Mechanical Properties of Acrylate Networks Formed by Visible Laser-Induced Polymerization. 2. Control of the Mechanical Properties[†]

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The mechanical properties of some acrylate networks formed by visible laser-induced polymerization were studied as a function of the initial molecular composition of the reacting mixture. The study included, besides some changes in the monomer composition, the influence of the acidity of the medium when ionizable dyes were used as photoinitiators. It was also shown that the mechanical strength of the network polymers can be significantly improved by the addition of inorganic fillers which have been surface treated with silane coupling agents containing polymerizable groups or by adding to the multifunctional acrylate monomers a solution containing a stronger preformed polymer. It was further observed that some of the physical properties of the parts formed may be anisotropic depending on the direction of laser scanning for photopolymer formation. The work also describes different attempts to obtain an elastomeric material by copolymerizing a flexible acrylated oligomer with the networking monomers.

Introduction

Photopolymerization of acrylic monomers has been used for many years in many different industrial applications.[1] Most of the time liquid monomers and oligomers are mixed with photoinitiators and co-initiators and a solid, network polymer structure is rapidly formed upon irradiation. In the majority of present industrial applications UV light sources are used, but recently visible light photoinitiators have been developed and these have started sharing the market for specific uses.[2]

In particular, a series of fluorone dyes together with amines as co-initiators have been found to be efficient free-radical initiators for the polymerization of double-bond-containing monomers, including acrylic, vinylic, and allylic double bond systems.[3] The initiation mechanism for these photopolymerizations has been carefully studied in many cases and involves, after dye excitation and intersystem crossing to the triplet state, electron donation from the amine co-initiator to the dye, and deprotonation of the amine cation radical to form a neutral free-radical species. The equations below, where M_1 represents the double-bond-containing monomer, describe the elementary steps involved:

$$\text{dye}\ (S_0) \rightarrow \text{dye*}\ (S_1) \qquad (1)$$

$$\text{dye*}\ (S_1) \rightarrow \text{dye*}\ (T_1) \qquad (2)$$

$$\text{dye*}\ (T_1) + \text{amine} \rightarrow \text{dye}^{\bullet -} + \text{amine}^{\bullet +} \qquad (3)$$

$$\text{amine}^{\bullet +} \rightarrow H^+ + \text{amine}^{\bullet} \qquad (4)$$

$$\text{amine}^{\bullet} + M_1 \rightarrow \text{polymer} \qquad (5)$$

To tailor photopolymers for different applications, we have recently tried to obtain a better understanding of the structure–polymer correlation in systems formed by visible photoinitiation. Prior to that, however, it was also necessary to understand how photopolymerization parameters affect photopolymer properties, and this was the subject of a previous report.[4]

The present work is aimed at testing how the mechanical properties of photopolymers are affected by structural modifications in the network. Most of these correlations have already been established by (nonphotochemical) purely thermal or thermochemical methods. Therefore, what is really being sought is to understand how some well-known experimental observations of "traditional" (thermal) polymer science can be efficiently adapted to applications involving photopolymerization procedures and techniques.

Among the various structural modifying factors tested were (a) the presence of peroxides in the monomer mixture, (b) the amount and type of diacrylate oligomer added to the initial multifunctional acrylates mixture, (c) the case of ionizable dyes, which depends on the initial acidity of the medium, (d) the presence of micron-size inorganic fillers the surface of which had, or had

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not, been treated with silane coupling agents containing polymerizable groups, such as vinyl or methacrylic, (e) the inclusion in the acrylate mixture of a solution containing a linear polymer, such as nylon 6,6, which is stronger (especially as measured by the tensile strength, σ, and Young's modulus, Y) than the network formed by the acrylates used. It was also observed that the parts formed may be physically anisotropic, depending on the scanning direction of the laser beam.

Experimental Section

Materials. The monomers and oligomers used were (a) poly(ethylene glycol-400), diacrylated, PEGA-400 (from Monomer-Polymer Laboratories, Inc.), (b) trimethylol propane triacrylate, TMPTA (Saret 357, from Sartomer Co.), (c) dipentaerythritol pentaacrylate, DPHPA (Sartomer 399, from Sartomer Co.), (d) poly(butadiene diacrylate), PBUA (from Scientific Polymer Products Inc.), (e) acrylated aliphatic urethane, PUA, with functionality 2 (from Monomer-Polymer Laboratories, Inc.). Monomer stabilizers were not removed because it has been observed that this generates an instability in the reaction mixture, with the polymerization starting before it is really intended. The measurements of mechanical properties of the materials is much more accurate if the monomers are used as received. The concentration of the monomers varied depending on the experiment performed but the composition of the basic monomer mixture utilized consisted of, in weight percent, PEGA (20), TMPTA (40), and DPHPA (40). Poly(hexamethylene adipamide), nylon 6,6, was purchased from the Aldrich Chemical Co. The peroxide used was also obtained from Aldrich. The fillers used included (a) siliconated fumed silica beads, CAB-O-SIL TS-720, from the CABOT Corp. The beads contained no polymerizable groups on the surfaces; (b) some 325-mesh ($\Phi < 45\ \mu$m) glass beads, surface treated with [3-(methacryloxy)propyl]trimethoxysilane, and (c) submicron-size aluminum silicate particles, surface treated with vinyltriethoxysilane; the last two items were supplied by Huls America Inc.

The main dye used as photoinitiator was a fluorone derivative (2,4-diiodo-6-butoxy-3-fluorone)[5] hereafter DIBF. Its concentration was varied from 5×10^{-4} to 1×10^{-3} M. Other dyes used in different experiments included the 2,4,5,7-tetraiodo (TIHF), the 2,7-di-*tert*-butyl (4,6-diiodo), (DBDIHF), and the 9-cyano (2,4,5,7-tetraiiodo), (CNTIHF, or NB, for new blue), fluorones. As co-initiators (electron donors in this case) the amines used were *N,N*-dimethyl-2,6-diisopropylaniline, DIDMA, from Carbolabs, Inc., and *N*-phenylglycine, NPG, from the Aldrich Chemical Co.

Sample Preparation. All the dyes (initiators) were dissolved in pure PEGA. When NPG was used as co-initiator, it was also added to pure PEGA, and the mixture of both solids in the oligomer was submitted to ultrasound for about 20 min. After this operation, the other multifunctional acrylates, TMPTA and DPHPA, were added to the system and the whole mixture submitted to ultrasound for 20 additional min. The mixture of these three monomers formed the basic standard recipe and will be henceforth referred to as STDR. When DIDMA was used as co-initiator, it was the last substance added to the to be reacted mixture, immediately before irradiation.

When other oligomers were incorporated, for example, PBUA and PUA, they were the last chemicals added to the basic STDR resin (unless if DIDMA was used as co-initiator). Special care was taken when PBUA was mixed with the acrylate monomers to assure homogeneity of the system immediately before irradiation. This precaution was taken because of the possibility of phase separation between the acrylates and PBUA. For studies of the influence of the acidity of the medium on the performance of ionizable dyes, a few drops of a 1.0 M solution of HCl in water were added to the STDR in order to obtain a final concentration of HCl around 10^{-2} M.

The inorganic fillers were also included at the final stage of sample preparation. Similar to what was described for the PBUA oligomer, special care was taken in providing a macroscopically homogeneous mixture by thoroughly stirring the monomers and fillers right before the photopolymerization.

Nylon 6,6 was added to the basic monomer mixture as a solution in methanol which also contained KCl and $CaCl_2$. The final concentration of Nylon in solution was estimated to be about 30%.

The photoreactive mixture was poured into dog-bone-shaped Teflon molds, 2.0 mm deep, 6.0 mm wide, with a gauge length of 70.0 mm and a total length of 150.0 mm. These dimensions do not strictly follow the specifications of the ASTM-D638-82a norm, but they are certainly suitable for comparison of the relative mechanical strength of the photopolymers formed under the small changes in composition studied.

The irradiation was carried out in air. An Ar^+ laser (Omnichrome, Model 543-200 MGS) was used as the radiation source. The laser beam was directed toward the sample by mirrors positioned above the Teflon molds. These mirrors were controlled by $x-y$ scanners (DX series servo controller, from General Scanning, Inc.) to form the dog-bone-shaped parts. The mirrors were driven by digitized computer data from a special file initially designed to generate a solid cube. If the z (vertical) transition is neglected, the file just controls the laser beam to generate a square. The file scale option was appropriately modified to span a little more than 200.0 × 200.0 mm square region, large enough to include all the dog-bone-shaped molds with the photosensitive mixtures. The laser power varied from 30.0 to 125.0 mW. The beam diameter was typically 2.0 mm. The speed control option of the file used was such that the laser beam was scanned over the samples at speeds between 1.3 and 13.0 mm/s. The laser beam was normally scanned parallel ($\parallel$) to the main (longer) axis of the dog-bone samples. For the studies of anisotropy a few samples were made with the main axis of the dog-bone Teflon molds rotated 90° with respect to the scanning direction. The mechanical and optical properties of such samples were determined and compared to the properties of the parallel scanned samples.

Mechanical Properties. Stress–strain tests were carried out at ambient temperature (typically 23 °C), with no strict humidity control, using the photopolymerized dog-bone-shaped samples prepared as described. The tests were performed using an L-500 instrument (Lloyd Instruments, Fareham, England), fitted with an NLC-500N load cell. The cross-head speed used was the slowest possible with this machine, 5.0 mm/s; the sample gauge length was 70.00 mm; and the width was 6.0 mm. In the case of the anisotropy studies both sets of samples were stress–strain tested in the direction of the longer axis of the dog bones.

This instrument was controlled by an MCM-4135T Goldstar PC booted with Lloyd's DAPMAT software. This analysis program allowed direct observation of the load versus elongation behavior of the sample during the tests. After the test ended, it also automatically displayed various physical parameters of interest, including stress at break (N mm^{-2}) and elongation at break, (absolute, in millimeters, and relative in percent), maximum load (N), work performed (N mm), and Young's modulus of elasticity (N mm^{-2}), among others.

Results and Discussion

Physical Anisotropy from Unidirectional Laser Scanning. As has been previously remarked, most of the samples were polymerized under scanning conditions such that the laser beam moved parallel to the longer axis of the dog-bone-shaped molds. Due to the partial bleaching of the dye photoinitiator present, the samples formed are quite clear with a light yellow tone. After they are formed, with the particular parallel

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[5] Shi, J.; Neckers, D. C. US Pat. Appl., May 20, 1991.

Table 1. Mechanical Properties of Photopolymers Made with the Standard Resin (STDR) Scanning the Laser either Parallel (∥) or Perpendicular (⊥) to the Main Axis of the Sample[a]

	σ (N mm^{-2})	Y (N mm^{-2})
parallel (∥) scanned samples	8.8	222.0
perpendicularly scanned sample (⊥)	5.0	232.0

[a] Dye DIBF at 5×10^{-4} M, DIDMA at 0.05 M; Ar$^+$ laser (514.5 nm): PI = 40.0 mW, Φ = 2.0 mm, scan rate = 9.0 mm/s.

scanning (∥) described above, it is macroscopically apparent that the samples are optically anisotropic: long, channel-like patterns are observed in the direction of the laser scanning. This optical anisotropy was easily checked by observing the sample under a polarizing microscope. Considerable increase in light transmitted was observed when both polarizers were set in the same direction as the laser beam was scanned.

The presence of optical anisotropy suggested a microscopic structural difference in the network due to the single scanning direction. This should also be evident in other physical characteristics of the samples, including the mechanical properties. To further explore the consequences of the anisotropic scanning, some photopolymer samples were prepared with the dog-bone molds main axis at 90° (perpendicular) to the laser scanning direction. The mechanical properties of these samples were determined by the stress–strain test and compared with the mechanical properties of samples prepared by parallel scanning of the laser beam. Table 1 displays the results obtained for both these samples. The anisotropy in the mechanical properties is clearly evident from these data, with the parallel scanned samples being stronger than those formed by perpendicular scanning.

This anisotropic effect is certainly related to the laser scanning procedure. Using the CUBE 100.DAT file and with the scanning parameters chosen for the experiment, the center of the laser beam is shifted sideways by about 2.0 mm from one scan vector to the next. Since the beam is Gaussian and 2.0 mm in diameter, it is expected that a small region of the monomer mixture, located between two consecutive scan vectors, will be exposed to a relatively low laser intensity. It is therefore expected that the overall structure will be composed of stronger network "channels", with interspersed weaker channels. When scannings in the parallel direction the strong network channels will be formed along the dog-bone main axis. Figure 1 depicts what was just described.

During the stress–strain test, the "load-cell" will measure mainly the force to break networks formed in the same direction as the samples (which are about 70.0 mm long) are pulled. For the samples made by perpendicular scanning, the width of the weaker region will be basically the same as for the parallel scanning. However, there are two differences between them. The first is that for the perpendicular scanned samples the "stronger" network regions, are now only 6.0 mm long, the width of the dog-bones central region. The second difference is that since in the pulling test the samples are always strained in the direction of the main axis of the dog bone, the stress test measured two different structural characteristics depending on the sample tested. For the parallel scanned samples the stress–strain test measures the force to break the long (70.0 mm) network "channel" structures formed during or immediately after the laser scanning. For the perpendicular scanned samples the test is not measuring directly the strength of the network but rather the "adhesion" force between adjacent networks. It is expected that this region between scanning lines has a smaller degree of polymerization because of the lower laser intensity in this region. It is also apparent that part of the network formed in this intermediate region is not formed immediately after the laser beam scanning. It is formed slowly and sideways with respect to the laser scanning direction, due to diffusion of some of the monomer molecules to the network channels formed directly at the laser beam path. Since on the border of these network there still may be some macroradicals, the polymerization (networking) still proceeds slowly. The main message left from these observations is that an isotropic scanning procedure is necessary if physically isotropic samples are to be made. However, even with unidirectional scanning, the anisotropy can be significantly reduced if the scanning file is designed in such a way as to allow a larger overlap between two consecutive scanning beams. The drawback is an increase in the overall scanning time.

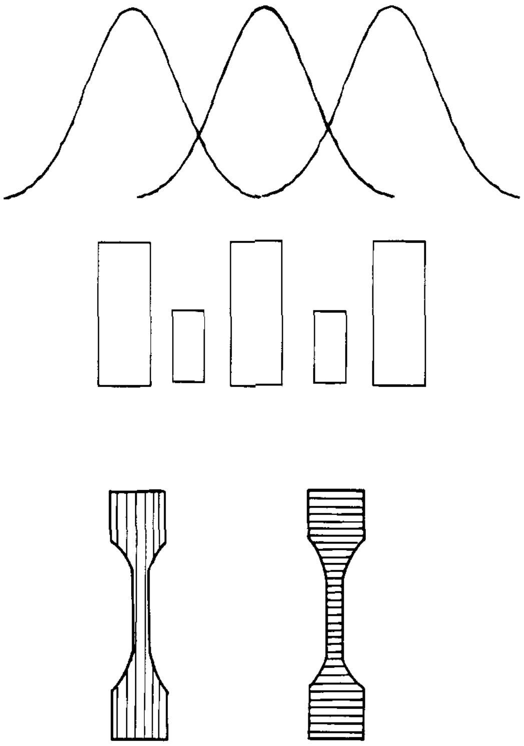

Figure 1. Diagrammatic representation of (a) the laser beam profile during three consecutive scanning vectors, (b) the relative laser intensity spatial distribution and the probability of polymer formation at these three scanning regions, and (c) direction of the laser vectors during the parallel and perpendicular scanning, relative to the dog-bone mold, for the physical anisotropy studies.

Mechanical Properties and the Acidity of the Medium. Although eqs 1–5 describe the basic mechanism of visible light-induced polymerization using fluorone dyes plus amine coinitiators, there are some structural features of the dyes which are not apparent from the equations. Figure 2a shows the general molecular structure of the fluorone dyes synthesized in our group. Table 2 displays the most common chemical

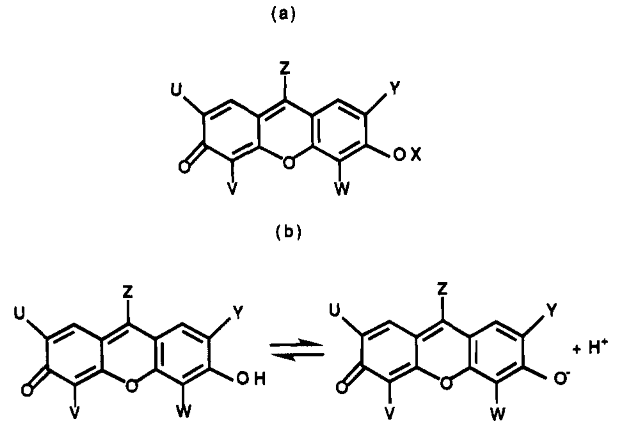

Figure 2. General structure of the fluorone dyes that can be used as visible photoinitiators of free-radical polymerization (a). Also shown is the equation establishing the equilibrium between the possible ionic and neutral forms of the ionizable dyes (b).

Table 2. Elements and Groups Corresponding to the Substituents in Each Position of the Fluorone Dyes General Structure Displayed in Figure 1a

U	V	W	X	Y	Z	dye acronym
H	H	H	H	H	H	HF
I	I	I	H	I	H	TIHF
I	I	I	H	I	CN	CNTIHF or NB
t-But	I	I	H	*t*-Bu	H	DBDIHF
I	I	H	C_2H_5	H	H	DIEF
I	I	H	C_4H_9	H	H	DIBF

Table 3. Mechanical Properties of Photopolymers Made with the Standard (STDR) Resin Using Different Ionizable Dyes and Changing the Acidity of the Medium

	σ (N mm^{-2})	Y (N mm^{-2})
TIHF[a]		
without HCl	3.0	132.4
with HCl	8.3	283.0
DBDIHF[a]		
without HCl	1.7	131.1
with HCl	2.1	150.4
NB[b]		
without HCl	0.6	7.3
with HCl	1.2	29.0

[a] Dye at 5 × 10^{-4}M, NPG at 0.05 M; Ar^+ laser (514.5 nm): PI = 50.0 mW, Φ = 2.0 mm, scan rate = 9.0 mm/s. [b] For the samples without HCl a HeNe laser (632.8 nm) was used at 35.0 mW, and for the samples with HCl an Ar^+ laser (514.5 nm), was used at the same power level; both lasers scanned at a rate of about 1.0 mm/s.

elements corresponding to each letter and the acronym used in each case. Particularly relevant to the discussion that follows is the atom or group represented by X. When X is hydrogen, as in TIHF, DBDIHF, and NB, the dye is ionizable since this H is a phenolic hydrogen. As a consequence, the dye may be present in a state of equilibrium between a neutral (protonated) and an anionic (unprotonated) form, as presented in Figure 2b. Equation 3 of the photopolymerization mechanism shows that an electron-transfer process occurs from the amine to the triplet excited state of the dye. It is obvious that the efficiency of this process is decreased if the acceptor is a negative ion.[6] The quantum yield of initiating radicals formed will decrease, and the overall polymerization rate will consequently decrease. We have previously reported the consequence of this decrease in the overall polymerization yield when comparing the mechanical properties of acrylate networks formed from the same monomer composition with different dyes.[4] TIHF and DBDIHF formed weaker materials than did DIEF, for example. Increasing the acidity of the system will increase the fraction of the dye molecules in the protonated neutral form. A thorough discussion of theoretical aspects of the influence of the state of ionization of the initiator on the polymerization process will be the subject of a separate report from our group.[7]

As would be anticipated, the mechanical properties of the polymers formed depend on the acidity of the medium. The standard monomer mixture (STDR) was used with different acidic dyes (TIHF, DBDIHF, and NB) as photoinitiators, in two sets of experiments. In the first series the mixture contained no added acid and in the second 1.0 M HCl was added to bring the final acid concentration to 0.01 M. The mechanical properties (Young's modulus and tensile strength) of the products were measured. Upon addition of the acid and homogenization of the system, the dye colors changed from the original orange (in the case of TIHF and DBDIHF) or blue (for NB) to red. These results are more apparent and quantitative if the spectra of the solutions before and after addition of HCl are compared. This is shown in Figure 3 where A, C, and E are the spectra of TIHF, DBDIHF, and NB, respectively, before the acid is added, and B, D, and F are the spectra of the same dyes in the monomer mixture with HCl at a concentration of roughly 10^{-2} M. A blue shift in all spectra, bringing the peak maxima close to 470 nm, occurs in all cases. This spectral feature seems to be a characteristic of all fluorone dyes in which the substituent Y is not a hydrogen.[3,5,8] For TIHF and DBDIHF this spectral shift does not necessitate a change of the excitation wavelength. More specifically, polymers are still formed using Ar^+ laser lines, the same source used before the acid was added. However, in the case of NB, as Figure 3F shows, the original band maximum at 648 nm almost entirely disappears and a new, broad absorption band appears in the 380–600 nm region. As a consequence, a HeNe laser, which emits at 632.8 nm, could not be used to initiate polymerization with NB in an acidic medium, and an Ar^+ laser had to be used instead. Table 3 displays the Young's modulus and tensile strength of polymers made with the above-mentioned ionizable dyes, in acidic and nonacidic media. The results clearly indicate that the dyes in a neutral form improve the overall polymerization process, as would be expected from the dependence of electron affinities of the dyes in their neutral and anionic forms. However, in addition to influencing the electron-transfer process, the acid may also participate in other steps that lead to the formation of free radicals. Evidence for such an effect comes from the work of Kotchetov and collaborators,[7] who observed a 20% increase in the total amount of C=C bonds disappearing when the polymerization was conducted in acidic media, even when a neutral dye was used as initiator. One possible explanation for this observation is that dye radical anions,

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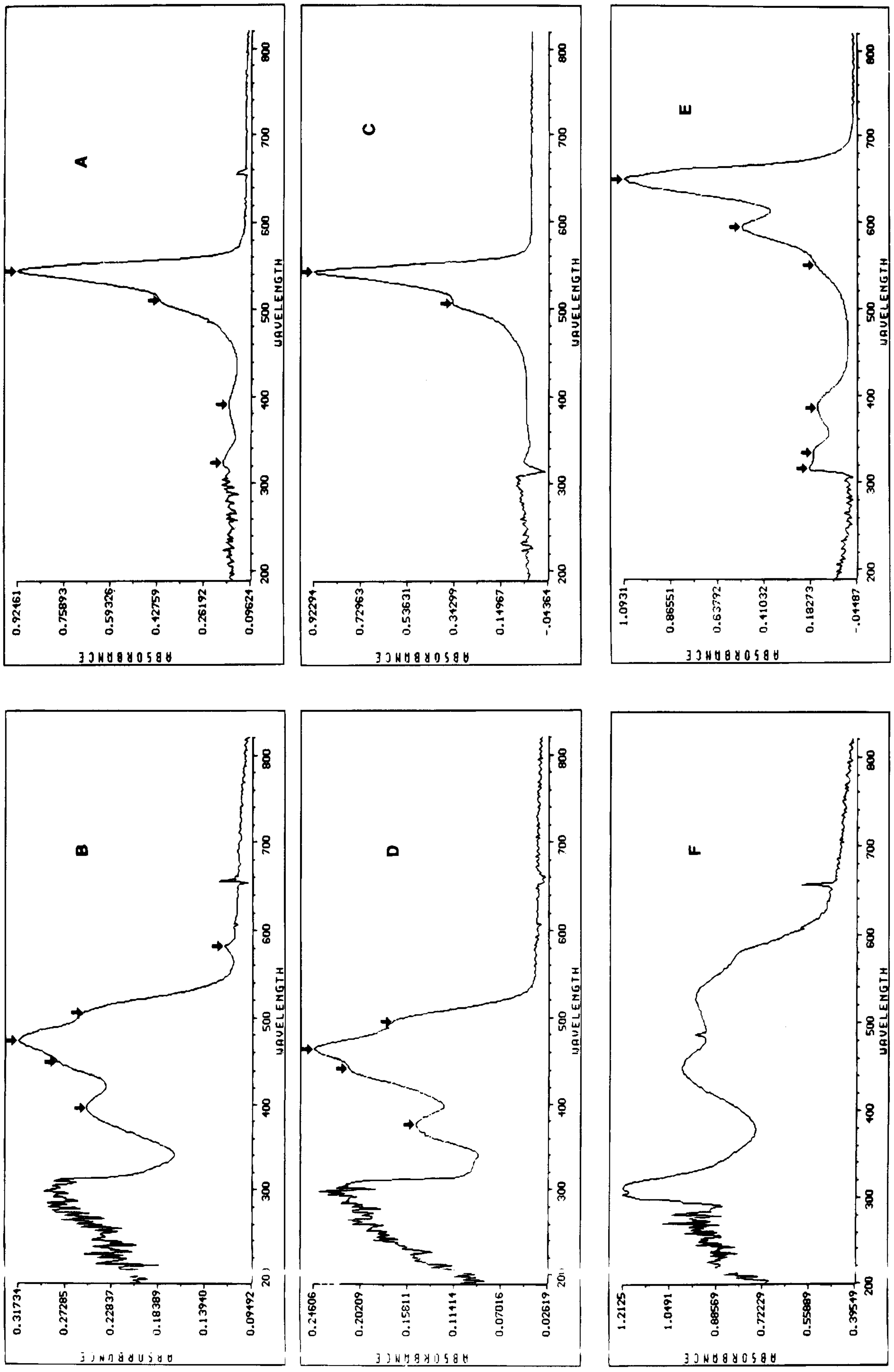

Figure 3. Spectra of the ionizable dyes TIFH, DBDIHF, and NB in a solution of the STDR, under acidic conditions (A, C, and E) and without any acid present (B, D, and F), respectively.

Table 4. Dependence of the Mechanical Properties of Photopolymers as a Function of the Type and Amount of Diacrylated Oligomer Used

	σ (N mm^{-2})	Y (N mm^{-2})
PBUA[a] (%)		
0	4.4	99.3
10	2.6	90.9
20	1.8	54.0
30	1.1	31.4
50	0.2	6.2
PEGA[b] (%)		
20	15.0	220.5
40	12.2	158.5
60	5.7	97.2
80	2.5	39.5
PUA[c] (%)		
0	3.8	65.7
10	4.4	73.7

[a] PBUA + STDR; DIBF: 5×10^{-4}M; DIDMA: 5×10^{-2} M; PI = 50.0 mW, Φ = 2.0 mm, scan rate = 13.5 mm/s. [b] PEGA (x/2) + TMPTA (x) + DPHPA (x); DIBF: 5×10^{-4}M; NPG: 5×10^{-2} M; PI = 100.0 mW, Φ = 2.0 mm, scan rate = 9.0 mm/s. [c] PUA + STDR; DIEF: 1×10^{-4} M, NPG: 5×10^{-2} M; PI = 70.0 mW, Φ = 2.0 mm, scan rate = 9.0 mm/s.

formed by photoelectron transfer, are destroyed by reaction with H$^+$. Equation 3b describes this process.

$$\text{dye}^- + \text{H}^+ \rightarrow \text{dye H} \qquad (3b)$$

Neutralization of the anionic dye radicals would inhibit their participation in deprotonation of the iminium radicals, formed from the co-initiators, to produce the neutral radicals which are probably the real initiators of growing polymer chains. It is also conceivable that neutral dye radicals add to monomers to start chains. However, we regard as more probable the hypothesis that very stable dye radicals participate in the process only as chain terminators.

Mechanical Properties and the Concentration of Diacrylated Oligomers. We have investigated the effect of varying the polyfunctionality in the prepolymer mix on properties of the products. One might anticipate that increasing the concentration of a diacrylate oligomer at the expense of tri- or pentaacrylated monomers have a deleterious effect on the mechanical properties of the products. Introduction of such an oligomer, with only two possible branching groups and separated by relatively long distances (much greater than the distance between the acrylic groups in TMPTA and DPHPA), will decrease cross-linking density. Cross-linking density is one of the major factors determining the mechanical strength of networked polymeric materials.[9] The effect of increasing the concentration of diacrylated oligomers on the mechanical properties of products formed under otherwise standard conditions is shown in Table 4. These results clearly indicate that the mechanical strength of the materials deteriorate as the relative amounts of diacrylated oligomers, as for PBUA and PEGA, is increased, in agreement with what is known for thermally or thermochemically made networks.[9,10] However, the results of Table 4 for the case of a diacrylated urethane oligomer, PUA, show a different trend, namely, an increase in both Young's modulus and tensile strength as the concentration of oligomer increases. This can be rationalized by the postulate that a second important factor is strong binding interaction between similarly constituted chains segments in the polymer molecules. The presence of polar groups, such as N—H and C═O, in the structure of the urethane oligomer, increases the possibility of interchain hydrogen bonding. In the case of PBUA the polymer chain is apolar and its conformation is mostly cis. These two factors work against any interchain or chain-to-monomer interaction. The dependence on both these factors has been observed in polymeric systems prepared by nonphotochemical procedures.[9-11] For the case of PEGA the fact that the polar groups are located in the main chain makes interchain interaction less likely, compared to polymers with polar side groups.

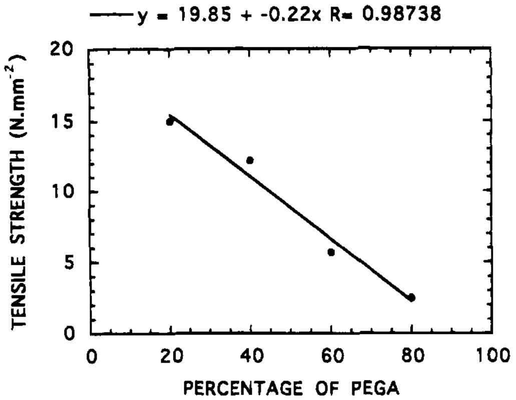

Figure 4. Stress-at-break of dog-bone parts made with the standard acrylate resin mixture, STDR, as a function of the amount of PEGA used.

The experimental error in measuring the mechanical properties of the dog-bone parts made depends on many factors. Some of these factors remain constant for different samples since they are mostly related to measurement techniques (thickness determination, stress—strain test procedure, etc.). It has been noted that error is also related to the homogeneity of the original reagent mixture; if the monomers and oligomers do not mix well, or worse, if they tend to phase separate, a larger spread in the mechanical properties, measurements is observed. Another observation is related to the specific properties measured: the Young's modulus tend always to be determined with greater precision than the tensile strength. Typical values for the standard deviation lie between 5 and 15% for the Young's modulus and 10 and 25% for the stress-at-break. These values are slightly higher for samples formed from less homogeneous mixtures or parts which end up visibly deformed (mainly due to high shrinkage) after the photopolymerization process.

Although we have no conceptual basis for development of a quantitative correlation between the chemical composition of the polymers and their mechanical properties, plots of both the stress-at-break (σ) and the Young's modulus against the percentage of PEGA, for example, show good linear relationships. This is depicted in Figures 4 and 5. It is also interesting to observe that the Young's modulus, which is measured with less error, has a much better linear correlation coefficient (r = 0.999) than the less precisely determined

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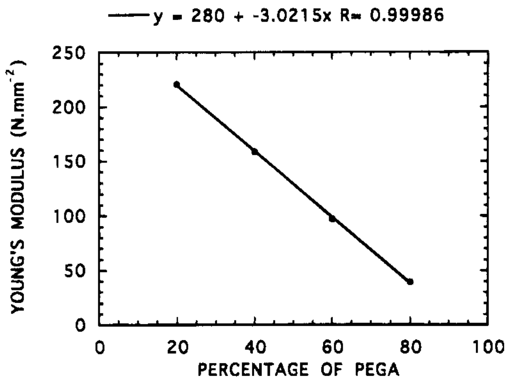

Figure 5. Young's modulus of elasticity of dog-bone parts made with the standard acrylate resin mixture, STDR, as a function of the amount of PEGA used.

Table 5. Dependence of the Mechanical Properties of a Photopolymer Containing a Diacrylate Oligomer as a Function of the Amount of Peroxide Dispersed in the Original Mixture[a]

LAUPEX (%)	σ (N mm^{-2})	Y (N mm^{-2})
0.0	1.1	30.0
0.5	2.0	68.2
1.0	3.5	135.7
1.0 $^{(2)}$	5.1	262.9

[a] PBUA (30%) + STDR + 2.5 wt % nonionic surfactants; DIBF (1.0×10^{-3} M), NPG (0.07 M); PI = 30.0 mW, $\Phi = 2.0$ mm, scan rate = 9.0 mm/s. [b] Ar$^+$ laser PI = 100.0 mW.

tensile strength ($r = 0.987$). It will remain at this stage as a mere observation, but more work will be performed to determine the extent of this correlation, with respect mainly to the concentration of monomers, oligomers, and fillers of different chemical structures.

Mechanical Properties and the Concentration of Peroxides. While the incorporation of an apolar and long-chain diacrylated polymer degrades the mechanical properties of a multifunctional acrylate matrix, probably by decreasing the cross-linking density, there are well-established other methods from polymer science to improve polymer properties. One such idea is the introduction of peroxides in the initial photoreactive mixture. Table 5 presents the Young's modulus of elasticity and tensile strength of acrylated networks containing fixed concentrations of a PBUA oligomer and different amounts of a peroxide. The results show that the mechanical properties of these network polymers can be substantially improved by the presence of organic peroxides in the original monomer mixture. Because oxy radicals formed from the thermolysis of peroxides are very reactive species, peroxides can be used as cross-linking agents in relatively inert polymers, especially polymers with saturated hydrocarbon-like structure. For example, dicumyl peroxide has been used to cross-link polyethylene.[12] Similarly one can use peroxides to cross-link unsaturated chains, such as those found in polybutadiene (PBU) based polymers. A typical mechanism for peroxide cross-linking involves hydrogen abstraction from the main PBU chain by an oxy radical, with consequent formation of a macroradical, and coupling of two radicals to produce interchain bonds. The final result is an increase in cross-linking density with substantial improvement in the mechanical strength, as observed in Table 5. Of course, to produce the effect, it is necessary that the peroxides decompose in the reaction mixture under irradiation of the Ar$^+$ laser. A mechanism to account for the effect of peroxides includes reaction with some of the intermediates as shown in the eqs 1–5 or directly with the amines in the mixtures.[13] Furthermore, since the polymerization is exothermic, some thermal homolysis of the peroxides may occur.

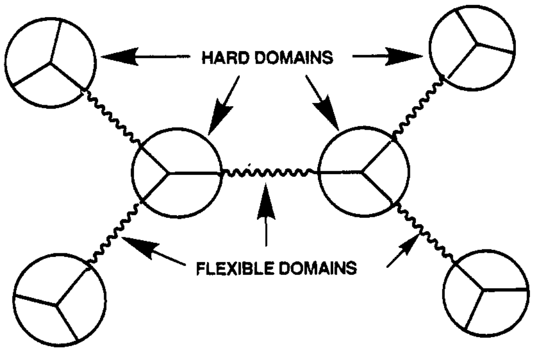

Figure 6. Ideal model of a possibly elastomeric structure formed between a small (and rigid) triacylate monomer and a flexible diacrylate oligomer.

Although incorporation of different types of peroxides has proven a possible way to reinforce some types of acrylated network matrices, this cannot be translated to manufacturing resins and industrial processing such as to reinforce the resins used in stereolithography. Though most peroxides have a very long (much greater than 100 h) half-life at ambient temperature, they still decompose under ambient conditions, though with a small decomposition rate. For industrial and other applications, long storage times of solutions containing peroxides may induce unacceptable prepolymerization and gelation. Consequently, other ways have to be devised in order to improve the mechanical properties of acrylated matrices made photochemically.

Since the presence of PBUA provided useful information on the effect of diacrylated species on the mechanical properties of acrylated networks, the original idea of including such oligomers in mixtures with small multifunctional acrylate molecules was directed toward obtaining flexible and elastic parts using stereolithography. Figure 6 displays the reasoning behind this idea. The cross-linked sites of the multifunctional acrylate monomers would behave similarly to the rigid domains of thermoplastic elastomers, such as the styrene–butadiene–styrene, SBS, triblock copolymers. The butadiene segments would provide the required flexibility and elasticity. Much to our initial surprise, the stress–strain testing of dog-bone samples containing 10, 20, 30, or even 50% of PBUA in the original reacting mixture did not show large elongation or even a "yield point". The explanation for these observations came from parallel studies on the percentage of acrylic double bonds (percent C=C) consumed by the photopolymerization reaction, determined by Fourier transform infrared spectroscopy, FTIR. The values of the percent C=C consumed for the mixtures studied under the photopolymerization conditions utilized, oscillated be-

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tween 28 and 36%.[14] In other words, it was apparent that most of the acrylic double bonds did not react. The conversion of acrylic C=C values was even lower when PBUA was added to the mixture. The significance of these results, as related to the preparation of flexible and elastic parts by photochemical stereolithography, is that, for most of the PBUA chains chemically included in the network, only one of the acrylic sites are bonded to other molecules. Many of them are not connected at all to other monomers or oligomers, and only very few of them have both sites connected to other reacting groups. Therefore, the molecular structure shown schematically in Figure 6 does not seem to be a good representation of the microscopic picture inside the acrylated matrix.

Mechanical Properties and the Presence of Fillers. Background in the formation of thermally made composites has also served as a guide to the production of reinforced photopolymers.[15] It has been determined that different types of fibers[16] and micron-size inorganic beads may function as additives to increase the strength properties of different types of polymers.[17] This is especially true if the reinforcing agent's surface has been treated with coupling agents, reagents containing polymerizable groups.[18] The most common coupling agents are methoxy-, ethoxy-, or chlorosilanes, and the polymerizable groups frequently encountered having acryloxy, methacryloxy, or vinyl moieties.[18] Although many aspects of the reinforcing process and the final bonding between the filler and the polymer matrix are still not fully understood,[19] it is normally accepted that the presence of the reactive groups containing double bonds is very effective in improving the bonding interaction between the filler and the matrix.[15-20] Since the fillers normally have mechanical properties (such as Young's modulus and tensile strength) much larger than those of the unfilled matrix, the addition of a filler with efficient coupling to the matrix will effectively add to the network the stronger mechanical characteristics of the filler.

The fillers used include (a) siliconated fumed silica beads (CAB-O-SIL HT-720), which have no coupling groups on the surface, (b) micron-size glass beads, o.d. < 45 μm, which have been surface treated with [(methacryloxy)propyl]trimethoxysilane, and (c) submicron-size aluminum silicate particles, which have been surface treated with vinyltriethoxysilane. The schematic representation of the chemical groups on the surface of the fillers is shown in Figure 7. Table 6 describes the monomers used with the different fillers, the polymerization conditions utilized, as well as the mechanical properties measured by stress−strain testing. The difference in the values of both σ and Y displayed in Table 6 for samples containing no fillers in the "glass beads" and in the "aluminum silicate" sections is due to the use of different scanning files when making the samples. However, the same scanning file was used to make samples with varying concentration of one particular filler. It is apparent from the results of Table 6 that the mechanical properties of the network formed with the particular monomers used are actually degraded by the presence of the CAB-O-SIL filler. Since silica has a higher Young's modulus and tensile strength than the unfilled acrylate matrix,[4,21] this result may indicate that the silica particles have not been ef-

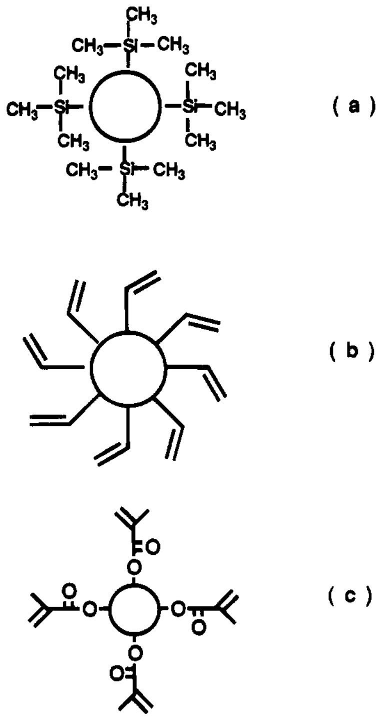

Figure 7. Schematic representation of three different types of surface treated fillers used to modify the photopolymers: Methylsilane-treated fumed silica (a), vinylsilane-treated aluminum silicate (b), and methacryloxysilane-treated glass beads (c).

Table 6. Modification of the Mechanical Properties of Photopolymers by the Addition of Inorganic Fillers

	σ (N mm^{-2})	Y (N mm^{-2})
CAB-O-SIL TS-720[a] (%)		
0.0	3.0	44.5
2.9	1.1	17.5
glass beads[b] (%)		
0.0	1.8	58.1
2.0	3.0	82.6
4.0	3.2	100.6
aluminum silicate[b] (%)		
0.0	0.5	19.0
2.0	1.4	57.6
4.0	2.2	111.4
9.0	5.5	243.0

[a] STDR; DIEF: 1×10^{-4} M; NPG: 0.05 M; PI = 100.0 mW, Φ = 2.0 mm, scan = 9.0 mm/s. [b] STDR + PBUA (30%, w); DIEF (1×10^{-3} M); NPG: 0.07 M; PI = 125.0 mW, Φ = 2.0 mm, scan = 9.0 mm/s.

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fectively "coupled" to the network. There are several possible explanations for this observation. First, the fact that the filler particles do not have active groups on their surfaces may preclude any significant modification of the properties of the acrylate polymers. Also, mainly because of the size of the particles and the different index of refraction compared to the monomers, the laser beam is highly scattered from the photoreactive mixture, thereby reducing the efficiency of the laser light in generating free radicals and inducing polymerization. The reinforcing mechanism of these fused silica particles in other types of polymers[22] is not expected to work with networks, because of the difference in molecular structure and morphology between the two structures.[9,22,23] With respect to the other two fillers, although some laser light may still be scattered by the fillers' particles, due to the difference in index of refraction, the presence of reactive double bonds on the fillers, surface seems to more than compensate for the decrease in laser efficiency, and the network is reinforced.

In principle, the observations encourage the view that there are different ways to strengthen photopolymers, give some notion on the magnitude of the effect that may be achieved, and provide preliminary information as to what fillers may be useful. The particle size also seems to play an important role in the final reinforcing process. Since methacrylic double bonds are more reactive than vinylic double bonds,[24] it would be expected that the glass beads should reinforce the polymer matrix more effectively than the aluminum silicate particles, contrary to what is experimentally observed.[25] This direct comparison is possible because the silicate and glass have comparable mechanical properties.

As mentioned before, one of our major interests is in application of the present results in stereolithography.[26] Although inorganic fillers, such as the glass and silicate beads, have proven to effectively reinforce some acrylate photopolymers, the direct application of these principles to make functional objects by stereolithography may face very tough barriers. A major problem is the partial sedimentation of the fillers, with consequent inhomogeneous distribution of material if the reactive mixture is left standing for long periods of time, which may occur in routine applications. A few possible ways to avoid this inhomogeneous distribution of fillers (or fibers) are being explored in parallel.[14] However, even with the present systems, model parts have been constructed by visible laser-induced stereolithography using prepolymer mixes containing up to 25% of glass fibers in the acrylate matrix.[27] New experiments are being performed to improve the density distribution throughout the polymer matrix.

Table 7. Reinforcement of the Photopolymers by the Addition of Other Polymers (Nylon 6,6)[a]

% nylon (est)	σ (N mm^{-2})	Y (N mm^{-2})
0.0	5.7	130.0
0.3	6.8	219.0
0.6	8.9	243.0
1.5	10.3	283.0

[a] STDR; DIBF at 5×10^{-4} M + NPG at 0.05 M; nylon 6,6 in solution of methanol + CaCl + KCl; Ar + laser at PI = 50.0 mW; scan rate = 13.0 mm/s.

Mechanical Properties and the Presence of a Solution of a Reinforcing Polymer. The last part of this paper presents a first attempt to significantly improve the mechanical properties of acrylate network polymers formed by stereolithography using a homogeneous solution of a polymer which is a strong fiber former in a liquid monomer dope. A similar experiment has been performed by Moussa and Decker.[28] However, in their experiment the photopolymerization of the multifunctional acrylates was carried out in a thin (15 μm thick) solid matrix of a linear and stronger polymer. In the experiments described below both the reinforcing polymer and the monomers are in a single liquid phase, and after irradiation the resulting material is a solid, with a semiinterpenetrating network structure.

The basic acrylate network polymer was formed from the same monomers used in the standard resin (STDR). As "reinforcing agent" poly(hexamethylene adipamide), nylon 6,6, was used. The nylon was first dissolved in a concentrated solution of calcium and magnesium chloride in methanol. The final concentration of nylon in the solution was estimated to be about 30%, from the weight of salts and solvent utilized. The initiator DIBF was used with DIDMA as co-initiator in solutions containing different concentrations of nylon. Table 7 shows the measured properties as well as the photopolymerization conditions and initial mixture composition. Nylon 6,6 is obviously an active reinforcement for the acrylate polymers.

Nylons are known to have high Young's modulus and very high tensile strength, properties attributed to hydrogen bonding between amide moieties in different chains. As a matter of fact, compared to some of the most common natural and synthetic materials, nylon 6,6 has the highest tensile strength per density ratio.[21] Therefore, there may be applications where the use of nylon 6,6 will provide an effective way to improve the mechanical properties of the network. The fate of the methanol after the photopolymerization process is not clear, though the sample is quite "dry" with no excessive liquid on its surface or slowly diffusing from inside. Because of the small amount of solution used, the methanol present does not represent a major impediment in using this system as a reinforcing agent. The initial acrylate monomers plus nylon−methanol solution mixture is homogeneous and so are the dog-bone samples formed. The results represent a first step toward the goal of using a homogeneous polymer reinforcing system in photopolymerization.

Conclusions

We have studied various aspects of visible light-induced polymerization to form acrylate polymers. The

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results can be logically related to mechanistic aspects of the polymerization steps, as well as to the control of the mechanical properties of the materials formed. It was shown that when some of the fluorone dyes are protonated, they are more efficient as initiators than when they are present in their anionic forms. It was also shown that the network polymers can be reinforced by a number of methods, including the use of inorganic fillers or solutions of polymers which are themselves strong fiber formers, such as nylon. Although these methods can be effectively used to improve the mechanical properties of the networks, some of them may not be appropriate to be used in stereolithography because of possible inhomogeneities in the system. The problem of separation of two-phase systems can be obviated by use of soluble reinforcing polymers, such as nylon, and additional ways of alleviating the problems due to sedimentation of the reinforcing agent are currently being explored.

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