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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. The work also describes different attempts to obtain an elastomeric material by copolymerizing a flexible acrylated oligomer with the networking monomers.

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Mechanical Properties of Acrylate Networks Formed
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by

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Prepared for RadTech

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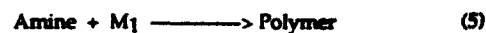
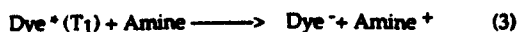
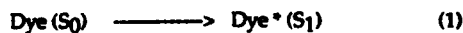
Abstract:

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 performed polymer. 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 a UV-light source is 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 have been utilized, together with amine co-initiators, as efficient free-radical sources for the polymerization of double-bond containing monomers, including acrylic, vinylic, and allylic double bond systems [3]. The initiator mechanism for these photopolymerizations has been carefully studied in many cases and involves, after dye excitation and intersystem crossing to the triplet state, an electron donation from the amine co-initiator to the dye, and rearrangement by deprotonation of the amine cation-radical to form a neutral free-radical species. The equations below describe the elementary steps involved.



where M_1 represents the double bond containing monomer.

In order 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 tests how the mechanical properties of photopolymers are affected by structural modifications in the network. Most of these correlations have already been established by (non-photochemical) thermal or thermochemical methods. Therefore, what is really being sought is to understand how the basic principles of "traditional" (thermal) polymer science can be efficiently adapted to applications involving photopolymerization procedures and techniques.

Among the various structural modifying factors 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, depending on the initial acidity of the medium; d) the presence of micrometric inorganic fillers which had, or had not, their surface treated with silane coupling agents containing polymerizable groups, like vinyl or methacrylic; e) the inclusion in the acrylate mixture of a solution containing a linear polymer, like Nylon 6,6, which is stronger (especially in the tensile strength, σ , and Young's modulus, Y) than the network formed by the acrylates used.

Experimental:**Materials:**

The monomers and oligomers used were: a) Polyethylene glycol-400, diacrylated, PEGA-400 (from Monomer-Polymer Laboratories, Inc.); b) Trimethylol propane triacrylate, TMPTA, (Sart 357, from Sartomer Co.); c) Dipentaerythritol pentaacrylate, DPHPA, (Sartomer 399, from Sartomer Co.); d) Polybutadiene diacrylate, PBUA, (from Scientific Polymer Products Inc.); e) Acrylated Aliphatic Urethane, PUA, with functionality 2, from Monomer-Polymer Laboratories, Inc. The

monomer's stabilizers were not removed because it has been observed that this procedure generates an instability in the reaction mixture, with the polymerization starting before it is really intended. The measured mechanical properties of the materials are 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), DHPA (40). Polyhexamethylene adipamide, Nylon 6,6 was purchased from the Aldrich Chem. Co. All the peroxides used were also obtained from Aldrich. The fillers used included: a) Siliconated fumed silica beads, CAB-O-SIL TS-720, from the CABOT Corp. These beads contained no polymerizable group on the surface. b) Some 325-mesh ($\Phi < 45$ mm) glass beads, surface treated with 3-(methacryloxy) propyltrimethoxysilane, and c) Sub-micrometric aluminum silicate particles, surface treated with vinyltriethoxysilane, these last two items 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} M to 1×10^{-3} M depending on the experiment performed. Other dyes used in different tests included the 2,4,5,7-tetraiodo (TIHF), the 2,7-di-*t*-butyl (4,5-diiodo), (DBDIHF), and the 9-cyano (2,4,5,7-tetraiodo), (CNTIHF, or NB, for New Blue), fluorones. As co-initiators (electron donors in this case) the amines used were *N,N*-dimethyl-2,6-diisopropylamine, DIDMA, from Carbolabs, Inc., and *N*-phenylglycine, NPG, from the Aldrich Chem. 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 minutes. After this operation, the other multifunctional acrylates, TMPTA and DHPA, were added to the system to be reacted and the whole mixture was again submitted to ultrasound for 20 more minutes. The mixture of these three monomers formed the basic standard resin used and it is from now 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 tested, for example, PBUA and PUA, they were the last chemicals added to the basic STDR resin, except if DIDMA was used as co-initiator. Special care was taken when PBUA was mixed with the acrylate monomers in terms of guaranteeing a final homogenous system right before irradiation. This was so because of the possibility of severe 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 around 10^{-2} M of HCl.

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 homogenous 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 plus KCl and CaCl_2 . The final concentration of Nylon in solution was estimated to be about 30% (w/w).

The photoreactive mixture was poured into dogbone-shaped Teflon molds, 2.0 mm deep, 6.0 mm wide, with a

gauge length of 70.0 mm, and a total length of 120.0 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 MCS) was used as the irradiation 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 dogbone-shaped parts. The mirrors were driven by digitized computer data from a special file initially designed to generate a solid cube. If the z 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 a 200.0×200.0 mm square region, large enough to include all the dogbone-shaped molds with the photosensitive mixtures. The laser power varied from 30.0 to 50.0 mW depending on the experiment performed. 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 2.6 and 8.6 mm/sec.

Mechanical Properties

Tensile strength tests were carried out at ambient temperature (typically 23 °C), with no strict humidity control, using the photopolymerized dogbone-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 crosshead 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.

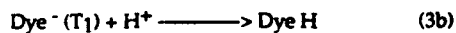
This instrument was controlled by an MCM-4135T Goldstar PC booted with Lloyd's DAPMAT software. This data analysis program allowed direct observation of the load versus elongation behavior of the sample during the tests. After the test ended, it also automatically displayed various physical parameters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

Results and Discussion:

Although Eqs. 1-5 describe the basic mechanism of the visible light-induced polymerization process using fluorone dyes plus amines, there is some structural information of the dyes which is not apparent from the equations. Figure 1a shows the general molecular structure of the dyes used. Table I displays what are the most common chemical elements corresponding to each letter and the acronym used in each case. Particularly relevant to the discussion that follows is the atom corresponding to Y. When Y is hydrogen, like in TIHF, DBDIHF and NB, the dye is ionizable since Y 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 1b. Eq. 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]. As a consequence, a

smaller number of free-radicals will be formed, and the overall polymerization rate decreases. We have previously reported the consequence of this decrease in 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. The ionized state of the dye, which is also an unprotonated state, can be neutralized (or reversed) to a protonated condition by increasing the acidity of the medium. This has been realized before and a thorough discussion of theoretical aspects of the influence of the ionizing state of the initiator on the polymerization process will be the subject of a separate report of our group [7].

The results to be discussed at this point correspond to a comparison between the mechanical properties of acrylate network polymers formed by visible light sensitive xanthene photoinitiators depending on the acidity of the medium. The standard monomer mixture (STDR) was used with different ionizable dyes (TIHF, DBDIHF and NB) as photoinitiators, and the mechanical properties (Young's modulus and tensile strength) of the materials formed were measured, first with the mixture containing no acid and then adding a few drops of HCl 1.0 M such that the final HCl concentration was 0.01M. The first observation was that, after adding the acid and homogenizing the system, the dye colors changed from the original orange (TIHF and DBDIHF) or blue (NB) to red, in all cases. These results are more apparent and quantitative if the spectra of the dyes before and after addition of HCl are compared. This is shown in Figure 2 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 clear blue shift in all spectra is observed with peak maximum close to 470 nm. This spectral appearance seems to be a characteristic of all fluorone dyes when Y is not a hydrogen [3,5,8]. For TIHF and DBDIHF this spectral shift does not restrict very much the wavelength of the irradiation source. More specifically, network polymers can still be formed using Ar⁺ laser lines, the same used before the acid was added. However, in the case of NB, as Fig. 2 *f* shows, the band maximum is shifted from the original 648 nm to the 380-600 nm region. As a consequence, a HeNe laser, which emits at 632.8 nm, could not be used to make polymers when NB was in an acidic medium. Table II displays the Young's modulus and tensile strength of polymers made with the above mentioned ionizable dyes, under acid and non-acidic media. The results clearly indicate that having the dye in a neutral form definitely improves the overall polymerization (cross-linking) process. The main reason being, as we suggested above, that the dye in the neutral state facilitates the electron transfer from the amine. However, besides influencing the electron transfer process, the acid may also participate in other molecular steps that lead to the formation of free-radicals. The evidence for this comes from the work of Kotchetov et. al. [7] where they observed a 20% increase in the percentage of C=C bond converted to single bond by the polymerization process in an acidic medium, even when a neutral dye was used as co-initiator. One possible explanation for this observation is that the presence of an H⁺ species helps quenching the dye anion. Eq. 3b below describes this process.



As a consequence, Eq. 3 is shifted to the right, a larger amount of amine cation-radicals are formed, and the polymerization becomes a more efficient process. Eq. 3b points to another interesting possibility: as soon as the dye is in a neutral radical state, it may also act as a polymerization initiator and this may increase the reaction yield. However, because of all the π delocalization present, this dye radical may be quite a stable species, acting most likely as a terminator of the polymerization rather than an initiator.

The first structural characteristic to be analyzed refers to the presence of diacrylates in a mixture of tri and pentaacrylated monomers. In principle, the increase in concentration of a diacrylate oligomer, under these circumstances, is expected to have a deleterious effect on the mechanical properties of the photopolymer formed. This is so because the 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 have, as main consequence, the decrease in average molecular weight in between cross-linking sites, and a consequent decrease in 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 photopolymers formed, using the visible photoinitiators previously described, is shown in Table III. These results clearly indicate that the mechanical strength of the materials deteriorate as the relative amounts of diacrylated oligomers is increased, like for PBUA and PEGA, in agreement with what is known for thermally or thermo-chemically made networks [9,10]. However, the results of Table III 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 stressing the second most important factor in determining the strength of network systems: the molecular structure of the network components. The presence of polar groups, like N-H and C=O, in the structure of the urethane oligomer, increases the possibility of hydrogen bonding with similar groups, or with C=O and C-O-C bonds from the smaller acrylate monomers. In the case of PBUA the polymer chain is apolar and its conformation is mostly *cis*, and 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 non-radiant sources [9,10,11]. 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.

While the addition of an apolar and less symmetrical diacrylated polymer structure degrades the mechanical properties of a multifunctional acrylate matrix, by decreasing the cross-linking density, the basic principles of polymer science also indicate other ways to improve polymer properties. One of the ideas explored during the course of this work was the introduction of peroxides in the initial photoreactive mixture. Table IV 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. Peroxides are extensively used as initiators of free-radical polymerizations: Thermally-induced

breakage of the O - O bond generates free-radicals which can propagate by reacting with the monomers. Because free-radicals centered on oxygen are very reactive species, peroxides have also been used as cross-linking agents to relatively inert polymers, even polymers with saturated C-C bonds. For example, polyethylene can be cross-linked by different peroxides [12]. However, there is no fundamental reason to not use peroxides to cross-link unsaturated chains, like polybutadiene (PBU) based polymers. The typical mechanism for the cross-linking process under these conditions involves hydrogen abstraction from the main PBU chain, with consequent formation of a macroradical, and recombination of two of these radicals for interchain bonding. The final result is an increase in cross-linking density with substantial improvement in the mechanical strength, as observed in Table IV. Prior to the cross-linking steps, the peroxide has to decompose inside the photoreactive mixture under irradiation of the Ar⁺ laser. There are a few possible ways this peroxide decomposition may take place, and they may well happen simultaneously. The peroxide may decompose by collisions with energetic species formed during the irradiation process, such as with the ionic and neutral free-radicals described in Eqs. 1-5. Besides this direct collision process, peroxides are known to be oxidizing agents for amines and, after the electron transfer step, rapid decomposition follows [13]. Also, the polymerization reaction of the acrylate monomers is a highly exothermic process, and the heat generated during this phase may further contribute to peroxide decomposition.

Besides the idea of trying to understand how the already established basic principles of polymer science could be translated into improving the strength of samples prepared by photopolymerization processes, it was also our concern to use this knowledge in forming functional objects by stereolithography. Although the presence of different types of peroxides has proven to be a possible way to reinforce some types of acrylated network matrices, it is unfortunate that its use cannot be easily translated to manufacturing resins and industrial processing. The reason is a very fundamental one: the fact that most peroxides have a very long (much greater than 100 hrs.) half-life at ambient temperature does not mean that they do not decompose under these conditions. It really means that the decomposition rate is just very small. Therefore, for industrial and other applications, long storage times of solutions containing peroxides may induce gelation and this is often unacceptable. Consequently, other ways have to be devised in order to improve the mechanical properties of acrylated matrices made photochemically.

Although the presence of PBUA provided some interesting and useful information on the effect of diacrylated species on the mechanical property of acrylated networks, the original idea of including such oligomer in mixtures with small multifunctional acrylate molecules was directed towards obtaining flexible and elastic parts using stereolithography. Figure 3 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, like the styrene-butadiene-styrene, SBS, triblock copolymers. The butadiene segments would provide the required flexibility and elasticity. Much to our initial surprise, the stress versus strain testing of dogbone samples containing 10, 20, 30 or even 50% of PBUA in the original reacting mixture did not show a large elongation, or even an "yield point". The explanation for these observations came from parallel studies on the percentage of C = C double bonds (% C=C)

converted to single bonds by the photopolymerization reaction. It was determined that the value of % C=C, for the monomers and oligomers used and under the photopolymerization conditions utilized, oscillated between 28 and 36% [14]. In other words, it was apparent that most of the acrylic double bonds did not react. These % C=C values are 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 visible light-induced 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 Fig. 3 does not seem to be a good representation of the microscopic picture inside the acrylated matrix.

The basic principles of thermal polymer science have also served as a guide to the reinforcement of photopolymers [15]. It has been determined that different types of fillers [16] and micrometric inorganic beads may function as additives to improve, strengthening, the mechanical properties of different types of polymers [17]. This is specially true if the reinforcing agent's surface has been treated with special chemicals, called coupling agents, containing polymerizable groups in their structure [18]. The most common coupling agents used are methoxy or ethoxy silanes and the polymerizable groups more frequently encountered have acryloxy, methacryloxy or vinyl moieties in their structures [18]. Although many aspects of the reinforcing process, and the final bonding between the filler agent and the polymer matrix, are still not fully understood [19], it is normally accepted that the presence of the reactive groups containing double bonds are very effective in improving the interaction between the filler and the matrix [15-20]. Since the fillers normally have mechanical properties (like the Young's modulus and tensile strength) much larger than 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 included: a) Siliconated fumed silica beads (CAB-O-SIL HT-720), which have no coupling groups on the surface; b) Micrometric glass beads, $\Phi < 45 \mu\text{m}$, which have their surface treated with methacryloxypropyltrimethoxy silane; c) Sub-micrometric aluminum silicate particles which have surface treated with vinyl triethoxy silane. These fillers are schematically represented in Figure 4. Table V describes the monomers used with the different fillers, the polymerization conditions utilized, as well as the mechanical properties measured by stress-strain testing. It is apparent from the results of Table V 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 is an indication that the silica particles have not been effectively "coupled" to the network. There are a few possible explanations for this observation. First, the fact that the filler particles do not have an active group on their surface precludes any additive effect to the acrylate polymer properties. 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. Therefore, the laser light is not so efficient 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 laser scattering may still be a wasting factor, the presence of the double bonds more than compensate the laser decrease in efficiency, and the network is reinforced.

In principle, the observations offer encouraging results on different ways to strengthening photopolymers, how effective it can be, and what kind of filler should be used. The particle size also seems to play an important role in the final reinforcing process; although methacrylates seem to be much easier polymerized than the vinyl groups [24], the finer aluminum silicate particles seem to be more effective in the reinforcing process and in promoting polymerization [25]. This direct comparison is possible because the silicate and glass have comparable mechanical properties.

As mentioned before for the case of peroxides, one of the major applications sought to apply the present results is in stereolithography [26]. Although the use of inorganic fillers, like the glass and silicate beads utilized, 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 to be surpassed. The main one is the partial sedimentation of the fillers with possible overall inhomogeneous distribution if the reactive mixture is left standing for long periods of time, which may be a real situation on routine applications. There are a few ways to bypass this inhomogeneous distribution of fillers (or fibers) which are being explored in parallel [14]. But, even at present, model parts have been constructed by visible laser-induced stereolithography containing up to 25% of glass fibers inside the acrylate matrix [27]. New experiments are being performed to improve the density distribution throughout the polymer matrix [14].

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 homogenous mixture of monomers and strong polymer solutions. A similar experiment has been performed by Moussa and Decker [28]. However, in their experiment the photopolymerization of the multifunctional acrylate monomers was carried out in a thin (50 μm) solid matrix of a linear 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, in a semi-interpenetrating network structure.

The basic acrylate network polymer was formed by the same monomers used in the standard resin (STDR). As "reinforcing agent" polyhexamethylene 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 dye DIBF was used with DIDMA as co-initiator and different percentages of the nylon solution were mixed. Table VI shows the measured properties as well as the photopolymerization conditions and initial mixture composition. It clearly shows that Nylon 6,6 is an active reinforcement for the acrylates.

Due to the possibility of selective hydrogen bonding between the polar groups of the amide moiety, nylons are known to have high Young's modulus and very high tensile strength. As a matter of fact, comparing to some of the most common natural and synthetic materials, Nylon 6,6 has one of the highest tensile strength per density

ratio [21]. Therefore, there may be applications where the use of Nylon 6,6 will be an effective way to improve the mechanical properties of the network. It is not clear, since it was not very carefully followed, the fate of the methanol after the photopolymerization process; the sample is quite "dry" with no excessive liquid on its surface or 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 very homogenous, and so are the dog-bone samples formed. The present results represent a first step towards the goal of using a homogenous system to reinforce photopolymers.

CONCLUSIONS:

We have studied various aspects of the visible light-induced polymerization of acrylate networks as 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 xanthene dyes are in their protonated structure, they can work more efficiently as free radical initiators. Many different ways to reinforce the network polymers were devised and explored, including the use of peroxides.

It was also shown that the network polymers can be reinforced by other methods, including the use of peroxides, inorganic fillers, or solutions of stronger polymers, like 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, mainly because of possible inhomogeneity in the system. Although in systems like using the nylon solution the results seem very encouraging, new ways to better solve this problem are also currently being explored.

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Figure Captions

Figure 1 : 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).

Figure 2: Spectra of the ionizable dyes TIHF, DBDIHF and NB in a solution of the STD, under acidic conditions (a, c and e) and without any acid present (b, d and f), respectively.

Figure 3: Ideal model of a possibly elastomeric structure formed between a small (and rigid) triacrylate monomer and a flexible diacrylate oligomer.

Figure 4: Schematic representation of three different types of surface treated fillers used to modify the photopolymers: Methyl silane treated fumed silica (a), vinyl silane treated aluminum silicate (b) and methacryloxy silane treated glass beads (c).

TABLE II

DEPENDENCE OF THE MECHANICAL PROPERTIES OF A
PHOTOPOLYMER CONTAINING DIACRYLATE OLIGOMERS AS A
FUNCTION OF THE AMOUNT OF PEROXIDE DISPERSED IN THE
ORIGINAL MIXTURE⁽¹⁾

LAUPEX (%)	σ (N.mm ⁻²)	Y (N.mm ⁻²)
1	0.05	0.7
2	0.19	2.4
5	0.30	5.4

⁽¹⁾-PBUA (50%) + Acrylated monomers; DBDIHF ($1.5 \times 10^{-3}M$),
NPG (0.05M); PI=100.0 mW, $\Phi=2.0$ mm, scan=9.0 mm/sec.

TABLE III

**ELEMENTS CORRESPONDING TO THE SUBSTITUENTS OF EACH
POSITION ON THE FLUORONE DYE STRUCTURE DISPLAYED IN
FIGURE 1**

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-but	H	DBDIHF
I	I	H	C ₄ H ₉	H	H	DIBF

TABLE IV

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)	γ (N.mm ⁻²)
TIHF⁽¹⁾		
wout/HCl	3.0	132.4
w/HCl	8.3	283.0
DBDIHF⁽¹⁾		
wout/HCl	1.7	131.1
w/HCl	2.1	150.4
NB⁽²⁾		
wout/HCl	0.6	7.3
w/HCl	1.2	29.0

(1) DYE AT 5×10^{-4} M, NPG AT 0.05 M; Ar⁺ LASER (514.5 nm) :
PI=50.0 mW, $\phi=2.0$ mm, SCAN= 9.0 mm/sec.

(2) USED A HeNe LASER (632.8 nm) AT 60.0 mW; SCAN AT
ABOUT 1.0 mm/sec.

TABLE V

MODIFICATION OF THE MECHANICAL PROPERTIES OF
PHOTOPOLYMERS BY THE ADDITION OF INORGANIC FILLERS(1)CAB-O-SIL
TS-720 (%) σ (N.mm⁻²) γ (N.mm⁻²)

0.0

44.5

2.9

17.5

GLASS
BEADS

0.0

58.1

2.0

82.6

4.0

100.6

47.0

273.0

ALUMINUM
SILICATE

0.0

0.5

19.0

2.0

1.4

57.6

4.0

2.2

111.4

9.0

5.5

243.0

(1) ORIGINAL MIXTURE CONTAINED ACRYLATES + PBUA.

TABLE VI

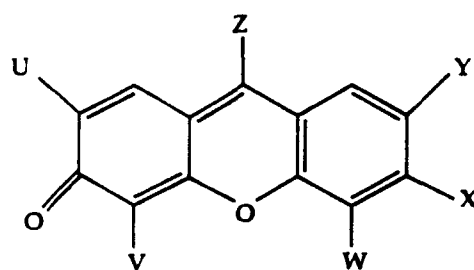
MECHANICAL PROPERTIES OF REINFORCED ACRYLATED
PHOTOPOLYMERS BY THE ADDITION OF A STRONGER POLYMER
(NYLON 6,6) IN SOLUTION

% NYLON (est.)	σ (N.mm ⁻²)	γ (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

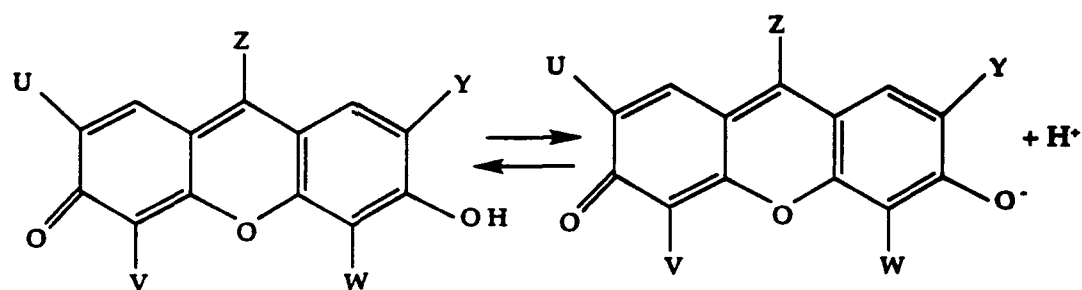
STDT [PEGA(20)+TMPTA(40)+DPHPA(40)]; DIBF (5×10^{-4} M) + NPG
(0.05M); NYLON 6,6 IN SOLUTION OF METHANOL + CaCl₂+KCl; PI =
50.0 mW ; scan = 13.0 mm/sec.

Figure 1

(a)



(b)



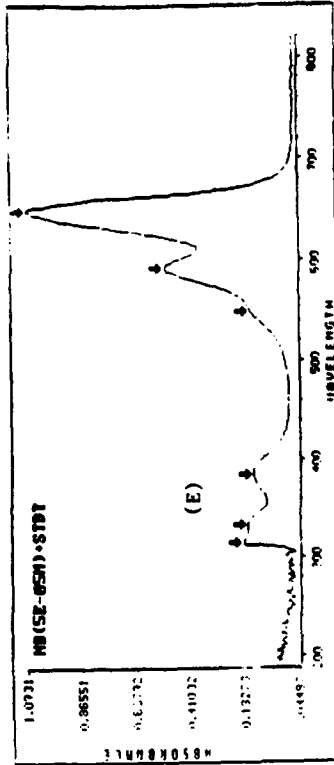
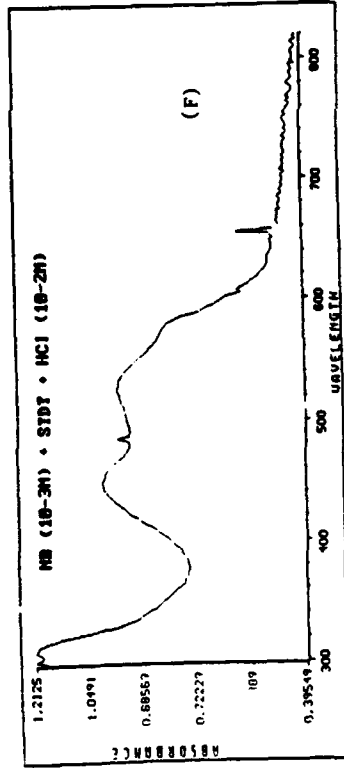
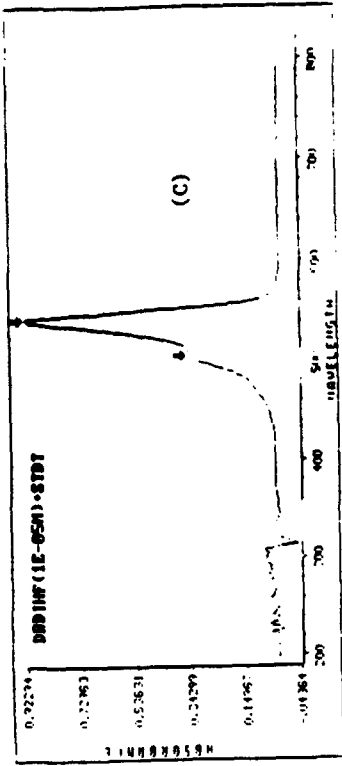
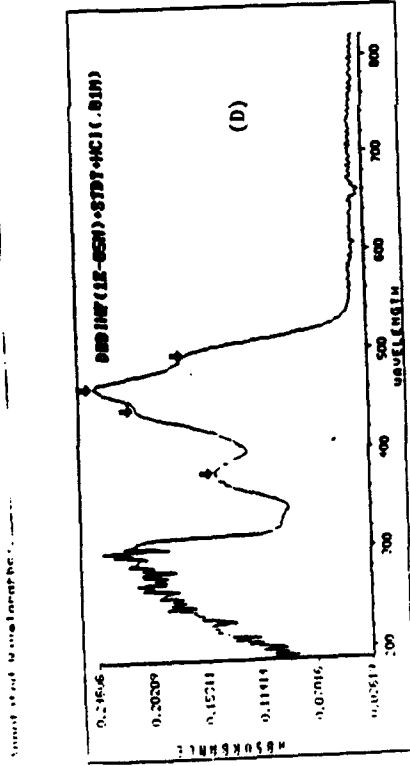
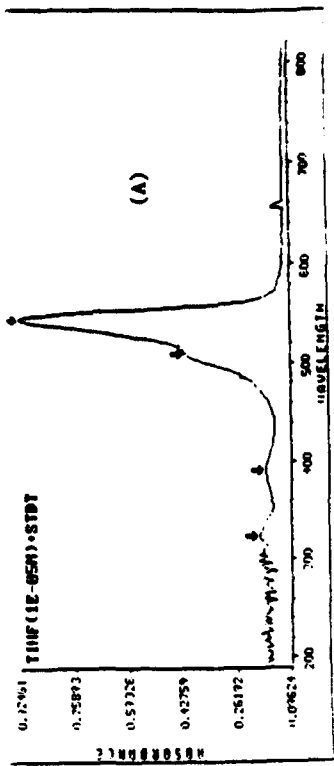
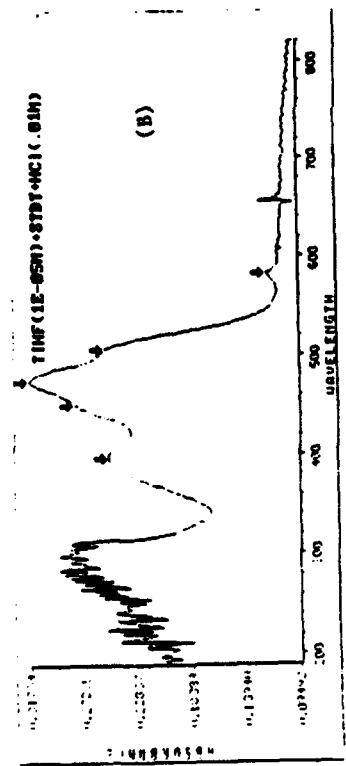


FIGURE 2

Figure 3

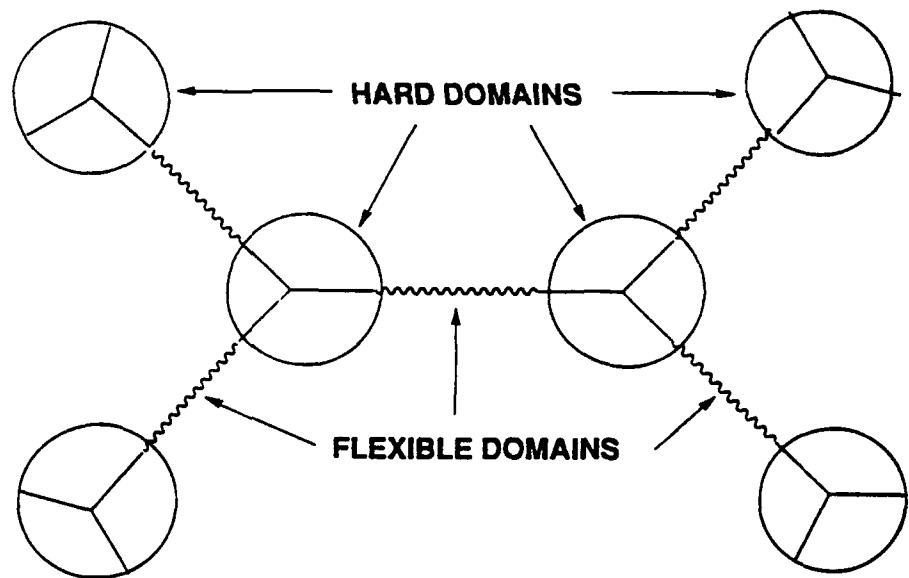


Figure 4

