

Transparent Fluorocarbon-Based Semi-II IPN Elastomers by High-Energy Radiation Methods

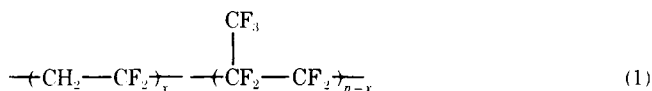
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Synopsis

Semi-II interpenetrating polymer network fluorocarbon elastomers were prepared by the addition of small amounts of a multifunctional monomer to the linear fluorocarbon polymer, followed by radiation polymerization *in situ*. The linear fluorocarbon is physically bound up with crosslinked network II, producing a semi-IPN of the second kind. Due to the high-energy radiation attack on the fluorocarbon backbone, a significant amount of graft copolymer forms which improves compatibility and yields clear, transparent elastomers. High-energy β and γ radiation produce very similar semi-IPN elastomers. Low-energy UV, which does not promote grafting, produces poorer-quality elastomers which show significantly less optical clarity, much lower strength, and higher creep. High-energy radiation also appears to destroy possible incipient crystallinity thought to be present in the linear fluorocarbon material.

INTRODUCTION

The fluorocarbon elastomers have the general structure



where n represents the degree of polymerization and x represents the number of vinylidene fluoride mers; the two mers are randomly distributed along the chain,¹ and the hydrogen present confers modest reactivity.

The glass transition temperature T_g depends on the ratio x/n but has a minimum near -15 to -20°C . Crosslinking can overcome the creep and tackiness normally exhibited by the linear polymer as well as improving other physical properties such as abrasion, solvent resistance, and toughness. Crosslinking tends to be difficult in fluorocarbons due to their inert chemical structure.^{2,3} Known crosslinking recipes include (a) diamines or peroxides, (b) MgO, an acid acceptor, and (c) carbon black or other fillers, and work by attacking the hydrogen on the backbone chain.^{1,4,5} These crosslinked materials are opaque to light, although the fluorocarbon homopolymers are relatively clear and transparent. In this paper, work is reported on the feasibility of obtaining a tough, transparent, crosslinked fluoroelastomer with reduced creep. A technique has been worked out for synthesizing such materials using a multifunctional monomer additive, followed by high-energy irradiation.

Interpenetrating Polymer Networks

At this point it may be useful to examine the definition of an interpenetrating polymer network, or IPN. The term IPN, in its broadest definition, signifies any material containing two polymers, each in network form, which have been synthesized or crosslinked in the immediate presence of each other.^{6b,7-10} The term crosslink indicates the covalent joining together of like polymer molecules to form a network. Other terms in common use include vulcanization and curing. In the following discussion, polymer I will indicate the first synthesized polymer and polymer II the second synthesized polymer. In this paper the fluorocarbon elastomer serves as polymer I. When only one of the polymers is crosslinked, the product is called a semi-IPN.^{11,12} If polymer I is crosslinked and polymer II is linear, the product is called a semi-IPN of the first kind (semi-I). If polymer I is linear and polymer II is crosslinked, a semi-IPN of the second kind (semi-II) results.

The present synthesis of a fluorocarbon based semi-II involves the addition of small amounts of the multifunctional monomer trimethylolpropane trimethacrylate (TMPTM) to the fluorocarbon elastomers, followed by polymerization *in situ* via high-energy radiation. The fluoroelastomer is physically bound up by the polymerized monomer. Without grafting, an idealized analogy would be sheaves of wheat bound up with baling wire, where the linear fluorocarbon chains are signified by the stalks of wheat and the baling wire is the crosslinked TMPTM network. As will be explored below, extensive grafting does occur, however, with considerable profit.

The term IPN also implies some kind of interpenetration of the two polymers. Full molecular interpenetration only occurs in the case of total compatibility of the two polymers (total solubility), while most IPNs along with polymer blends, blocks, and grafts phase separate to a greater or lesser extent. The last is important if one wants a high-impact resistant plastic or certain types of thermoplastic elastomers. Suppression of phase separation is required for high clarity.¹³⁻¹⁵

Opacity Considerations

The concept of optical opacity is important for this work and shall be discussed briefly. This property depends on the amount of light scattered by the material, which is proportional to the square of the difference of the refractive index of the two components and the sixth power of the radius of the dispersed phase, assuming very small particles.¹⁶ Therefore, optical transparency depends on the type of phase separation and domain size. If the refractive indices of the two polymers match, the mixtures should be clear.^{6b}

High-energy radiation attacks the fluorocarbon polymer backbone, creating a significant amount of graft copolymer. This grafting increases mutual solubility of the two components, reducing the refractive index difference of the phases¹⁷ or may produce smaller phases,^{14,18,19} both results tending to improve transparency.

An alternate route to optical clarity lies in the use of thermodynamically soluble blends.²⁰

EXPERIMENTAL

A Viton A type, high-viscosity series of fluoroelastomers were obtained from DuPont de Nemours Co., in an extruded chunk form. Trimethylolpropane trimethacrylate (TMPTM) was obtained from Monomer-Polymer Laboratory, and *n*-butyl acrylate was obtained from Borden Chemical. The energy sources included a Co-60 gamma source and a UV source located at Lehigh University and a beta source located at Radiation Dynamics, Inc., Long Island, New York. Samples of fluorocarbon elastomers containing between 0% and 7% TMPTM were prepared for one series, and samples containing 1% TMPTM and 15%–30% *n*-butyl acrylate were prepared for a second series. Because of the low boiling point of the *n*-butyl acrylate monomer, evaporation and homogeneous mixing were a problem at lower concentration levels.

The fluorocarbon elastomers were mixed with the monomers in a Brabender Plasticorder to provide homogeneous mixing. The monomer was added on a weight percent basis. For UV-irradiated samples, 0.5% benzoin was included as an activator. The mixtures were compression molded at 120°C between Mylar sheets to form slabs of dimensions 4 in. × 6 in. × 0.03 in. These slabs were then irradiated without the removal of the Mylar to reduce the oxygen level and provide smooth, clean surfaces.

β - and γ -irradiation levels were between 0 and 10 Mrad, while the UV dose was for 24 hr, provided by two lamps. Each lamp contained two 48 in. long tubular ultraviolet lights (General Electric F40BL, $\lambda = 350$ nm). Each lamp was situated about 4 in. from either face of the sample to provide continuous uniform exposure of the UV light over the entirety of the sample.

Studies on the irradiated samples included (1) qualitative and quantitative optical comparisons with the linear fluoroelastomer, (2) shear modulus G at room temperature, (3) shear modulus versus temperature, (4) shear modulus–creep measurements at 100°C, (5) stress relaxation and creep recovery measurements, (6) dynamic mechanical spectroscopy (DMS), (7) swelling and extraction studies, and (8) stress–strain studies. Characterization 1 was done on a double-beam Beckmann DK-2A recording spectrophotometer at $\lambda = 460$ μm . Samples were clamped between two glass microscope slides with a drop of silicone oil between the sample surfaces and glass slides. Two slides with a drop of oil between them were used as a reference. Methods 2, 3, and 4 were obtained on a Gehman torsional stiffness tester.²² The results were reported as $3G$, which corresponds to Young's modulus. Method 5 was done on a stress relaxometer, and method 6 on a Rheovibron Model DDVII from -80 to $+30^\circ\text{C}$ at 110 Hz. Experiment 7 was done in test tubes, while experiment 8 involved an Instron. The Instron provides a means of elongating the sample at a constant rate; the stress is measured as a function of time. The samples were cut into dumbbell shape in order that the ultimate failure take place at the center of the sample and not be affected by any stress concentration at the instrument jaws.

RESULTS

Gehman Torsion and DMS

Gehman torsion studies as a function of time, temperature, monomer II level, and radiation dose level provided a means for studying glass transition behavior and creep moduli of the semi-II systems. Dynamic mechanical spectroscopy also allowed the study of the glass transition behavior of these materials and to obtain detailed information about molecular mixing from the loss modulus peaks.

The modulus-time creep curve, Figure 1, for γ -irradiated fluorocarbon samples containing 3% TMPTM show that at higher radiation doses the materials possess improved creep resistance at 100°C. This elevated temperature was selected to yield measurable creep values in a reasonable time span. In particular, the 6.3-Mrad sample shows almost a flat curve for long times. By contrast, creep behavior remains significant at lower dose levels at all times of observation.

Figure 2 shows the modulus-temperature curve for the 3% TMPTM, 6.3-Mrad sample (above). A single T_g at about -20°C is observed for this semi-II composition, the same T_g as for the linear fluorocarbon homopolymer, shown as the dashed line. The addition of the TMPTM network appears to broaden the lower portion of the glass transition, so the rubbery plateau is not fully reached until approximately 80°C , explaining the significant short time creep for this sample in Figure 1 and suggesting modest phase segregation between the fluorocarbon elastomer and the TMPTM network. Creep curves for analogous samples irradiated with beta radiation are presented in Figure 3. Also included is the creep curve for a similar sample irradiated with low-energy UV and appropriate blank compositions, all at $100 \pm 2^\circ\text{C}$.

As with the γ -irradiated samples, the 3% TMPTM samples, irradiated in the upper range of 5.0 to 7.5 Mrad of beta radiation, demonstrate good creep resistance. The 5% TMPTM sample also shows excellent creep resistance, but for an unknown reason appears convex downward at long times. This may be related to the slow relaxation of the phase-segregated acrylic portion of the 5% TMPTM samples, as indicated by their turbidity (see below). However, even the inclusion of only 1% TMPTM provides an obvious (but inadequate) reduction in the creep behavior of the fluorocarbon elastomer.

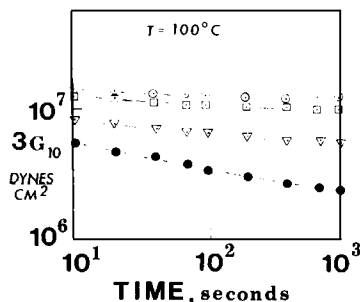


Fig. 1. Modulus-time creep curves at 100°C for γ -irradiated fluorocarbon samples containing 3% TMPTM. High radiation doses impart good creep resistance: (○) 6.30 Mrad; (□) 4.96 Mrad; (△) 1.58 Mrad; (●) 0.80 Mrad.

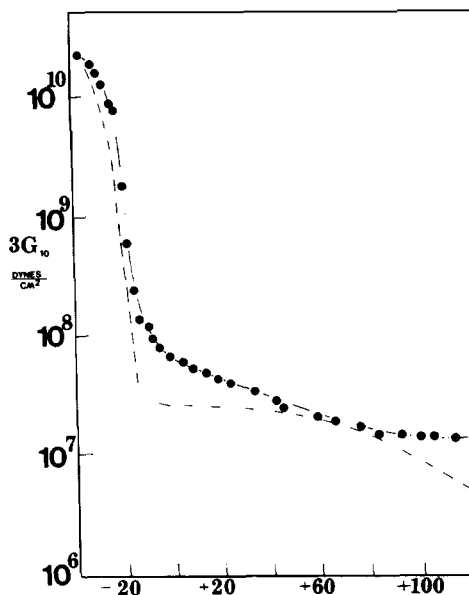


Fig. 2. Modulus-temperature curve for γ -irradiated 3% TMPTM, 6.3-Mrad sample. A single T_g at about -20°C observed: (---) linear polymer; (●) crosslinked material.

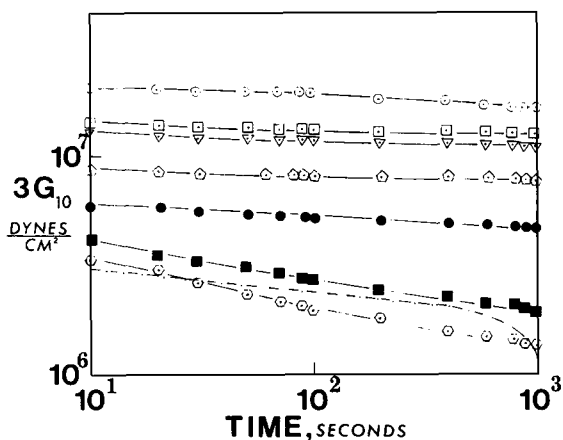


Fig. 3. Modulus-time creep curves for fluorocarbon samples irradiated with β radiation or UV. Good creep resistance observed at high dose levels and TMPTM concentrations: \circ 5% TMPTM, 5.0 Mrad; \square 3% TMPTM, 5.0 Mrad; ∇ 3% TMPTM, 7.5 Mrad; \triangle 1% TMPTM, 7.5 Mrad.

Low-energy UV produces samples that show only modest reduction in their creep behavior at the 3% TMPTM concentration level. While the initial modulus is slightly raised, the creep behavior is almost identical with that of an unirradiated sample containing 3% TMPTM. As discussed below, the low-energy UV is believed to be less effective in promoting the mutual grafting of the two components.

The temperature dependence of the dynamic storage modulus E' and the dynamic loss modulus E'' for the 3% sample irradiated with 5.0 Mrad of β radiation is illustrated in Figure 4. The 7.5-Mrad sample follows identical E' and

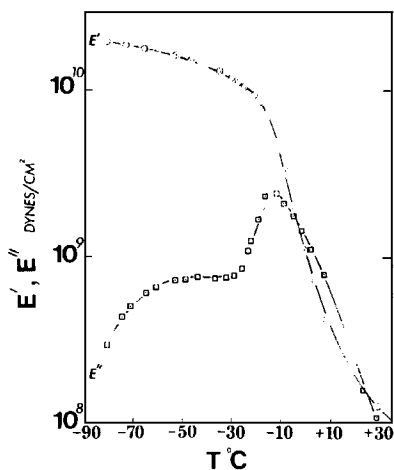


Fig. 4. Temperature dependence of dynamic modulus E' and dynamic loss modulus E'' for fluorocarbon elastomer samples irradiated at 5.0 Mrad with β radiation.

E'' curves. At 110 Hz, the apparent T_g is about -13°C . At 0.1 Hz, a value of about -30°C would be obtained for T_g , using the time-temperature superposition principles; this result is in rough agreement with the T_g obtained for the corresponding γ -irradiated sample (Fig. 2).

Table I lists the 10-sec modulus at room temperature for fluorocarbon elastomer samples containing 0%, 1%, 3%, or 5% TMPTM and irradiated over a range of 0 to 10.0 Mrad with β radiation. The 10-sec modulus remains relatively constant at a constant TMPTM concentration over the dose level range of 2.5 to 10.0 Mrad. This was also observed with the gamma-irradiation samples of similar compositions. The samples containing 1% TMPTM show little increase in modulus over the homopolymer, whereas the 3% and 5% samples show a slight increase. No significant differences between the 3% and 5% TMPTM samples, based on room-temperature modulus, can be noted. The fluorocarbon blanks (0% TMPTM) show a steady decline in modulus with increasing dose rate.

In the absence of radiation (0 Mrad), the TMPTM exhibits a plasticizing effect. Table I shows the modulus drops from 5.1×10^7 dynes/cm² for the unirradiated homopolymer to 2.7×10^7 dynes/cm² for the unirradiated fluorocarbon containing 3% TMPTM.

The drop from 5.1 to 3.1×10^7 dynes/cm² on first irradiating the 0% TMPTM sample may indicate the destruction of some molecular order, such as incipient crystallization. At a constant dose level of 7.5 Mrad (Table II), the 10-sec

TABLE I
Room-Temperature Modulus ($3G$) for β -Irradiated Fluorocarbon Samples

Dose, Mrad	$3G$ at 20°C , dynes/cm ²			
	0% TMPTM	1% TMPTM	3% TMPTM	5% TMPTM
0.0	5.1×10^7	—	2.7×10^7	—
2.5	3.1×10^7	3.4×10^7	4.3×10^7	4.1×10^7
5.0	2.9×10^7	2.9×10^7	4.0×10^7	4.1×10^7
7.5	2.9×10^7	3.6×10^7	4.3×10^7	4.8×10^7
10.0	2.5×10^7	2.8×10^7	3.9×10^7	4.5×10^7

TABLE II
Room-Temperature Modulus ($3G$) for Fluorocarbon Samples Irradiated at 7.5 Mrad with β -Radiation

% TMPTM	$3G$ at 20°C, dynes/cm ²
0.0	2.9×10^7
1.0	3.6×10^7
2.0	3.5×10^7
3.0	4.3×10^7
4.0	3.3×10^7
5.0	4.8×10^7
7.0	6.4×10^7

modulus increases with increasing TMPTM concentration as predicted by the theory of rubber elasticity. Above the 3% TMPTM level, the materials become hazy or turbid, suggestive of significant phase separation. This will be discussed further below.

The substitution of *n*-butyl acrylate (plus 1% TMPTM as crosslinker) for the TMPTM to form a lightly crosslinked polymer, network II, subsequently lowered the modulus of the homopolymer. In Figure 5, the modulus is seen generally to decrease as the concentration level on *n*-butyl acrylate is increased. Haziness was significantly present in these materials, especially at high *n*-butyl acrylate concentration and low β levels, indicating phase separation usually encountered in graft copolymer and IPN materials. Similar samples polymerized by UV radiation were highly opaque.

Stress Relaxation and Creep Recovery

Stress relaxation studies are analogous to creep studies but are more amenable to theoretical treatment. In stress relaxation studies, the sample is elongated by a definite amount and the force necessary to maintain this elongation is

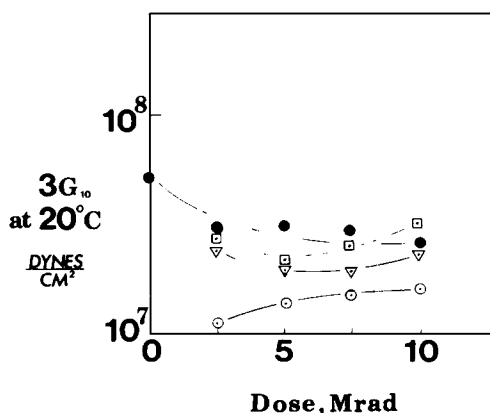


Fig. 5. Room-temperature modulus vs. β radiation dose level for fluoroelastomers at average *n*-butyl acrylate concentrations of 0%–30% with 1% TMPTM as crosslinking agent. Acrylate tends to lower the modulus of the homopolymer: (●) 0% butyl acrylate; (□) 15% butyl acrylate; (▽) 20% butyl acrylate; (○) 30% butyl acrylate.

measured as a function of time. A time-dependent Young's modulus $E_r(t)$ is so obtained. Creep recovery then follows as the stress is removed. During creep recovery, the sample length is measured as a function of time. A linear material is expected to recover slower and to a lesser extent than a crosslinked sample, because only physical crosslinks of a temporary nature are present.

Figure 6 illustrates the results of the stress relaxation studies. The downward slope of the relaxation curve is much greater for the fluorocarbon homopolymer blank due to its uncrosslinked linear state. The 3% TMPTM samples show only slight stress relaxation. Irradiation with 5.0 or 7.5 Mrad of beta radiation produces almost identical relaxation and creep recovery behavior, indicating complete polymerization at 5 Mrad.

Table III shows the recovered length of the stretched samples after 4 days. Creep recovery is much faster for the semi-II samples containing β -irradiated TMPTM than its linear counterpart. Originally stretched about 50% for 24 hr, the crosslinked systems recovered to within 4% or 5% of their initial length. The blank sample recovered to within only 18% of its initial length, indicating important differences in such practical properties as permanent set.

Turbidity

In order to determine quantitatively the actual light transmittance of the semi-II compositions, a clarity study was undertaken. The amount of light ($\lambda = 460 \mu\text{m}$) transmitted by the samples was determined by experiment. From the transmission data so obtained, the turbidity τ was calculated by means of Beer's law²³:

$$I = I_0 e^{-\tau x} \quad (2)$$

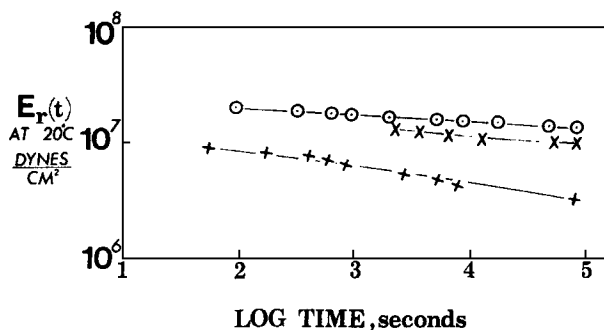


Fig. 6. Stress relaxation curves for fluoroelastomer samples irradiated with β radiation. 3% TMPTM reduces the relaxation behavior of the homopolymer substantially: (○) 3% TMPTM, 7.5 Mrad; (×) 3% TMPTM, 5.0 Mrad; (+) 0% TMPTM, 0.0 Mrad.

TABLE III
Creep Recovery Table for Fluorocarbon Elastomers, β -Irradiated

Sample	Original length, cm	Stretched (24 hr) length, cm	Length after 4 days Recovery, cm	% Recovery
3% TMPTM, 5.0 Mrad	2.46	3.46	2.58	95
3% TMPTM, 7.5 Mrad	2.57	3.55	2.68	96
0% TMPTM, 0.0 Mrad	2.40	3.75	2.83	82

where x represents the sample thickness, I_0 equals 100% transmittance, and I equals the recorded transmittance.

Due to the nature of the double-beam experiment, reflection of light by the front and back surface of the samples was internally corrected. The fluorocarbon sample was placed between two glass slides with a drop of silicone oil between the faces of the sample and the slides. Because the medium through which the light traveled before entering the sample (glass and silicone oil) has approximately the same refractive index as the fluorocarbon material, no significant internal reflection was expected. As described above, the "blank" in the other beam consisted of two glass slides with a drop of silicone oil between them.

Tables IV through VII list the turbidity data of the several samples irradiated with γ radiation, β radiation, or UV.

The materials containing 3% TMPTM irradiated with γ or β radiation have similar optical properties, with somewhat higher levels of turbidity than the linear fluorocarbon homopolymer. The turbidity of the unirradiated fluorocarbon homopolymer provides a baseline comparison for determining the actual increase in turbidity created by the addition of the second polymer network. It is interesting to note that the initial addition of 3% TMPTM increases turbidity somewhat. Upon irradiation, the turbidity actually decreases again. At higher concentration levels of TMPTM (5%), even after polymerization, a much greater degree of turbidity can be noted.

Table IV shows the turbidity level of the fluorocarbon samples as functions of TMPTM level and β -irradiation dose level. The value of $\tau = 0.15$ for the 3% TMPTM and 5-Mrad irradiation should be noted as the lowest value for the TMPTM-containing samples. At 5% TMPTM, the turbidity jumps, indicating increased haze and probably phase separation.

Table V explores the turbidity of 3% TMPTM samples as a function of γ -irradiation dose. As with Table IV, the turbidities are low, indicating a high degree of optical clarities.

For the *n*-butyl acrylate (1% TMPTM) system, Table VI, turbidity decreases as dose level increases at 15% and 20% concentration levels. At higher concentrations, a minimum is observed for reasons not yet clear.

Table VII shows the turbidity of the UV-irradiated samples containing *n*-butyl acrylate (1% TMPTM) or TMPTM. In both cases, the turbidity is significantly greater than similar samples polymerized by β or γ radiation.

TABLE IV
Turbidity (τ) of β -Irradiated Fluorocarbon Samples Calculated Using Beer's Law^a

% TMPTM	Dose, Mrad	I	Turbidity τ
0.0	0.0	88	0.10
0.0	5.0	85	0.12
3.0	0.0	51	0.45
3.0	2.5	70	0.20
3.0	5.0	78	0.15
3.0	7.5	60	0.29
3.0	10.0	61	0.30
5.0	2.5	37	0.71
5.0	5.0	40	0.65
5.0	7.5	20	1.14
5.0	10.0	18	1.26

^a $I = I_0 e^{-\tau x}$ ($\lambda = 460 \mu\text{m}$).

TABLE V
Turbidity (τ) of γ -Irradiated Fluorocarbon Samples Calculated Using Beer's Law^a

% TMPTM	Dose, Mrad	I	Turbidity τ
3	1.3	65	0.24
3	2.5	60	0.28
3	3.8	64	0.25
3	5.2	62	0.26
3	6.2	63	0.25

$$^a I = I_0 e^{-\tau x} (\lambda = 460 \mu\text{m}).$$

TABLE VI
Turbidity (τ) of β -Irradiated Fluorocarbon/Acrylic IPN Samples Calculated Using Beer's Law^a

% Butyl acrylate (1% TMPTM)	Dose, Mrad	I	Turbidity τ
15	2.5	33	0.64
15	5.0	56	0.32
15	7.5	60	0.38
15	10.0	68	0.32
20	2.5	17	1.07
20	5.0	54	0.46
20	7.5	57	0.32
20	10.0	64	0.29
25	2.5	6	1.31
25	5.0	44	0.50
25	7.5	30	0.61
25	10.0	18	0.88
30	2.5	5	1.41
30	5.0	44	0.50
30	7.5	36	0.56
30	10.0	25	0.85

$$^a I = I_0 e^{-\tau x} (\lambda = 460 \mu\text{m}).$$

TABLE VII
Turbidity (τ) of UV-Irradiated Fluorocarbon Samples Calculated Using Beer's Law^a

Composition	I	Turbidity τ
15% Butyl acrylate (1% TMPTM)	3	2.12
20% Butyl acrylate (1% TMPTM)	18	1.18
25% Butyl acrylate (1% TMPTM)	22	0.91
30% Butyl acrylate (1% TMPTM)	25	0.85
1% TMPTM	82	0.14
3% TMPTM	50	0.46

$$^a I = I_0 e^{-\tau x} (\lambda = 460 \mu\text{m}).$$

The decided jump in turbidity for the *n*-butyl acrylate system and at higher levels of TMPTM may be related to phase separation.^{6a} The greater clarity of the high-energy β - or γ -irradiated materials over the UV-irradiated materials probably results from reduced phase segregation, greater compatibility, etc., as induced by higher grafting levels.

Swelling and Extraction

Swelling and extraction studies were performed on selected fluorocarbon elastomer samples to determine the crosslink density (network chain segments between crosslinks) and the % extractable material in each sample. The results are tabulated in Table VIII. Acetone was used as solvent or swelling agent since it dissolved the untreated linear fluorocarbon homopolymer.

The Flory–Rehner equation (24) was used to calculate the moles of active network chains (n) per cm^3 :

$$-\ln(1 - v_2) + v_2 + \chi_1 v_2^2 = V_1 n (v_2^{1/3} - v_2/2) \quad (3)$$

where v_2 is the volume fraction of polymer in the swollen mass, V_1 is the molar volume of the solvent, and χ_1 is the Flory solvent–interaction parameter.

The moles of active network chains per cm^3 are seen to be functions of both the radiation dose and the percent of TMPTM, as shown in Table VIII. In general, the crosslink density increases up to 3% TMPTM and 5 Mrad of radiation, then stays nearly constant.

Even if no crosslinking monomer was present, irradiated fluorocarbon homopolymer samples did not dissolve, but only swelled in acetone. As the radiation dose level increased from 2.5 to 10.0 Mrad, the % extractables decreased at constant TMPTM level, and hence it was concluded that some additional crosslinks are introduced. With 1% TMPTM, there is no significant change over the irradiated homopolymer in either % extractables or moles of active chains. With 3% and 5% TMPTM samples irradiated with β radiation, as the dose level increases, the % extractables material decreases, moles of active chains increase, and hence it can be concluded that crosslink density increases.

In comparison, the low-energy UV-irradiated samples (containing 3% TMPTM) showed 85% extractable material, indicating a very low level of true crosslinking. Even the β -irradiated fluorocarbon homopolymer samples (with

TABLE VIII
Crosslink Density and % Extracted Material for Various Fluorocarbon Samples Using Acetone as Solvent

Sample	Dose Mrad	Moles active chain ^a	% Extracted
Blank	0.0	dissolved	100
Blank	2.5	1.65×10^{-5}	60
Blank	5.0	2.76×10^{-5}	34
Blank	7.5	4.86×10^{-5}	24
Blank	10.0	6.10×10^{-5}	21
1% TMPTM	5.0	4.54×10^{-5}	31
1% TMPTM	7.5	4.97×10^{-5}	24
3% TMPTM	2.5	1.75×10^{-4}	29
3% TMPTM	5.0	1.87×10^{-4}	21
3% TMPTM	7.5	1.22×10^{-4}	21
3% TMPTM	10.0	2.34×10^{-4}	16
5% TMPTM	2.5	1.31×10^{-4}	32
5% TMPTM	5.0	1.80×10^{-4}	22
5% TMPTM	7.5	2.45×10^{-4}	16
5% TMPTM	10.0	1.73×10^{-4}	10
3% TMPTM	UV	2.45×10^{-5}	85

^a Calculated by the Flory–Rehner Equation.

no TMPTM) contained lower amounts of extractables than the UV-irradiated systems. Hence, the high energy of the β irradiation alone is shown to introduce significant crosslinks. However, the combination of β radiation and TMPTM gave the highest crosslink level.

Stress-Strain Mechanical Studies

Stress-strain curves were obtained for several 3% TMPTM, 5-Mrad samples on an Instron. A fully formulated silicone rubber sample and a blank, untreated fluorocarbon elastomer were included for comparison. Typical results are illustrated in Figure 7. While the silicone rubber had about a 30% higher tensile stress to break, the elongation to break for the fluorocarbon elastomers was nearly twice as high, reaching values of approximately 600%. The detailed data for all the specimens is summarized in Table IX. As shown, the tensile strength on specimen E2 was abnormally low, more than three standard deviations away from the average values excluding it. Therefore, that result should be discarded. Perhaps the sample contained an extraneous flaw.

The area under the stress-strain curves yields the energy required to break the samples. As shown in Table X, the value for the fluorocarbon elastomer exceeds the value for the silicone rubber by a factor of about 2. The units are ergs/cm^3 and represent absolute equivalent values of work needed to fail a unit cube of the material in the tensile mode. As explained above, the actual samples were cut in the form of standard dumbbell shapes.

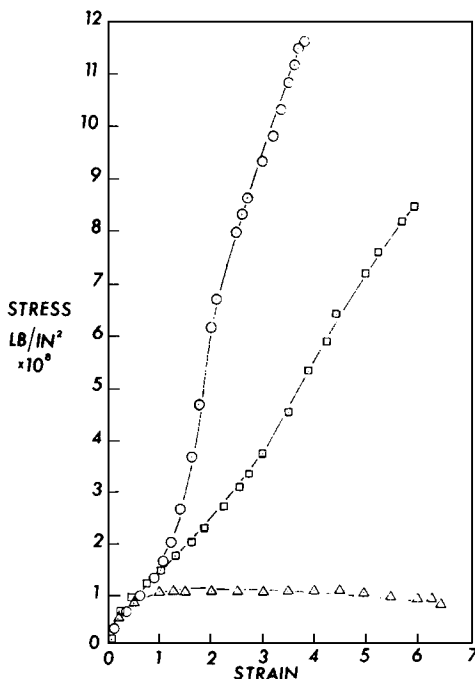


Fig. 7. Stress-strain of fluorocarbon elastomers compared with fully formulated silicone rubber: (○) silicone rubber; (□) 3% TMPTM, 5.0 Mrad; (△) blank fluorocarbon.

TABLE IX
Ultimate Tensile Strength and % Elongation at Break for Various Fluorocarbon Elastomer Samples and Silicone Rubber^a

Sample	Ultimate tensile strength at break, psi	% Elongation at break
E 1 (3% TMPTM, 5.0 Mrad)	900	440
E 2 (3% TMPTM, 5.0 Mrad)	580	520
E 3 (3% TMPTM, 5.0 Mrad)	850	630
S 1 (3% TMPTM, 7.5 Mrad)	870	360
S 2 (3% TMPTM, 7.5 Mrad)	760	490
S 3 (3% TMPTM, 7.5 Mrad)	850	590
S 4 (blank linear fluorocarbon)	110	120
Silicone rubber	1177	380

^a Sample S 4 began to yield at a load of 1.5 lb. The tensile strength reported is the maximum just prior to yielding. Sample E 2 has a questionable value for the ultimate tensile strength at break. Average tensile strength at break: including sample E 2, AVG. = 800 psi; excluding sample E 2, AVG. = 840 psi. Standard deviation of ultimate tensile strength: including sample E 2, $\Sigma = 118$ psi; excluding sample E 2, $\Sigma = 52$ psi.

TABLE X
Energy Required to Break Selected Samples^a

Sample	Energy to break, ergs/cm ³
Fluorocarbon elastomer (3% TMPTM, 5.0 Mrad)	3.35×10^8
Blank linear fluorocarbon	8.90×10^7
Silicone rubber	1.47×10^8

^a The energy to break is calculated by graphically integrating a graph of stress vs strain. The values reported pertain to a unit volume of material.

DISCUSSION

Grafting

Both β and γ radiation can attack the fluorocarbon polymer backbone, generating a certain amount of grafts with monomer II, polymer II chains, or fully formed networks present. This grafting between the two phases, induced by the high-energy radiation, increases compatibility and/or reduces phase domain size.

If two incompatible polymers are mixed, the individual polymer domains normally retain the glass transitions of their respective parent homopolymers; therefore, such a material should be expected to exhibit two principal glass transitions. If significant molecular mixing takes place, the transitions will be broadened and/or their T_g values will be closer. Correspondingly, two maxima will be observed in the mechanical loss spectrum.^{6a}

The semi-II consisting of the fluorocarbon elastomer and TMPTM behaves much like a homopolymer, having only one principal glass transition and one maximum in the mechanical loss spectrum (E''), as shown in Figure 4. This is probably due to the low concentration of the TMPTM component and/or to the grafting induced by the high-energy radiation and indicates a lack of significant phase separation.

The optical properties of the semi-II strongly suggest the presence of grafting. While β - and γ -irradiated samples tended to remain clear, the UV-irradiated samples always exhibited significant haze levels (compare Table VII turbidity values with those listed in Tables IV, V, and VI). High clarity can be maintained if phase separation is suppressed, phase domains are made smaller, and/or the composition within the phases is made more alike.^{25,26} Unfortunately, the present data cannot distinguish between these possibilities.

A critical concentration level for TMPTM appears to be about 3%, above which the material becomes hazy, indicating the formation of two distinct phases. High-turbidity materials are characteristic of graft copolymers containing appreciable amounts of polymer II.

Further evidence for high-energy grafting is the fact that the UV-irradiated 3% TMPTM samples have a great amount (80%) of extractable material compared to about 20% extractables for similar beta-irradiated systems (see Table VIII). It is concluded that the β radiation forms a more monolithic network by grafting the fluorocarbon chains to the TMPTM network joining the chains together more efficiently and hence reducing the extractable material.

High-Energy Radiation Effects on Fluorocarbon Homopolymer

Other phenomena observed in this study suggest that high-energy radiation, in the absence of crosslinking monomer, has two effects:

1. The "as is" elastomer may have some kind of molecular order such as incipient crystallinity, which is destroyed by radiation. This would account for the apparent decrease in modulus of fluorocarbon homopolymer samples irradiated with γ or β radiation (see Table I). Some degree of crystallinity may be present in the raw fluorocarbon material, which reinforces and strengthens the homopolymer.^{6c} If radiation destroys this crystallinity, the material's modulus necessarily decreases. Addition of TMPTM followed by high-energy β or γ irradiation provides a crosslinked network which binds up the linear fluorocarbon and participates in a significant degree of grafting. This reduces creep but has no significant effect on modulus, because elastomer modulus is a measure of both physical and chemical crosslinks and the former predominate in numbers in lightly crosslinked systems.

2. Some crosslinking of the chains occurs to form a network structure. The irradiated fluorocarbon homopolymer even in the absence of TMPTM does not dissolve in acetone (Table VIII), suggesting that the chains are no longer free but linked together into a network. Further, as radiation dose level increases, less and less material is extracted and the moles of active chains increase. Continued crosslinking at higher dose levels is suggested.

Physical Entanglements Versus Chemical Crosslinks

In both γ - and β -irradiated systems, it was observed that the modulus remained relatively constant at a constant TMPTM concentration over a dose level range of 2.5 to 10.0 Mrad (Table I). This constant modulus can be attributed to the fact that physical entanglements most likely outnumber chemical crosslinks, as mentioned above (see schematic diagram in Fig. 8). As the dose level increases, the increase in modulus measurements is only modest because of the

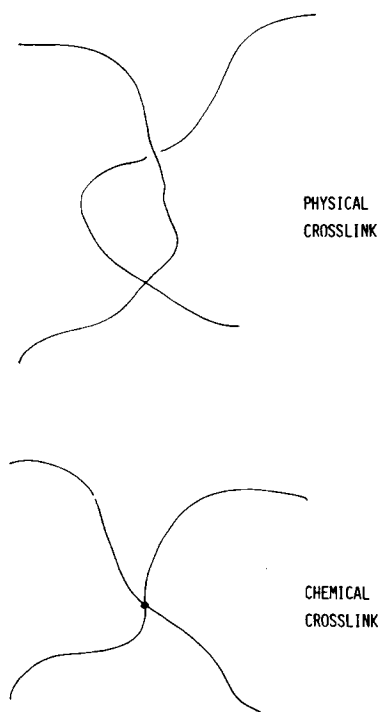


Fig. 8. Schematic illustration of a physical crosslink and chemical crosslink. Chemical crosslink anchors chains whereas physical crosslink is an entanglement, subject to slippage.

far greater number of physical entanglements (see Table XI). Under present experimental conditions, it may be that the modulus, through the equation

$$G = nRT \quad (4)$$

is measuring both the physical and chemical crosslinks while swelling is a better measure of chemical crosslinks.

Tabulated in Table XI are selected values of n (moles of active network chains) calculated by the Flory–Rehner equation, eq. (3), which probably accounts for only chemical crosslinks, while the equation $G = nRT$ accounts for both physical and chemical crosslinks. In all cases, as expected, the values are higher for the latter due to physical entanglements. This difference represents moles of physical entanglements, shown in the last column of Table XI. It is significant

TABLE XI
Moles Active Chains

Sample	Flory-Rehner Eq.	$3G$	Moles physical crosslinks
Blank, 7.5 Mrad	4.9×10^{-5}	3.9×10^{-4}	3.4×10^{-4}
1% TMPTM, 7.5 Mrad	5.0×10^{-5}	4.9×10^{-4}	4.4×10^{-4}
3% TMPTM, 5.0 Mrad	1.9×10^{-4}	5.4×10^{-4}	3.5×10^{-4}
3% TMPTM, 7.5 Mrad	1.2×10^{-4}	5.8×10^{-4}	4.6×10^{-4}
5% TMPTM, 5.0 Mrad	1.8×10^{-4}	4.9×10^{-4}	3.1×10^{-4}
5% TMPTM, 7.5 Mrad	2.5×10^{-4}	6.7×10^{-4}	4.3×10^{-4}
3% TMPTM, UV	2.5×10^{-5}	4.3×10^{-4}	1.9×10^{-4}

that these values are greater than the moles of active chains attributed to chemical crosslinks.

It should be noted that the physical crosslink level remains constant near 4×10^{-4} mol/cm³, as would be expected because the entanglement of fluorocarbon chains remains nearly the same. This value corresponds to an M_c value of 5×10^3 g/mol. Most elastomers have physical entanglement M_c values between 4×10^3 and 15×10^3 g/mol.

Comparison of β Radiation, γ Radiation, and UV

From the data presented it appears that the high-energy radiation polymerization method produces greater grafting than the low-energy UV. If clear, low-creep materials are desired, β and γ irradiation is preferred over UV-irradiation polymerization methods.

β and γ radiation are apparently quite similar. Many of the samples showed comparable properties when irradiated by β or γ radiation at similar dose levels. However, in the turbidity study, it was observed that β irradiation produced somewhat clearer samples (compare Table IV to Table V).

There are slight differences in the actual reaction process. One difference between γ and β radiation is the actual rate of irradiation, which may affect the oxygen uptake of the system. In the slower polymerization induced by γ irradiation, there is more time for oxygen to diffuse into the material. The oxygen may react to form peroxides and hydroperoxides, which decompose to yield two free radicals of which one may generate one homopolymer II polymer molecule and one a graft copolymer site.¹⁸ In the absence of oxygen, direct grafting to TMPTM is encouraged, increasing grafting. Overall, β radiation appears to be more efficient and less time consuming.

Optimum Materials

The major properties sought in this research program were a fluorocarbon-based elastomer with reduced creep and great toughness combined with optical clarity. On the basis of mechanical and physical studies, the 3% level of TMPTM appears to be the best. Although creep and % extractable materials are lower at higher TMPTM levels (5%), optical considerations make 3% the necessary upper concentration limit.

High-energy radiation obviously provides materials superior to UV. Optimum properties were obtained between the dose levels of 5.0 and 7.5 Mrad of both γ and β radiation. This recipe clearly remains unoptimized but, as a feasibility study, provides a path by which the fully formulated material can be achieved.

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