

Elastomeric Electron Beam-Cured Coatings: Structure-Property Relationships. II. Chain Transfer Agents

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Synopsis

Properties of electron beam-cured film from 100% reactive mixtures consisting of polyester diacrylourethane oligomer, copolymerizing monomer, and chain transfer agents were investigated. The inclusion of chain transfer agent in such polymerization reaction was aimed to reducing the degree of polymerization of the double at each end of the oligomer, which is believed to be responsible for the low extensibility of these films. In general, these agents were found to result in some retardation in the polymerization reaction, but none of them influenced the mechanical properties of the cured films except mercapto-functional agents, which were found to drastically affect these properties. By the addition of a mere 2% to 3% of these agents it was possible to toughen the EB-cured films by increasing both the extensibility and breaking strength. This confirms the above speculation and brings the properties of these films to a level almost comparable to those of linear polyurethanes.

INTRODUCTION

In part I,¹ radiation-induced crosslinking of polyester diacrylourethane oligomer was found to produce films with somewhat lower extensibility than expected. This was speculated to be due to high functionality of crosslinks, which should be equal to the degree of polymerization of the double bond at each end of the oligomer. Addition of active monomer did not change this structure except in the case of diethylaminoethyl acrylate.

In this work, addition of small amounts of chain transfer agents was investigated. Ideally, the intervention of such agents, in the kinetic chain reaction of radical addition to double bond, will only result in reducing the degree of polymerization without affecting the rate of polymerization. However, other complicating reactions can take place, depending on each particular system, and they may retard or inhibit the polymerization reaction.

The chain transfer agents used in this study are all characterized by having a labile hydrogen or halogen which can easily be abstracted by the growing polymer. However, of all the agents used in these systems, only mercapto-functional agents produced the desired effect. This may be due to the high reaction rate of thiol addition to double bond, a reaction which is well known in the literature and is the subject of many reviews.²⁻⁴ The transfer process of monothiol agent involves several steps, in the first of which a growing polymer chain attacks a thiol molecule to yield a stable polymer molecule and a new thiyl radical. This radical in turn adds to a monomer molecule to form an intermediate radical. Lowering of the molecular weight occurs when, on the average, the intermediate radical reacts more rapidly with the unsaturated substrate than with another chain transfer molecule. If the latter is the predominant reaction,

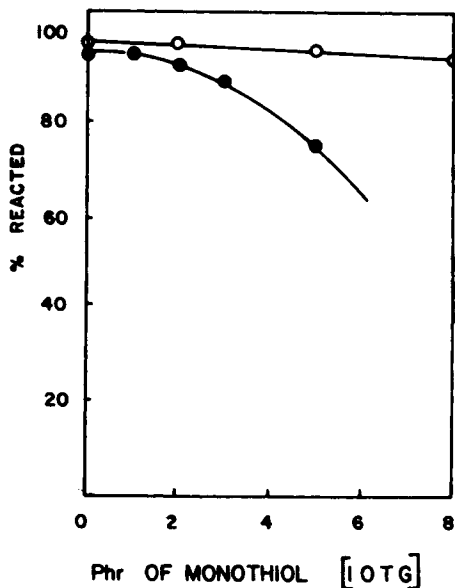


Fig. 1. Percent conversion as function of IOTG concentration. MW: (O) 1200; (●) 4600.

the resulting product will not be a polymer at all but rather a collection of small molecules including the one-to-one adduct of the chain transfer agent to the double bond.

Monothiols, with one —SH group per molecule, have been used by many investigators³ to cut down on the degree of polymerization and regulating or reducing crosslinking density in the vulcanization of natural rubber. Polythiols on the other hand were used as a crosslinking promoter in radiation curing of chlorobutyl and polydiene elastomers.^{5,6} In these cases the addition of one thiol group to the double bond will lead to grafting of the agent to the rubber chain. The reaction of the second and third thiol groups will lead to crosslinking.

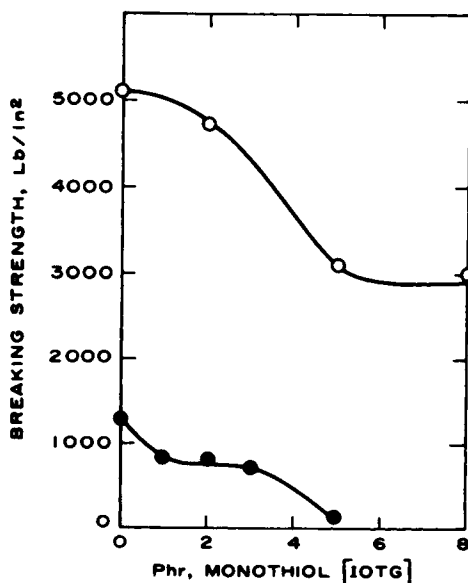


Fig. 2. Breaking strength as function of IOTG concentration. MW: (O) 1200; (●) 4600.

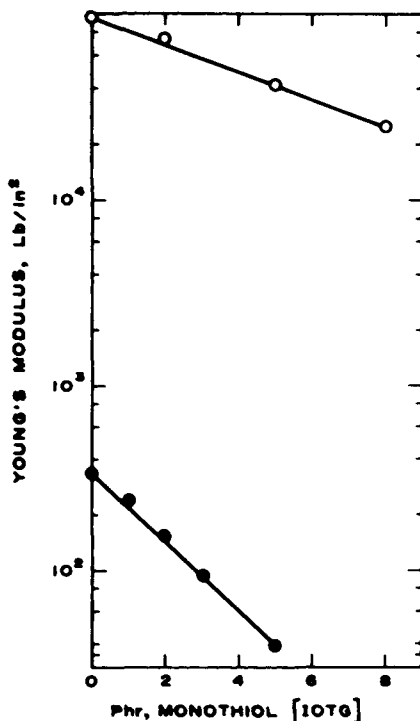


Fig. 3. Young's modulus as function of IOTG concentration. MW: (○) 1200; (●) 4600.

EXPERIMENTAL

Description of the materials, and processing and testing are given in part I.¹

EXPERIMENTAL RESULTS

Oligomer or Oligomer-Monomer Systems With Chain Transfer

In this study attention was given to the use of well-defined chain transfer agents. Such agents were mixed in small proportions (0.5% to 3%) with mixtures containing 75% of oligomer MW 4600 and 25% V-pyrol, and the films were irradiated at 5 Mrad. The results for percent conversion as well as physical properties are given in Table I.

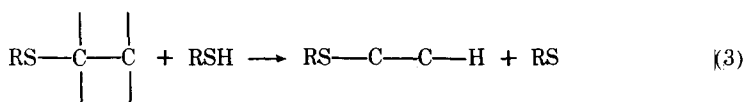
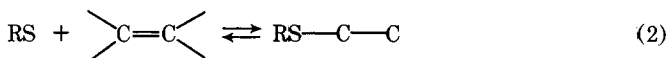
As can be seen, the addition of chain transfer agents generally resulted in a decrease in percent conversion of the system while none of them influences the percent elongation of the film, except IOTG (monothiol), where elongations up to 415% were obtained.

Initial studies were conducted by mixing IOTG with otherwise neat oligomer MW 1000 and 4600 in concentrations of 1% to 8%. The percent conversion at 5 Mrad as a function of monothiol addition is given in Figure 1. Physical properties of the cured films are shown in Figures 2-4 as a function of monothiol concentration.

The percent conversion decreased with increasing amounts of IOTG in the system, the effect being more pronounced with high molecular weight oligomer.

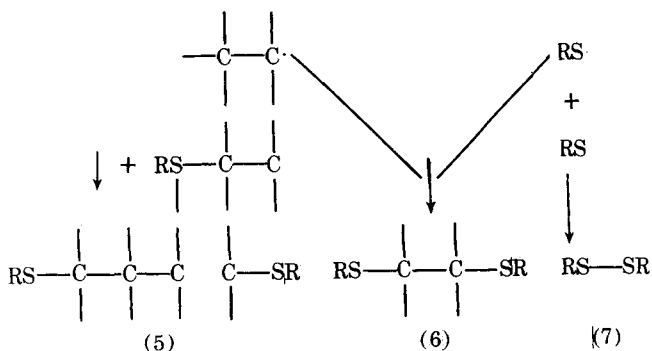
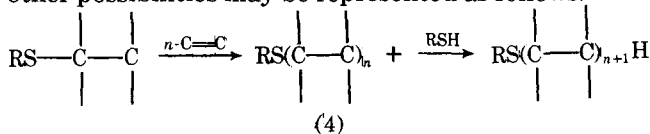
The breaking strength and modulus decreased, while percent elongation increased with increase of IOTG in the mixture.

It is believed that the basis of the above observation is the high reaction rate of thiol addition to double bond of the oligomer. The reaction mechanism² involves the formation of the thiyl radical by hydrogen abstraction, which subsequently adds to the double bond to form a new radical, the latter reacting with a thiol molecule to give the final product, a new thiyl radical. This can be represented as follows:



Both the addition of thiyl radicals, eq. (2), and the chain transfer, eq. (3), are normally exothermic, with the result that the overall reaction is fast and has a kinetic chain between a few hundred and several thousand cycles.^{7,8}

It was claimed that high yield of 1:1 product (i.e., one thiol to one C=C) can be obtained according to the above reactions if monomer with low C=C reactivity was used. It was also implied that different variables, such as the polarity and bulkiness of groups attached to both thiol and olefin, the stability of the radicals, and the ratio of thiol to C=C, etc., can affect the course of the reaction. A number of other possibilities may be represented as follows:



Reaction (4) can be a competing one, especially with highly reactive C=C like acrylate.

Kharasch,⁹ in working with an equimolar quantity of methyl acrylate and monothiol in the presence of peroxide and ultraviolet radiation, was able to isolate a high yield of 2:1 and 3:1 telomer in addition to 1:1 product and a small amount of higher olefin product. On the other hand, Crezlak¹⁰ used a small amount of monothiol during the catalytic polymerization of methyl methacrylate to obtain various low degrees of polymerization ranging from 27 to 129.

In this case, since the molar ratio of monothiol to acrylate was between that

TABLE I
Effect of Chain Transfer Agents on Film's Physical Properties

Formula	Breaking strength, psi	% Elongation	Young's modulus, psi	% Gel
1. 75% oligomer MW 4600 + 25% V-pyrol	2,353	240	1,755	95
2. 1 + 2% acetone	2,222	195	1,473	87
3. 1 + 2% diethyl phosphite	2,334	231	672	92
4. 1 + 2% IOTG (isooctyl thioglycolate)	1,892	415	410	91
5. 1 + 2% methyl ethyl ketone	1,636	237	875	91
6. 1 + 2% DBPA	502	167	259	76
7. 1 + 0.5% DBPA	561	176	383	82
8. 1 + 2% CBr ₄	—	—	—	43

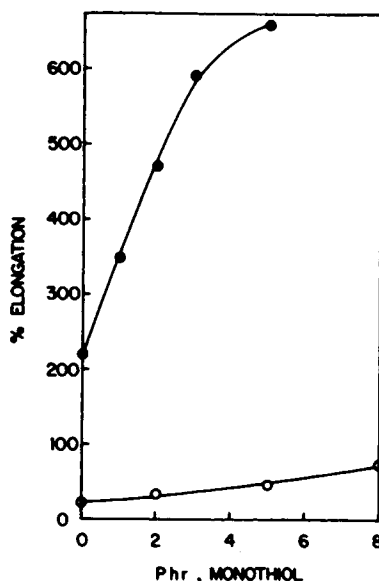


Fig. 4. Percent elongation as function of IOTG concentration. MW: (○) 1200; (●) 4600.

used by Kharasch and Crezlak, all possibilities can exist, but the predominant structure must be made of interconnected segments of low degree of polymerization, since the percent gel was high. This loose structure can explain the high extensibility of the film. At the same time, formation of 1:1 or telomeric products at both ends of the oligomer must have been responsible for the observed decrease in percent conversion.

The effect of adding monothiol to oligomer of molecular weight 4600 with different monomers was investigated. The oligomer-monomer ratio was kept at 75:25, to which additions of 1% to 5% of isooctyl thioglycolate (IOTG) was made. The monomers used were N-vinylpyrrolidone (V-pyrol), isobornyl acrylate (IBOA), tetrahydrofurfural acrylate (THFA), N-(1,1-dimethyl-3-dimethylaminopropyl) acrylamide (DMAA), and N,N-diethylaminoethyl acrylate (DAEA). As expected, the percentage conversion was found to decrease slightly with increasing IOTG addition. Figure 5 shows this trend.

As far as physical properties are concerned, it was found that the addition of IOTG had either a positive, negative, or practically no effect, depending on the nature of the monomer used. This is presented in Figures 6-10.

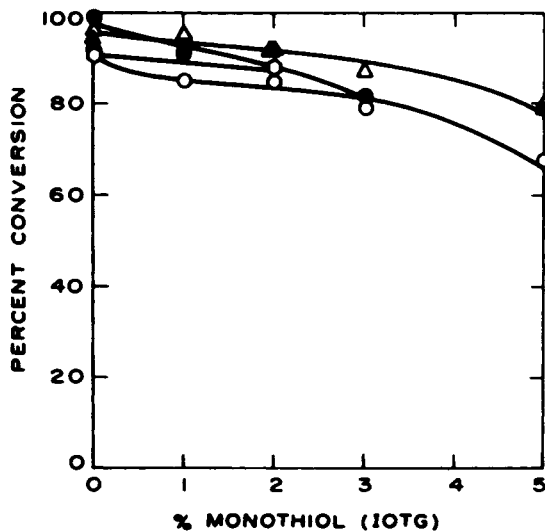


Fig. 5. Percent conversion as function of IOTG addition. Dose 5 Mrad. (▲) THFA; (●) DMAPA; (△) V-pyrol; (○) DEAEA; (○) IBOA.

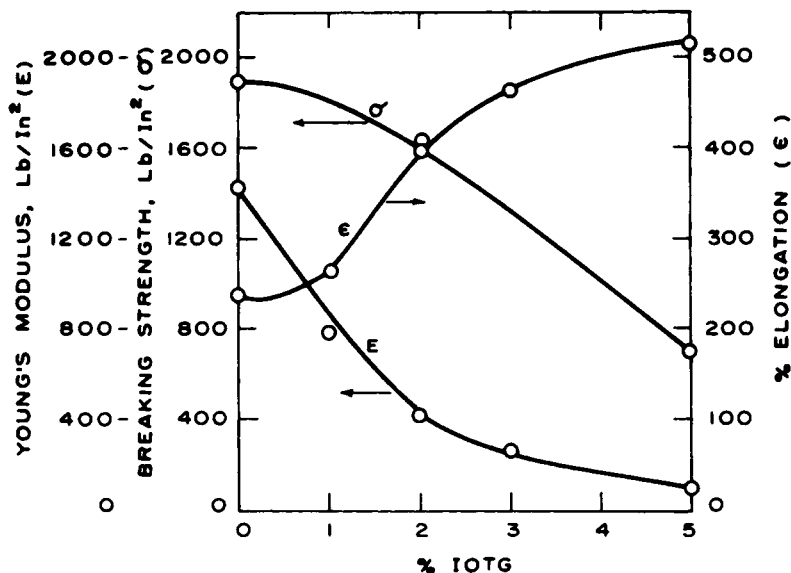


Fig. 6. Physical properties as function of IOTG addition (75% MW 4600; 25% V-pyrol). Dose 5 Mrad.

Encouraged by the above-mentioned results, it was decided to explore the effect of using polythiol on the properties of these films. In this work the polythiol used was trimethylolpropane tris-3-mercaptopropionate (TMTMP), which contains three terminal SH groups. In this case 1:1 product is more desirable since it will limit the crosslinking functionality to 3. The TMTMP addition was adjusted to 1/3 to 1/2 mole of oligomer, i.e., one SH group for every double bond in the oligomer. The first phase of the work included the use of pure oligomers. The percentage conversion as well as the physical properties for different oligomer molecular weight are shown in Table II. As can be seen from this table,

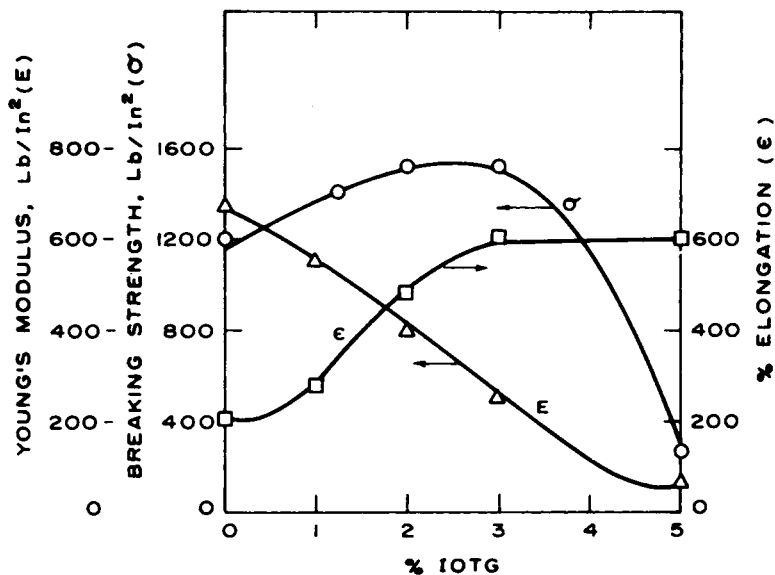


Fig. 7. Physical properties as function of IOTG addition (75% MW 4600; 25% IBOA). Dose 5 Mrad.

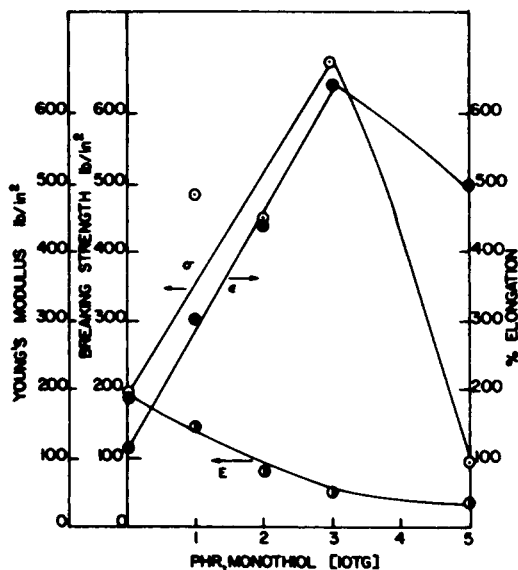


Fig. 8. Physical properties as function of IOTG concentration in 75% 4600 MW oligomer and 25% THFA.

the TMTMP addition greatly enhanced the extensibility of the films and reduced the modulus. However, the breaking strength was found to increase with the higher molecular weight oligomer but to decrease with low molecular weight oligomer.

The percent conversion as a function of trithiol concentration is given in Figure 11, which shows that the percent conversion remained at a high level (96%) up to 4% addition, after which it dropped continuously with increased trithiol ad-

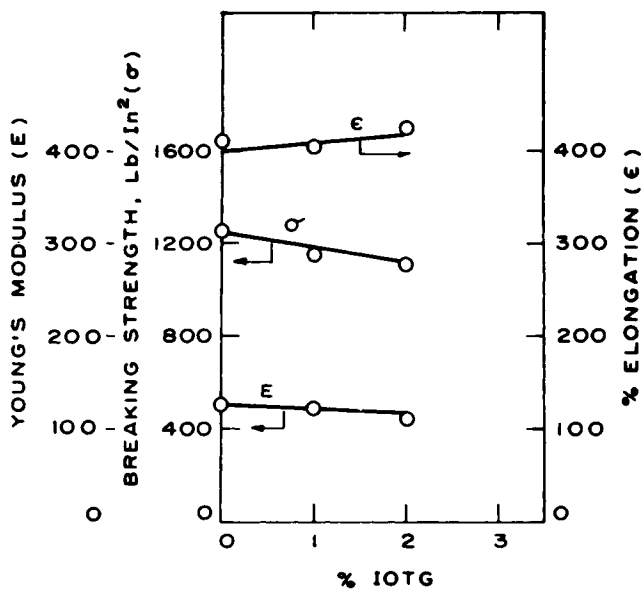


Fig. 9. Physical properties as function of IOTG addition (75% MW 4600; 25% DEAEA). Dose 5 Mrad.

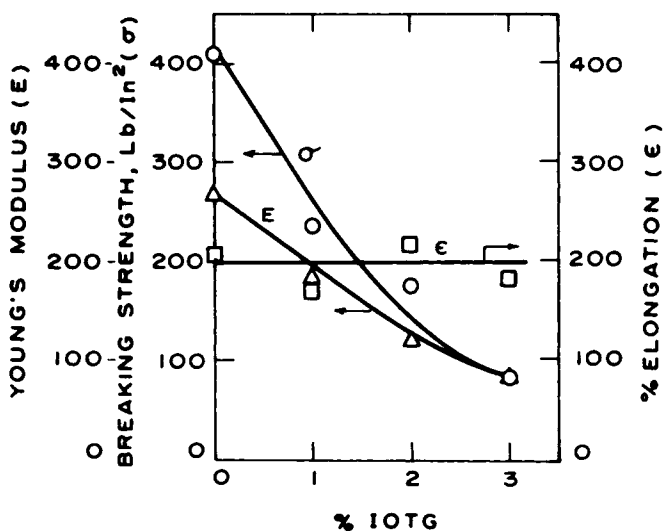


Fig. 10. Physical properties as function of IOTG addition (75% MW 4600; 25% DMAPA). Dose 5 Mrad.

dition. The effect of radiation dose on percent conversion was investigated for some of the above mixtures. The results shown in Figure 12 indicated that the percent conversion went up sharply with low dose and then leveled off above 1 Mrad.

The physical properties of films cured at high dose (3 or 5 Mrad) are shown in Figure 13 as a function of trithiol concentration. The breaking strength dipped slightly before climbing to a sharp maximum at 4% trithiol concentration. The percent elongation increased considerably with trithiol addition and leveled off beyond about 5.5%. The modulus decreased with trithiol addition.

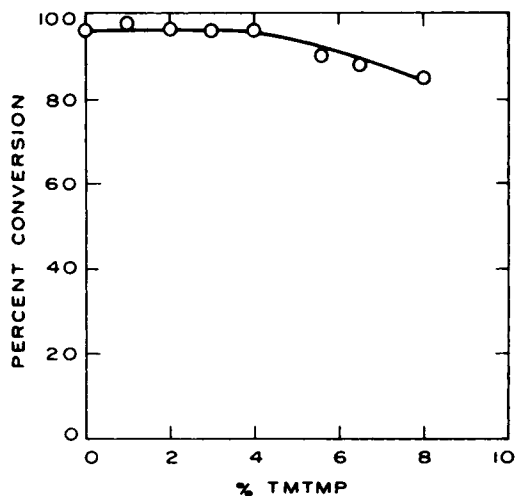


Fig. 11. Percent conversion of 4600 MW oligomer as function of TMTMP addition. Dose 5 Mrad.

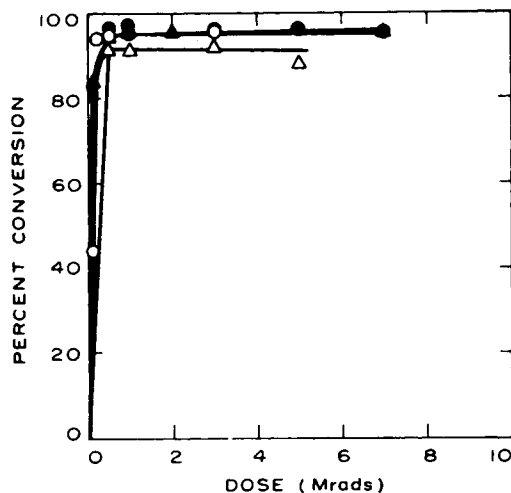


Fig. 12. Percent conversion of mixture containing 4600 MW oligomer and TMTMP, as function of dose. (O) 100% MW 4600; (▲) 100% MW 4600 + 3% TMTMP; (●) 100% MW 4600 + 4% TMTMP; (Δ) 100% MW 4600 + 6.5% TMTMP.

The behavior of breaking strength can be explained as follows. In the absence of trithiol one may expect a high degree of functionality of crosslinking, as previously described. This obscures the effect of the high molecular weight of the oligomer. With slight addition of trithiol some trifunctionality will exist, giving rise to a structure of a mixed nature, possibly accounting for the dip in breaking strength. As more trithiol is added, trifunctionality prevails and the structure becomes more regular with the sharp peak of breaking strength. The fact that this peak does not coincide with the calculated trithiol percentage based on 1:1 equivalent may be due to the formation of small amount of other telomers.

Similar experiments were performed on films made from the less viscous oligomer-monomer mixtures. One mixture consists of 75% 4600 MW oligomer and 25% V-pyrol, and the other consists of 70% 6000 MW oligomer with 30% V-pyrol.

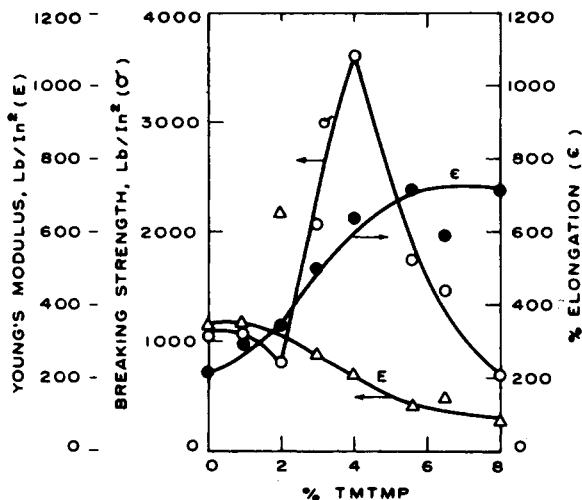


Fig. 13. Physical properties of 4600 MW oligomer as function of TMTMP addition.

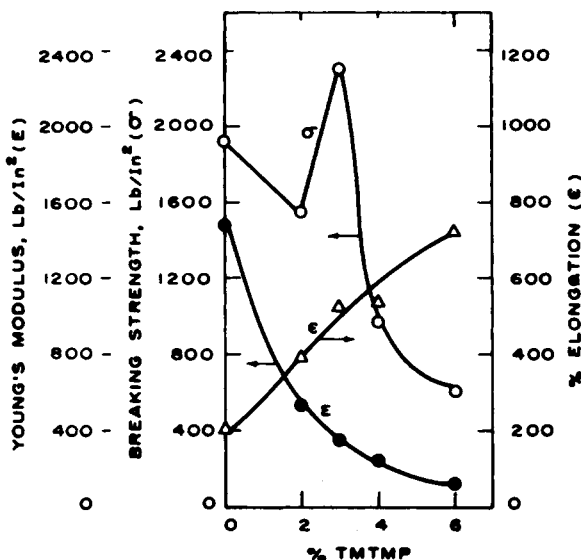


Fig. 14. Physical properties of a mixture of 4600 MW oligomer (75%) and V-pyrol (25%) as function of TMTMP addition.

The results obtained showed that the percent conversion was not impaired by the addition of up to 3% trithiol for the former mixture and 2% for the latter. Physical properties of the films showed generally the same trend as those of films obtained from pure oligomer, but at a maximum in breaking strength corresponding to 3% and 2% trithiol, respectively (Figs. 14 and 15). The stress-strain diagrams of the films with and without trithiol addition are shown in Figure 16 for comparison. It can be seen that as a result of this addition the breaking strength increased by 35%, percent elongation increased by 100%, and toughness increased by about 200%.

It seems that the phenomena described above are quite general. They have been duplicated in our laboratory by addition of small amounts of mercaptans to several commercial, proprietary radiation-curable formulations, and others

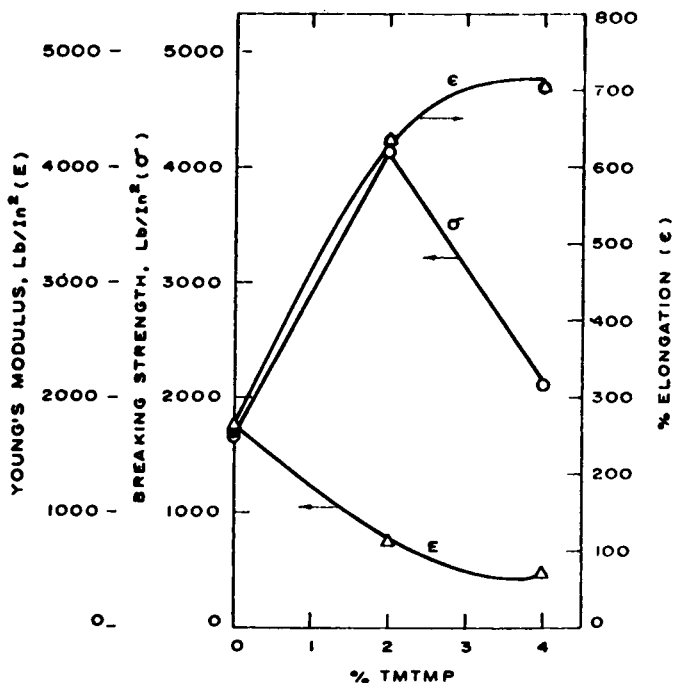


Fig. 15. Physical properties of films from 6000 MW oligomer and V-pyrol as function of TMTMP addition.

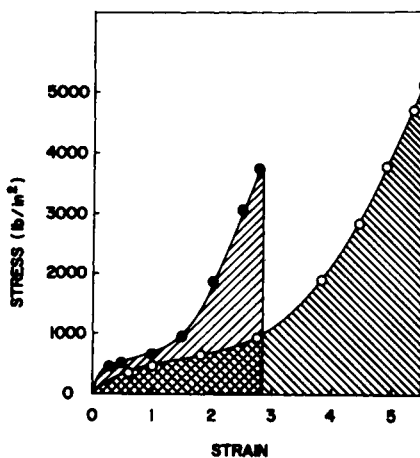


Fig. 16. Stress-strain diagrams of films with and without trithiol addition. (●) Formula (1) = 70% MW 6000 + 30% V-pyrol; (○) formula (2) = (1) + 3% silicone surfactant + 2% trithiol.

have observed similar results.¹¹ The lack of success with other chain transfer agents remains unexplained but may be related to the higher reactivity of thiyl radical. In summary, it is thus useful to compare the range of properties obtained with the variety of films produced in this work with electron beam curing¹ and those of conventional films used in textile applications in a plot of breaking strength versus percent elongation (Fig. 17). It can be seen that electron beam-cured films cover a wide range of properties, from very strong and relatively brittle films to very extensible and soft films, with some having a superior

TABLE II
Effect of TMTMP Addition on Properties and Percent Conversion of Films Irradiated at 5 Mrad

Formulation	Breaking strength, psi	% Elongation	Young's modulus, psi	% Conversion
1. 100% oligomer MW 1000	6768	17	134,000	99.0
1. 100% oligomer MW 1000 + 21% TMTMP	1165	206	463	98.2
2. 100% oligomer MW 3000	2120	139	614	96.0
2. 100% oligomer MW 3000 + 8.8% TMTMP	1901	543	212	90.0
3. 100% oligomer MW 4600	1044	218	338	96
3. 100% oligomer MW 4600 + 5.6% TMTMP	1737	713	125	90

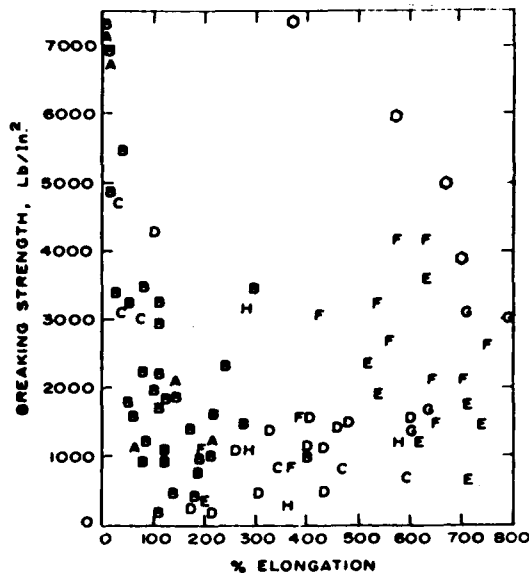


Fig. 17. Electron-beam-cured and conventionally cured film properties. A, oligomer; B, A + monomer; C, A + monothiol; D, B + monothiol; E, A + trithiol; F, B + trithiol; G, Hycar latices; H, Rhoplex lat. F; O, thermoplastic urethanes.

toughness, i.e., high extensibility and strength. The films are seen to fall within the range of those conventionally produced.

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Received June 26, 1978

Revised August 11, 1978