrum of additive-free film of cured resin.

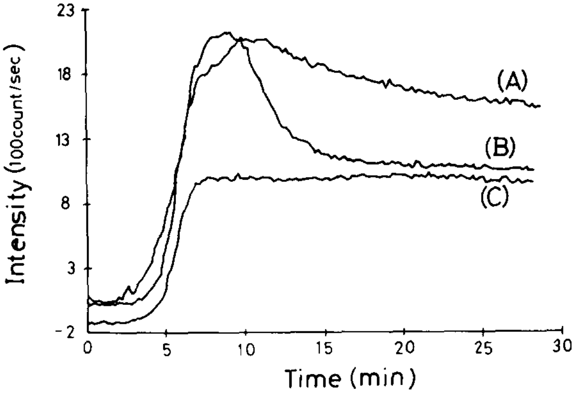

Fig. 6. Change in the chemiluminescence intensity of films of cured resin containing additives. A, additive-free; B, 1% TPL; C, 1% 770. Heating condition: 20°C/min from ambient temperature to 120°C and held for 30 min.

measured (Fig. 6). In the case of the additive-free sample (Fig. 6B), the intensity increased rapidly up to 100°C and after the maximum intensity (120°C, held for 30 min) decreased slowly (Fig. 6A). Although the TPL-containing sample showed similar behavior, the subsequent decrease in intensity was much more rapid than that of the additive-free sample. The steep increase in intensity in the early stages of heating was not found for the sample containing 770 and a constant intensity was observed when the temperature was held at 120°C (Fig. 6C).

It is believed that the chemiluminescence intensity is proportional to the amount of carbonyl groups in the excited state, which are derived from the hydroperoxide.[12,13] Thus it is assumed that the intensity increment in the lower temperature region originates from the hydroperoxide formed by photo-scission of the urethane bond and in the higher temperature region from the hydroperoxide formed by thermal oxidation of the resin.

Although 770 and TPL both inhibit the formation of hydroperoxide, their functions are quite different, and assumed to be as follows; 770 inhibits the initial formation of photo-derived hydroperoxide, and TPL, which has been known to be a hydroperoxide decomposer,[14] decomposes the hydroperoxide formed by photo-degradation and thermal oxidation.

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