Fermi National Accelerator Laboratory

FERMILAB-TM-1784

Development of Radiation Hard Scintillators

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May 1992

Presented at the International Conference on Radiation-Tolerant Scintillators and Detectors, Tallahassee, Florida, April 28-May 2, 1992.

Operated by Universities Research Association Inc. under Contract No. DE-AC02-76CHO3000 with the United States Department of Energy

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ABSTRACT

Substantial improvements have been made in the radiation hardness of plastic scintillators. Cylinders of scintillating materials 2.2 cm in diameter and 1 cm thick have been exposed to 10 Mrads of gamma rays at a dose rate of 1 Mrad/h in a nitrogen atmosphere. One of the formulations tested showed an immediate decrease in pulse height of only 4% and has remained stable for 12 days while annealing in air. By comparison a commercial PVT scintillator showed an immediate decrease of 58% and after 43 days of annealing in air it improved to a 14% loss. The formulated sample consisted of 70 parts by weight of Dow polystyrene, 30 pbw of pentaphenyltrimethyltrisiloxane (Dow Corning DC 705 oil), 2 pbw of p-terphenyl, 0.2 pbw of tetraphenylbutadiene, and 0.5 pbw of UVASIL299LM from Ferro.

KEYWORDS

Plastic Scintillator; Scintillator; Radhard; Radiation Resistant; Polystyrene

INTRODUCTION

A radiation hard plastic scintillator can be defined as a scintillator that does not exhibit a large decrease in light output when exposed to ionizing radiation and which can recover a substantial amount of its light output in a short time after being irradiated. A fast recovery after high dose rate irradiation may imply a smaller change in light output during low dose rate exposure to the same integrated dose. Significant improvements in radiation hardness have been achieved by combining with the base plastic, additives which can be expected to increase the diffusion rate of reactive species within the plastic and by using antiradiation (antirad) chemicals to scavenge peroxides and free radicals and by selecting the best primary and secondary wavelength shifters. The diffusion rate modifiers and antirad chemicals are seen to be synergistic. Many non-traditional plastics have also been examined as scintillator bases. None of these have given scintillators as good as the styrene family of plastics. For the most part, commercial polymers, not the usual monomers have been used as starting materials, and tests have been confined to readily available chemicals instead of synthesizing special compounds. Thus it is felt that the results can be scaled up readily to produce any desired amount of material. To further demonstrate that contention, materials have been prepared in a mixing extruder to make injection

molding pellets. We have also injection molded scintillator plates from pellets. One of the better rad hard formulations has been cast into 11.4 x 11.4 x .31 cm plates which have had keyhole shaped grooves machined into the plates for fiber insertion and radiation testing.

METHODS

Sample Preparation

Standard samples are cut from fabricated cylinders 2.2 cm in diameter. The samples are 1 cm thick and are carefully polished before testing. The cylinders are made by two methods. Samples containing diffusion enhancers such as the DC 705 oil are mixed together in a glass beaker surrounded by an aluminum temperature controlled block. The temperature is held at 343°C. The mixing is done by a glass stirring rod and a slow flow of nitrogen gas is directed into the beaker while stirring. When the mixture appears uniform it is removed from the aluminum block and put in a vacuum bell jar for debubblizing. It is then poured into a mold released glass tube and allowed to cool. Removal may be facilitated by cooling in a freezer. This method has the disadvantage of causing some yellowing from thermal degradation at this high temperature. A special apparatus is now being built to mix high viscosity materials under vacuum and then inject them directly into a mold. Tests with a prototype apparatus indicate that temperatures as low as 150°C may be enough and samples of excellent clarity are produced. Commercially, a Banbury type mixer could be used.

The second method is to combine the materials in a mixing extruder. To achieve a uniform feed of ingredients into the mixing extruder, the plastic pellets and the finely ground powdered shifters and antirads are premixed by tumbling with a very small amount of DC705 oil. The oil coats the pellets and causes the powders to stick uniformly to their surface. The cooled extruded strand is then chopped into pellets and injection or compression molded into cylinders. Compression molding uses much less material and thus is the process of choice. It has been found that bubble free cylinders are obtained by heating the pellets in a split cylindrical mold under very light pressure until molding temperature is reached. A few cold pellets are then introduced into the top of the mold under the piston and pressure is applied. The cold pellets allow air to escape from the hot mass below. For polystyrene, temperatures of 180°C and forces of 1000 kg were used.

Samples were made in sets of three. One served as a control and the other two were irradiated. Afterward one sample was annealed in air and one in nitrogen. Prior to irradiation, the samples were sealed into stainless steel tubes. The air was then evacuated through a needle valve and the tube was backfilled with nitrogen gas to a slight positive pressure, then sealed. The tubes were then shipped to the University of Michigan for irradiation. The irradiation was done in the Cobalt 60 facility. All samples reported here were irradiated at 1 Mrad/h to a total of 10 Mrad.

Testing

Three types of testing were done on each sample. They were, measurement of the visible and near ultraviolet optical transmission spectra, measurement of the light output from incident radiation, and measurement of the annealing response. The

latter was measured as the time change of light output or optical transmission or the size of the visually discolored zone.

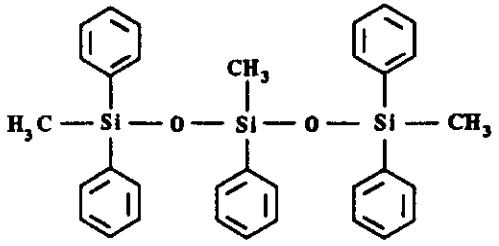
The optical transmission was measured with a Hewlett Packard Model 8451A spectrophotometer. Each sample was measured against air as a reference and also against an identical control sample. An irradiated sample measured against its control gives a direct measure of radiation induced change except for any small changes due to surface reflections etc. that may vary somewhat between measurements. The same variations are present when measuring against air, but if the sample appears unchanged at long visible wavelengths, as is the usual case, then before and after spectra may be normalized to the same value at these long wavelengths. After the normalization, the short wavelength changes are readily seen and may be compared with the other method. Transmission spectra are taken before irradiation, immediately after irradiation, and when pulse height measurements indicate that all annealing has occurred and the light output has stabilized. The primary interest in the optical measurements is to separate out how much of the decrease in light output with irradiation is due to absorption of light by formed color centers and how much may be due to other phenomena such as direct damage of shifter molecules.

Light output measurements are taken with a Hamamatsu R2154 photomultiplier tube. The sample is placed face down in the center of the photomultiplier tube face using a bit of methyl silicone oil to insure optical contact. A cobalt 60 source is placed in contact with the upper surface of the sample. The whole assembly is inside a black box. The photomultiplier output is connected to a Lecroy QVT model 3001 multichannel analyzer operating in the charge mode. The pulse height spectrum is displayed on an oscilloscope and the light output is taken as the voltage of the high charge edge of the spectrum measured at half height. The high voltage to the photomultiplier tube is adjusted before each set of measurements to give a consistent reading from a standard size sample made of polyvinyltoluene scintillator (Bicron BC408, chosen because of its exceptionally high light output). All results are reported in percent of PVT. Measurements are taken before irradiation, immediately after irradiation, and at periodic intervals until the pulse height becomes stable indicating that annealing is complete.

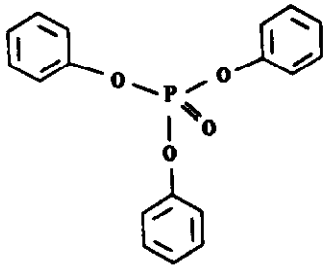
Annealing was also monitored by observing the visual changes in the sample. After irradiation, the samples are usually darkened in color from their initial clear state. Most often the color is yellow (indicating absorption of blue light) but sometimes in non-styrene base plastics is brown, black, or even bluish. With time the colored area seems to shrink inside the sample. A clear edge is usually evident between the more intensely colored interior zone and the less intensely colored area just below the surface of the sample. Periodic measurements are made with a ruler of the depth of the less intensely colored zone. Measurements are made to the nearest .04mm and are continued until the zone reaches the center of the sample at which point the more intensely colored zone disappears. Comparison of the annealing time by this method (called depth annealing) with the annealing time by pulse height measurement gives another indication of damage processes other than transmission loss. Both annealing measurements give information about recoverable and permanent damage processes.

EFFECTS OF DIFFUSION ENHANCERS

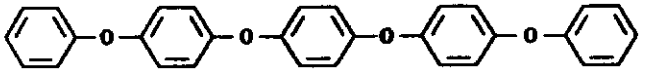
The reason for adding diffusion enhancers to the base plastic is to speed the anneal rate, both the oxygen anneal rate and internal anneal rate of recombining free radicals or other colored radiation byproducts. Figures 1 and 2 give the structural



Dow Corning DC705 Pentaphenyltrimethyltrisiloxane



Triphenylphosphate



Monsanto Santovac-5 Pentaphenylether

Fig. 1. Chemical structure of diffusion enhancers

formulas for some of the diffusion enhancers we have been considering. A small sample of the Santovac-5 has been obtained but not yet tested because of its very high price of over $2000/gal. The triphenylphosphate is a low cost material commonly used in PVC plastics. It has too high a vapor pressure to use by the method of combining ingredients in an open beaker. Therefore it is presently being tested in an epoxy based scintillator and if it shows promise there it will be tried again in polystyrene using the closed mixer-molder we are building. The HB-40 partially hydrogenated p-terphenyl shows some promise and should be inexpensive, but it must be distilled before use to eliminate it's yellow color. The before irradiation light output is not as high (60% of PVT) as with other materials, but the drop after irradiation is less, so the material warrants further investigation, especially so when concentration effects are considered. The HB-40 contains 3% non-hydrogenated p-terphenyl which complicates the question of how much primary shifter to add, if any.

Up to this point, the major effort has been on the higher light output formulations obtained using pentaphenyltrimethyltrisiloxane, which also appears more effective at increasing annealing rates. This material has been obtained as the common

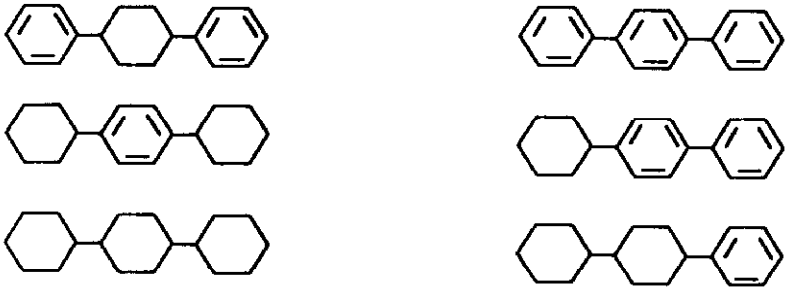


Fig. 2. Monsanto partially hydrogenated p-terphenyl

laboratory diffusion pump oil sold by Dow Corning as DC705 oil. Its cost is high at $94/lb, but not prohibitive. Figure 3 shows the effect of this oil on the radiation hardness. The base material is considered to be a mixture of Dow polystyrene XU-70252.00 and the DC705 oil. The ordinate in Fig. 3 is the % oil in the base mixture. Two parts-by-weight (pbw) of p-terphenyl as a primary shifter were added to 100 pbw of base mixture. The secondary shifter was 0.2 pbw of POPOP. The upper part of the figure shows a gradually increasing pulse height with % oil. This may indicate that the oil is a more efficient scintillator than the polystyrene. However, it is true that the first samples made were of the lower concentrations, so it is possible that the effect is only an artifact of improving technique. Nevertheless, the DC705 must be at least as efficient as the polystyrene. The lower portion of the figure shows the pulse height immediately after irradiation. There is no effect until the oil concentration reaches 30% after which there is a rapid improvement in radiation hardness. Figure 4 shows the pulse height annealing curves for samples with varying percentages of oil in the base mixture.

The 30% oil curve shows a significantly higher anneal rate, and the 32.5%, 35%, and 40% show similar but even higher rates. Figure 5 shows the depth anneal rate for the same samples. The effect of the oil concentration is even more dramatic, in fact the 40% oil sample showed no visual signs of yellowing. It should be noted that the 40% oil sample is undoubtedly too soft for practical application but the other concentrations may be acceptable. Mechanical testing will begin soon. No evidence of migration of the oil or the shifters has been observed. Plates 11.4 X 11.4 X 0.31cm have been cast from the 30% oil formulation and successfully machined with grooves for the insertion of shifter fibers. Figure 6 shows the absorption and emission curves measured for the DC705.

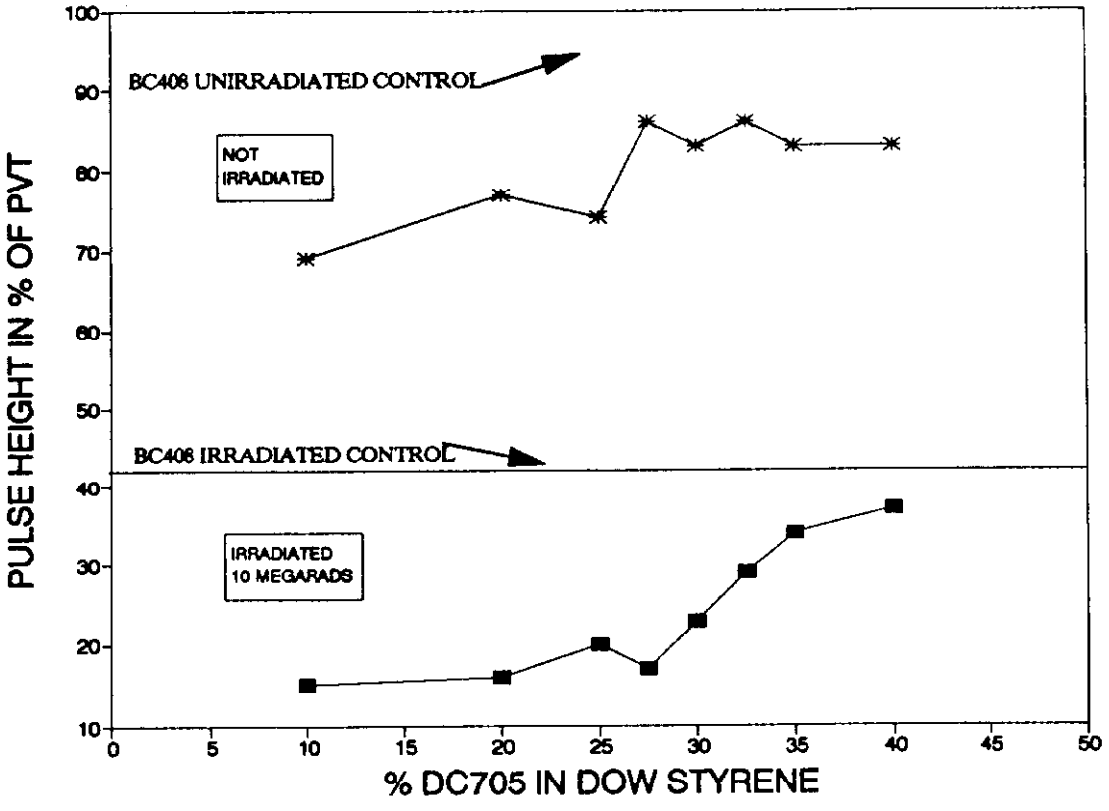


Fig. 3. Effect of DC705 concentration

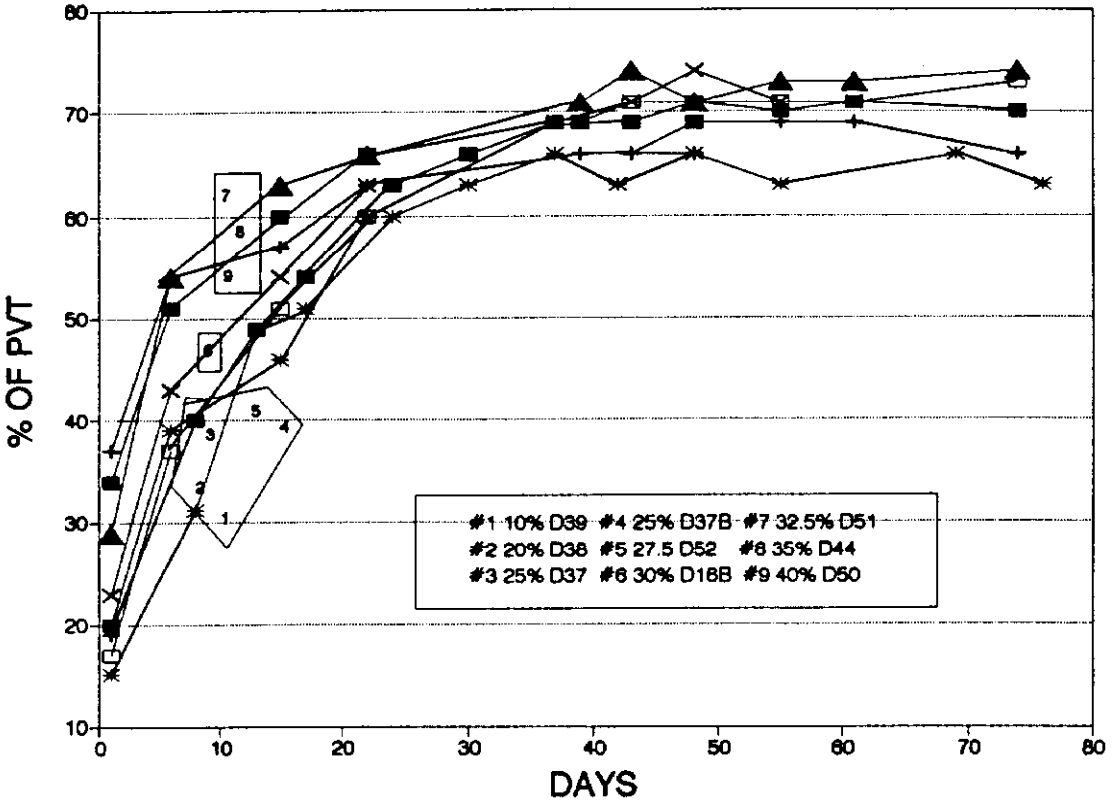


Fig. 4. Effect of oil content on pulse height annealing

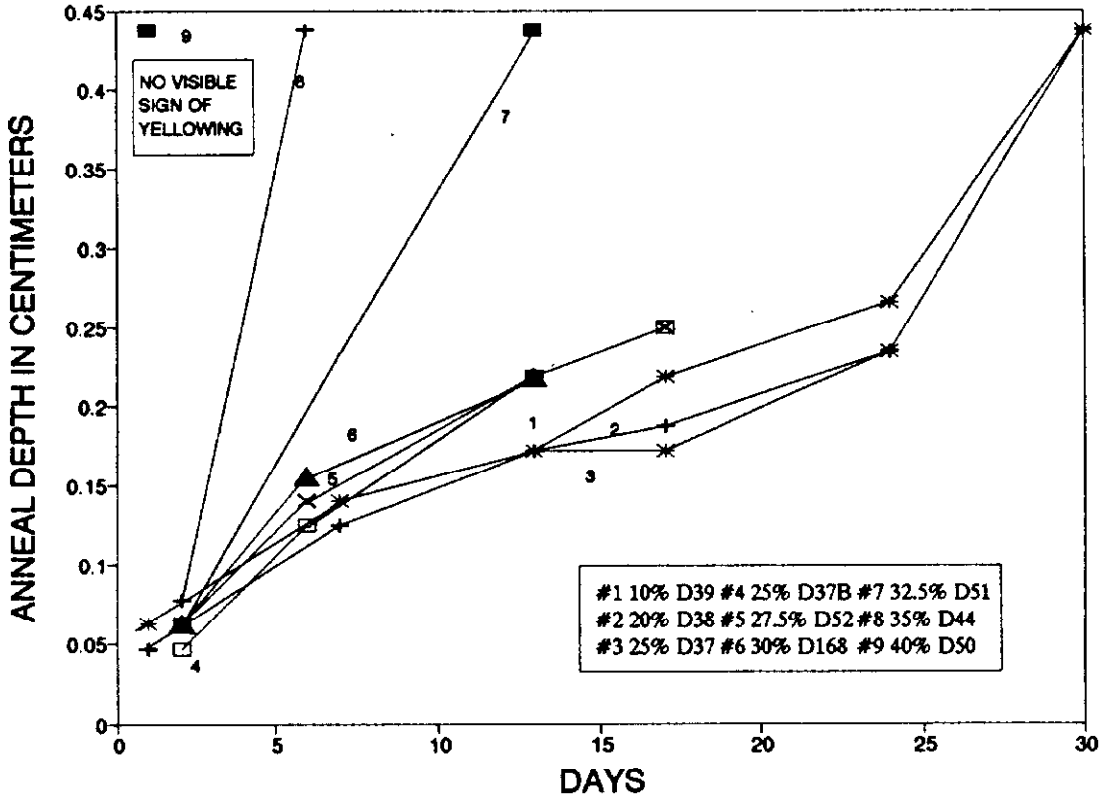


Fig. 5. Effect of oil content on anneal rate (% oil is given in the table)

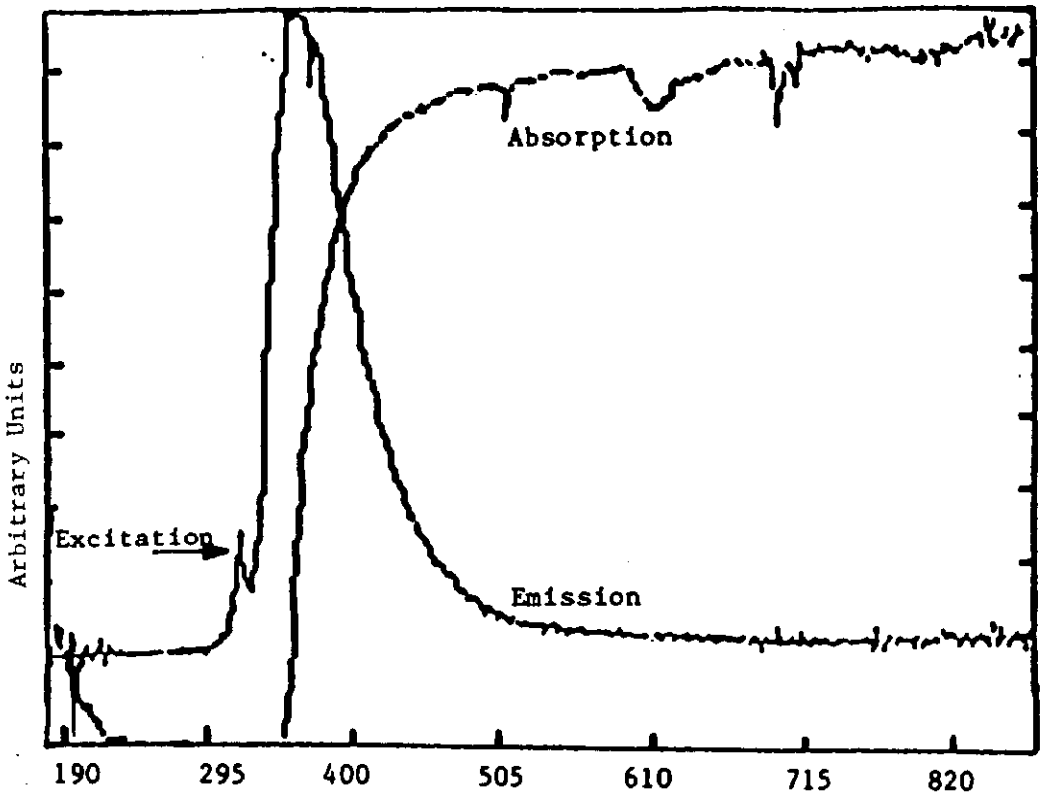


Fig. 6. Emission and absorption spectra of DC705

The measured decay time of a sample consisting of 70 pbw of Dow polystyrene, 30 pbw of DC705, 2 pbw of p-terphenyl, and 0.2 pbw of POPOP was 4 nanoseconds full width at half height. Thus it is seen that the DC705 has not caused an increase in the decay time of the scintillator. The measured decay time of an identical formulation except that the secondary shifter is TPBD (tetraphenylbutadiene) instead of POPOP was 5 nanoseconds full width at half height.

In the search for a less expensive diffusion enhancer than the DC705, another Dow oil has been tried. This is DC710 which is a phenylmethylpolysiloxane with trimethyl termination. When the formulation containing this oil cooled down it turned opaque white. Microscopic examination showed many small globular inclusions which are probably the oil coming out of solution in the polystyrene. The structure of this oil is not so very different from that of the DC705 oil, but its solubility is very different. The stability of the formulated scintillators is extremely sensitive to the relative solubility of all the ingredients.

EFFECT OF ANTIRADIATION ADDITIVES

Ten different antirad agents have been tried, some are free radical scavengers and some are antioxidants. All are common additives for thermoplastics to protect them from thermal and ultraviolet degradation. Most fall into four categories of chemicals, the hindered phenols, the hindered amines, the phosphites, and the thioethers. The thioethers and the hindered phenols are said to be synergistic. Mitsubishi International supplied samples of LA-57 and LA-77 which are hindered amines, AO-80 which is a hindered phenol, HP-10 which is a phosphite, and AO-412S which is a thioether. Enichem supplied samples of UVASIL 299 and UVASIL 299LM which are hindered amines. Ferro supplied a sample of UV-CHEK AM-340

which is a hindered phenol. Triphenylphosphite and triphenylphosphine were obtained from a chemical supply house. Figures 7 and 8 show the structural formulas of these materials. Figure 9 compares the effectiveness of the antirads in a formulation consisting of 70 pbw Dow polystyrene, 30 pbw DC705, 2 pbw p-terphenyl, .2 pbw POPOP, and .5 pbw of antirad. The light output as % of PVT is shown both before and after irradiation to 10 Mrads. Bicron BC408 is shown as a standard of comparison as is a sample without any antirad. All of the antirads were somewhat effective, with the UVASIL 299LM and the HP-10 being most effective. Anecdotal information says that antirads are not effective in making rad hard scintillators and if this is true it appears that the DC705 has made them effective in this case. This may be because the oil has increased the mobility of the antirads making it possible for them to reach the site of the damage. In this light, it is especially interesting that the UVASIL 299 is not as effective as the UVASIL 299LM which is identical except for its lower molecular weight and therefore increased mobility. It is possible that at higher concentrations of antirad the diffusion enhancing effect of the oil is not so necessary, but since some of the antirads may have an adverse effect on light output before irradiation it may be important to be able to keep their concentrations low.

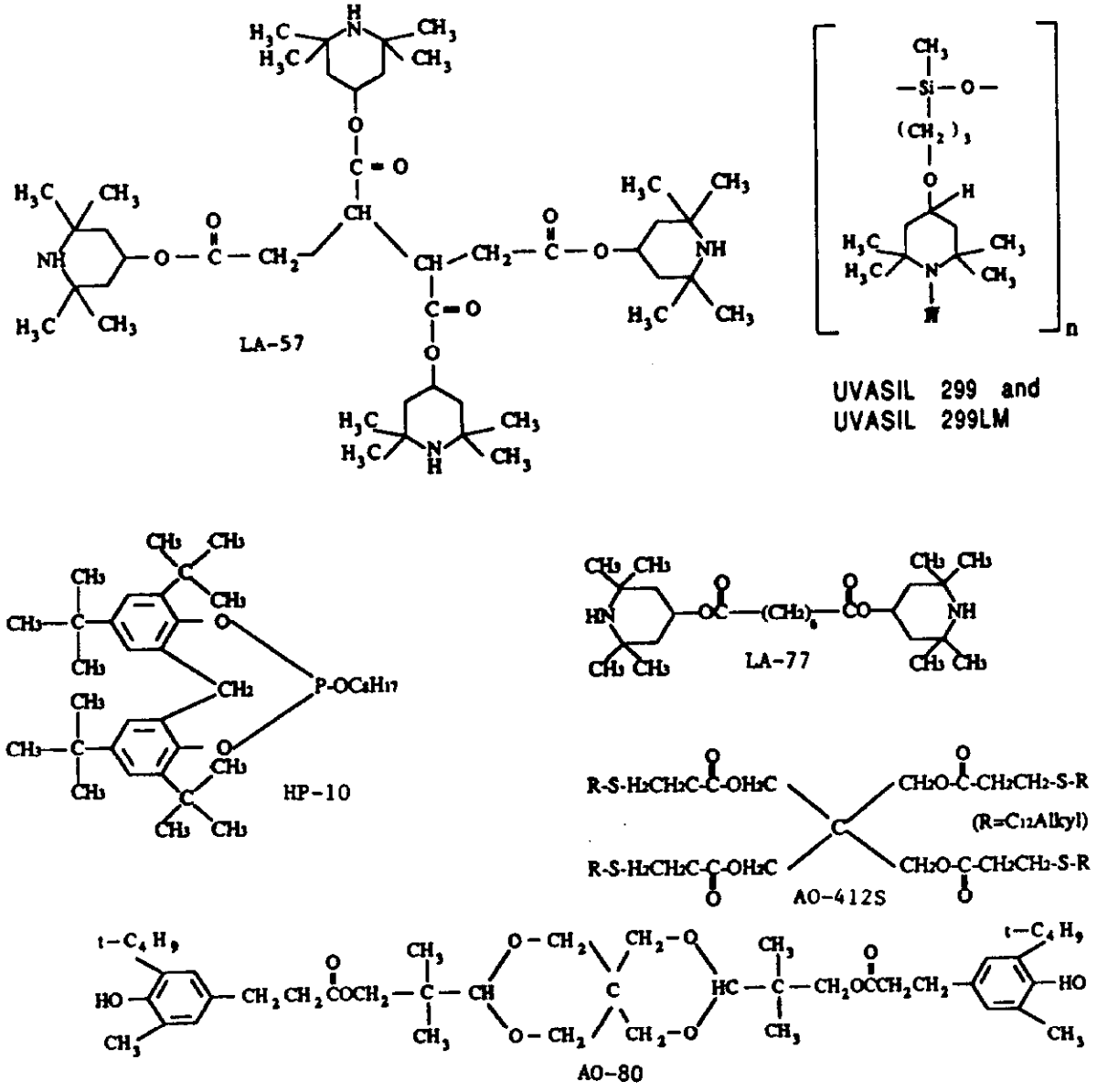
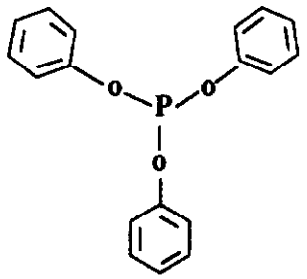
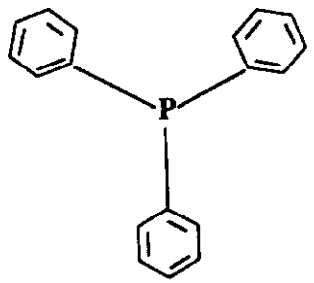


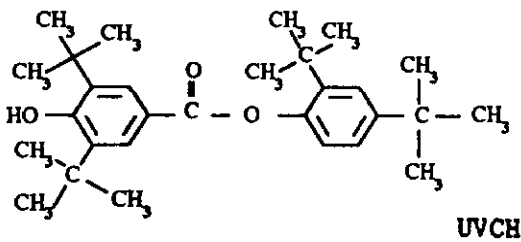
Fig. 7. Chemical structure of antirads



TRIPHENYL PHOSPHITE



TRIPHENYL PHOSPHINE



UVCHEK AM-340

Fig. 8. Chemical structure of antirads

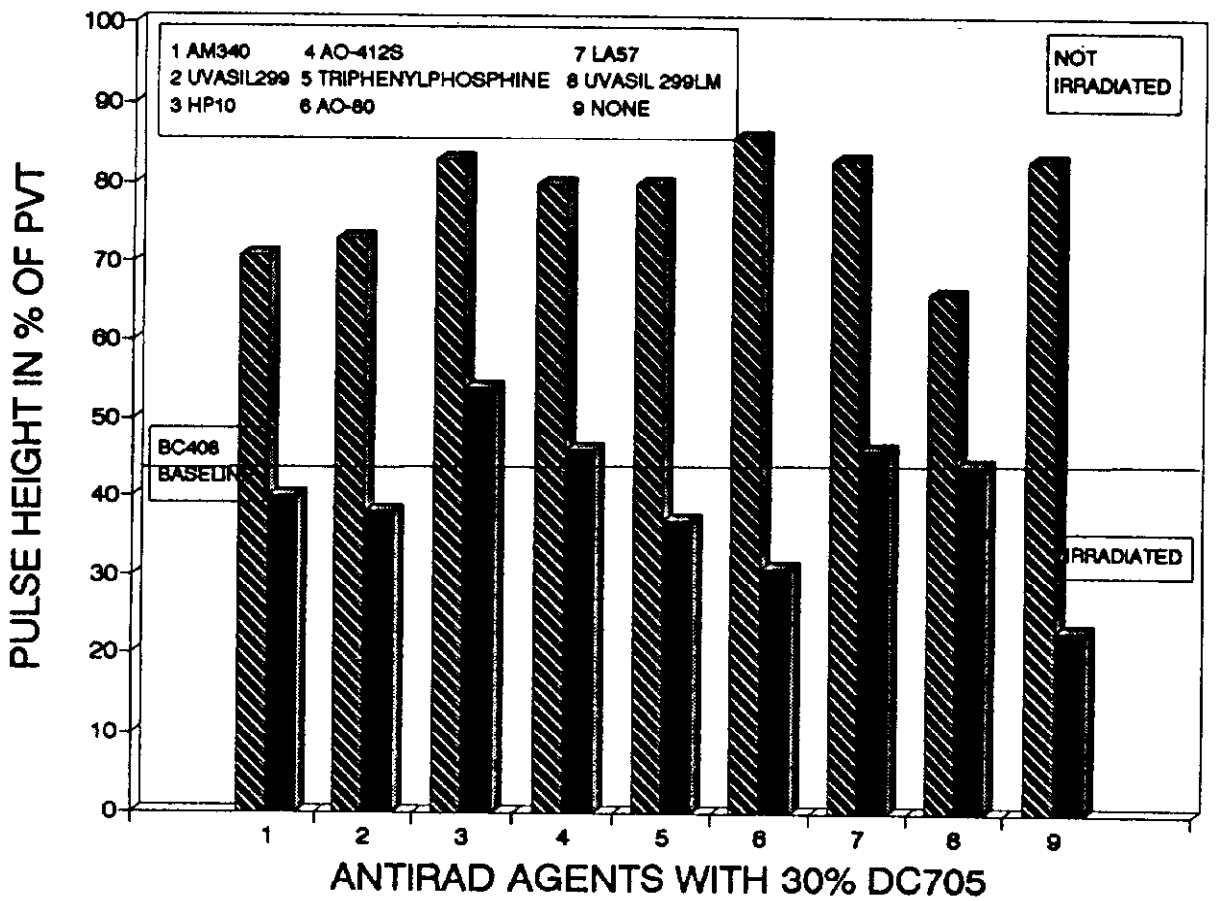


Fig. 9. Comparison of antirad agents

Concentration studies of the interaction of oil and antirads are planned. Figure 10 shows very clearly how increasing the oil content increases the effectiveness of the antirad UVASIL 299LM. Figure 11 shows the effect of the antirads (and triphenyphosphate) on depth anneal rates. It is not surprising that 3 of the antirad protected formulations show no depth anneal rate since they show no visual discoloration after irradiation, but it is surprising that the other materials show large positive and negative effects on anneal rate even though they are present only in low concentrations.

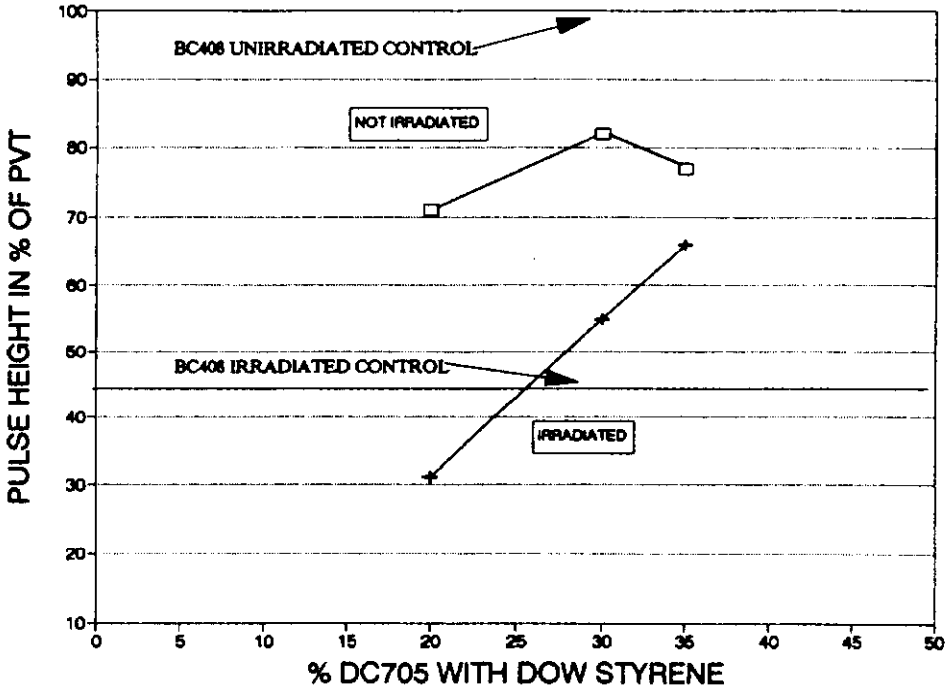


Fig. 10. Antirad effect (UVASIL299LM) vs. DC705 oil concentration

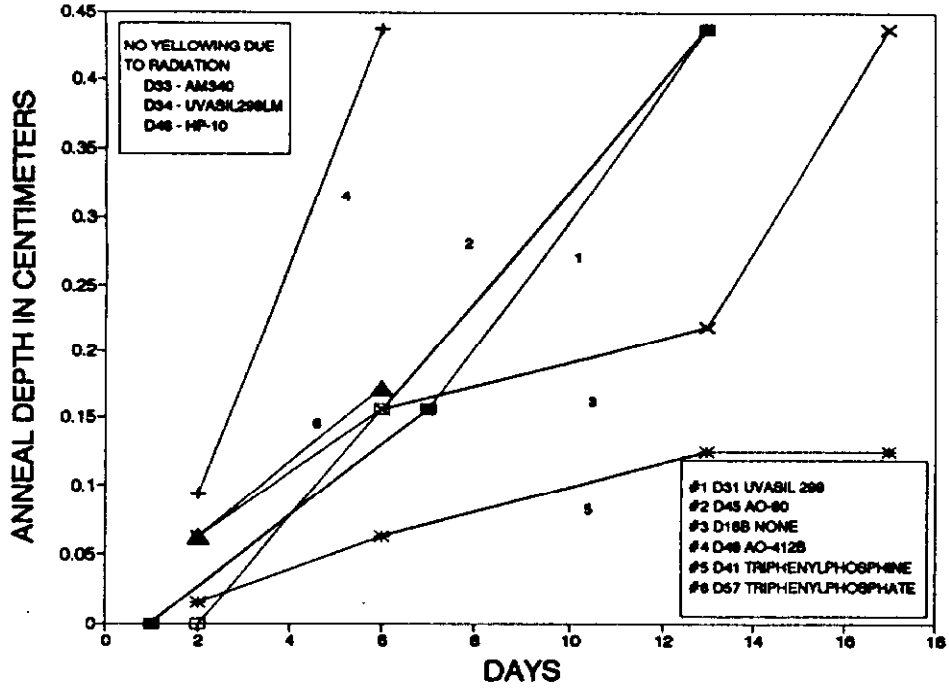


Fig. 11. Effect of antirads on anneal rates

EFFECT OF SHIFTERS

Figure 12 shows the structural formulas of the various primary and secondary shifters we have been considering. Figure 13 shows the effect of varying the concentration of POPOP.

The formulation consists of 100 pbw Dow polystyrene, 2 pbw of p-terphenyl, and x pbw of POPOP. The PPH on the abscissa stands for parts by weight per hundred of base material (polymer and oil if present). The upper part of the figure shows a slight increase in pre-irradiation light output with increasing amounts of POPOP. The highest concentration sample is slightly down perhaps due to self absorption. The lower portion of the figure shows that after irradiation the light output goes down with increasing POPOP concentration. The higher concentration samples are visually more yellow. Other studies with a POPOP derivative have shown it to be radiation resistant. It is possible that POPOP may be complexing with a radiation produced damage site to produce a color center. Figure 14 gives the pulse height annealing curves of these samples. It can be seen that all anneal at about the same rate.

As the POPOP concentration increases, the light output after annealing increases also. However, this seems to follow the increase in light output with POPOP concentration before irradiation. The permanent damage after annealing is constant at about 10% and not a function of POPOP concentration. Figure 15 shows the effect of varying POPOP concentration in a formulation containing oil. The base material is 70 pbw of Dow polystyrene and 30 pbw of DC705 oil. The shifters are 2 pbw of p-terphenyl and x pbw of POPOP. The lower curve is the light output after the 10 Mrads of gamma irradiation. It has the same general shape as the curve for the samples without oil shown in Fig. 13, but for all concentrations the light output of the oil-containing samples is significantly higher.

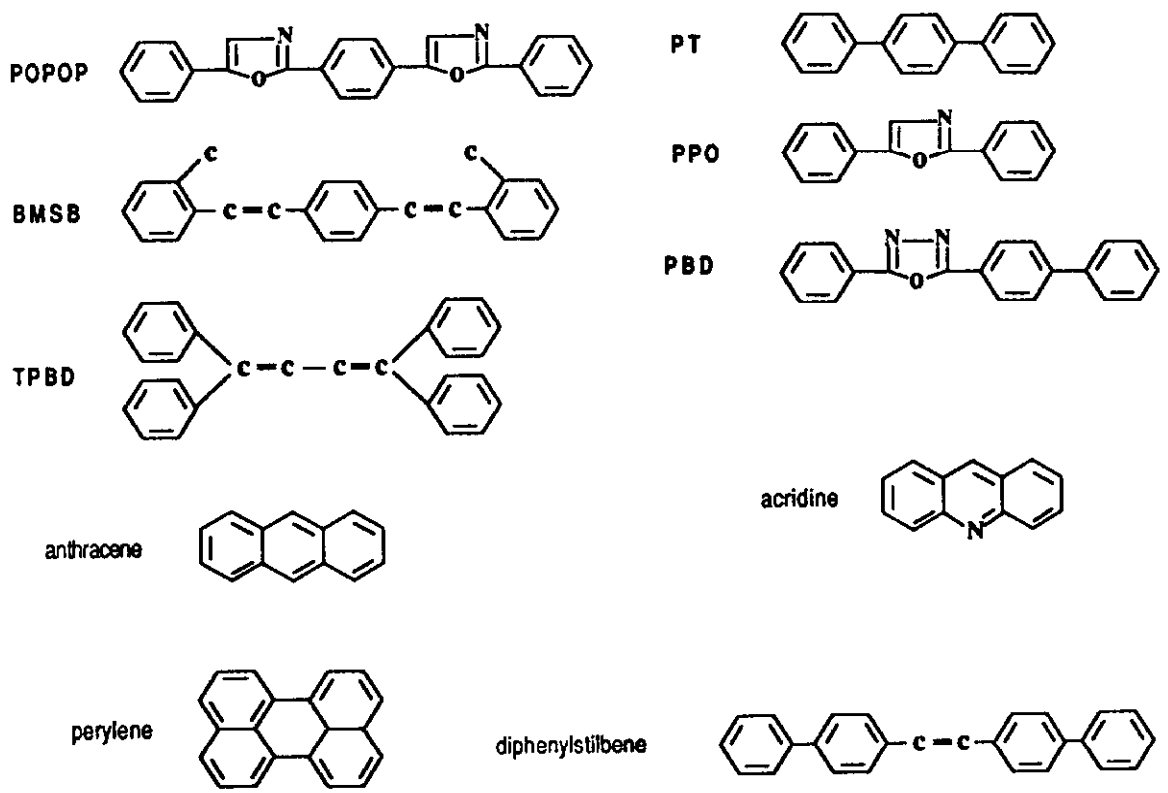


Fig. 12. Chemical structures of shifters

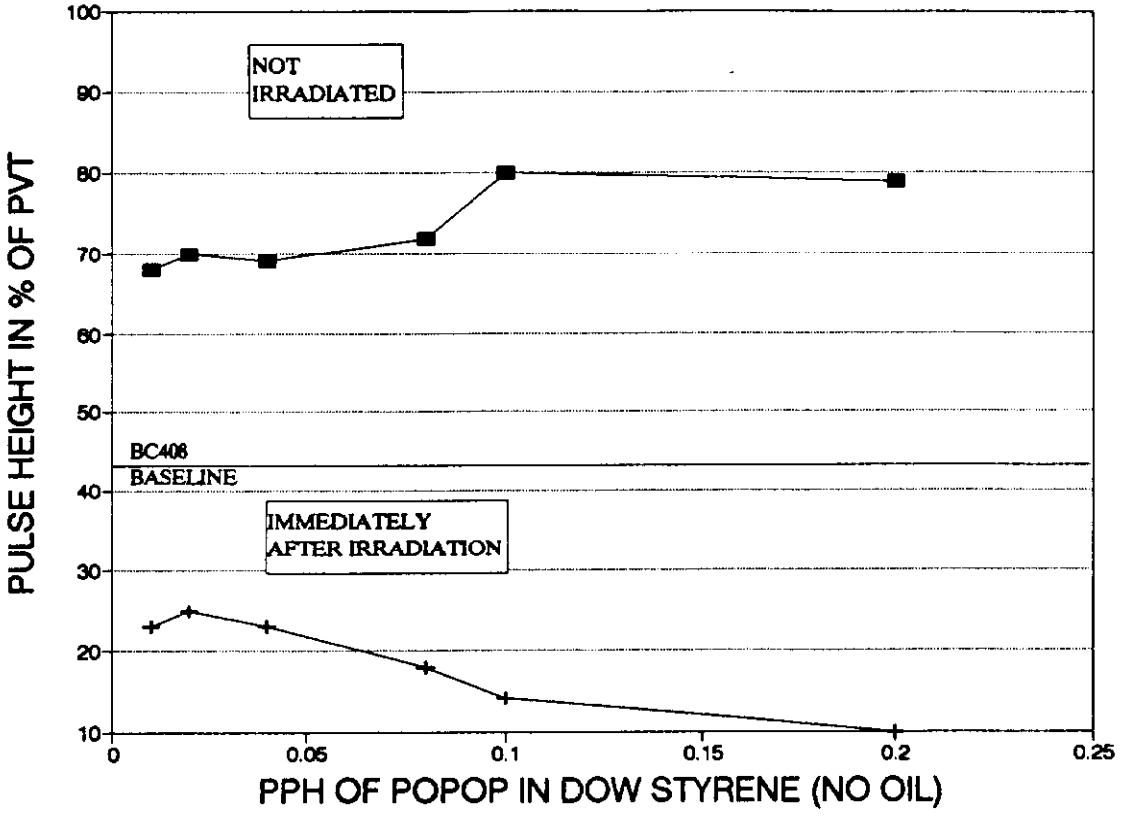


Fig. 13. Effect of POPOP concentration

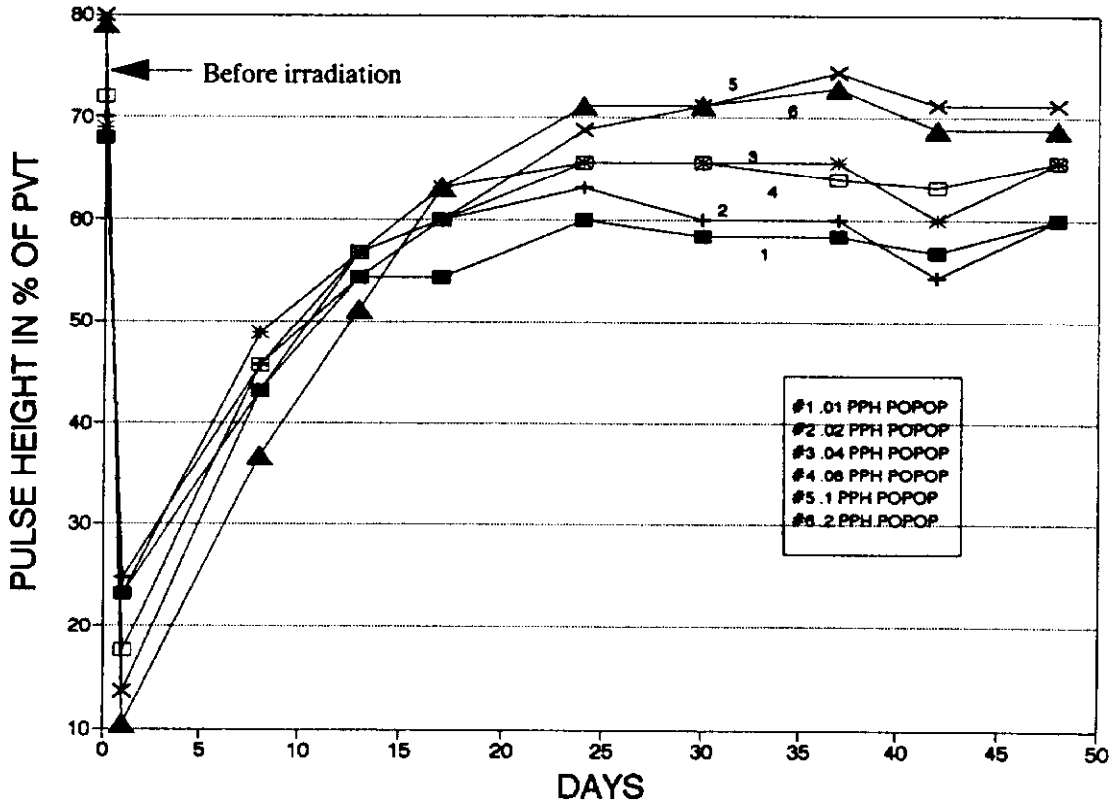


Fig. 14. Effect of POPOP concentration on pulse height annealing

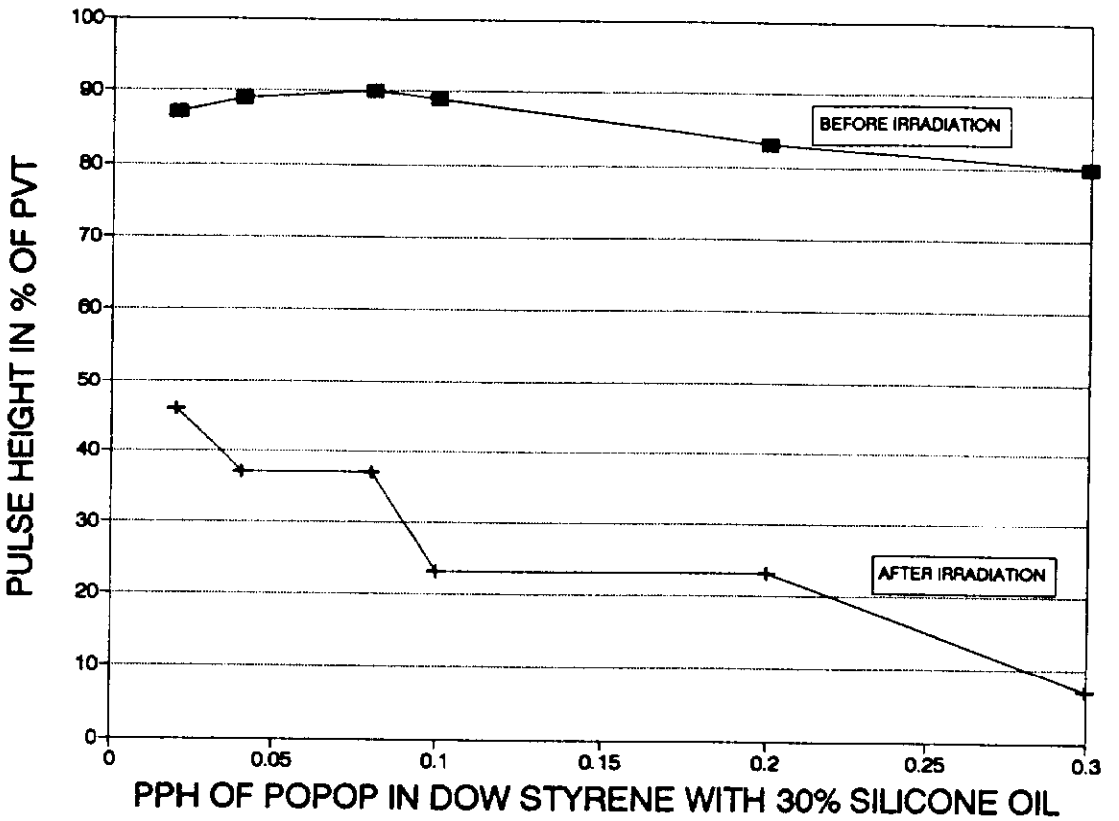


Fig. 15. Effect of POPOP concentration with 30% DC705

The upper curve is the light output before irradiation, and it does not show the increase in light with POPOP concentration that was apparent with the no-oil samples of Fig. 13. The oil seems to have enhanced the light output at the lower POPOP concentrations, both before and after irradiation. Figure 16 gives the pulse height annealing curves for these samples. The most significant facts apparent are that these oil-containing samples seem to be annealed after about 12 days while the non-oil samples shown in figure 14 took about 25 days to anneal, and the oil containing samples did not recover as much of their original light output. The oil not only increased the permanent damage, expressed as % change, but may have caused the highest POPOP concentrations to further increase the permanent damage.

Figure 17 shows the results when using varying concentrations of TPBD instead of POPOP. These are also samples with a base containing 30% DC705 oil. Fortunately, increasing amounts of TPBD are seen to increase the light output both before and after the 10 Mrads, and the damage caused by the radiation is much less than for the POPOP samples. As can be seen from Fig. 10, a POPOP sample with a 35% oil base and the addition of an antirad is about as good as a TPBD sample with a 30% oil base and no antirad (the .2 PPH point in Fig. 17). Of course an antirad-containing sample with TPBD has been made with the result reported in the abstract, namely a decrease in light output of only 4% after 10 Mrads and a pre-irradiation light output of 74% of PVT (Bicron BC408). The price to be paid so far is the 74% pre-irradiation output compared to 83% for a sample without antirad. Figure 18 gives the pulse height annealing curves for the TPBD samples.

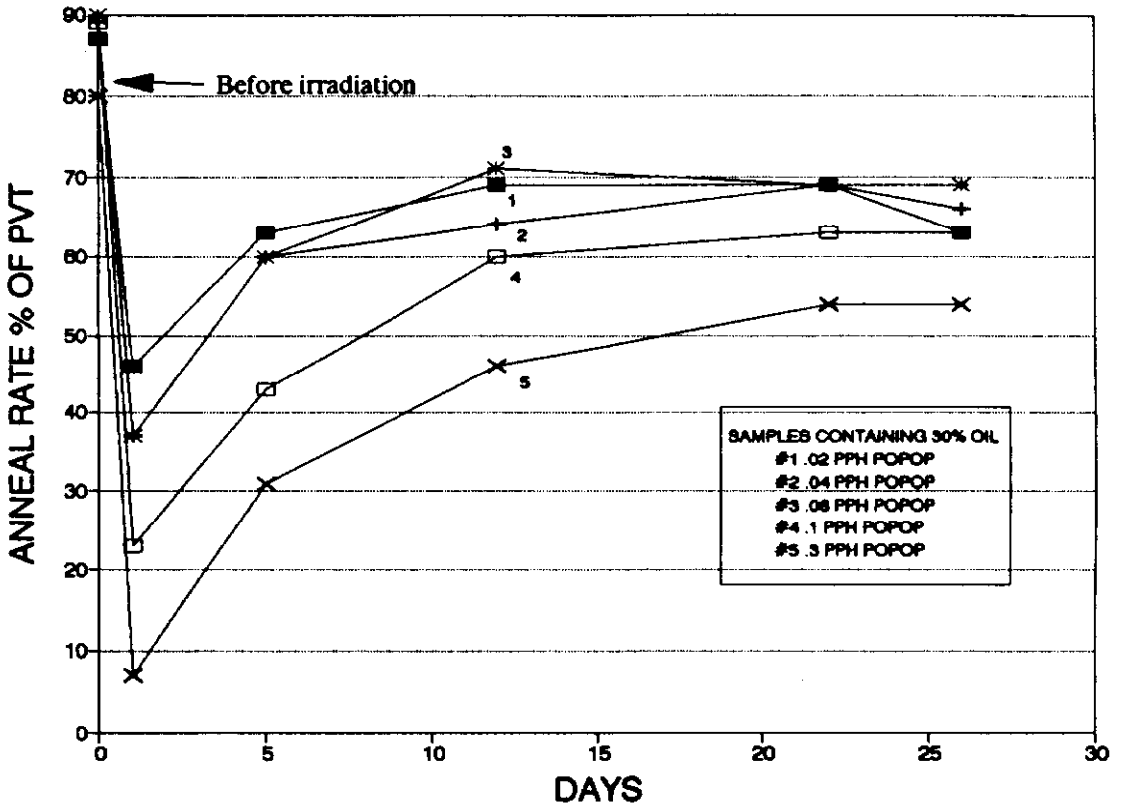


Fig. 16. Effect of POPOP concentration on pulse height annealing with 30% DC705

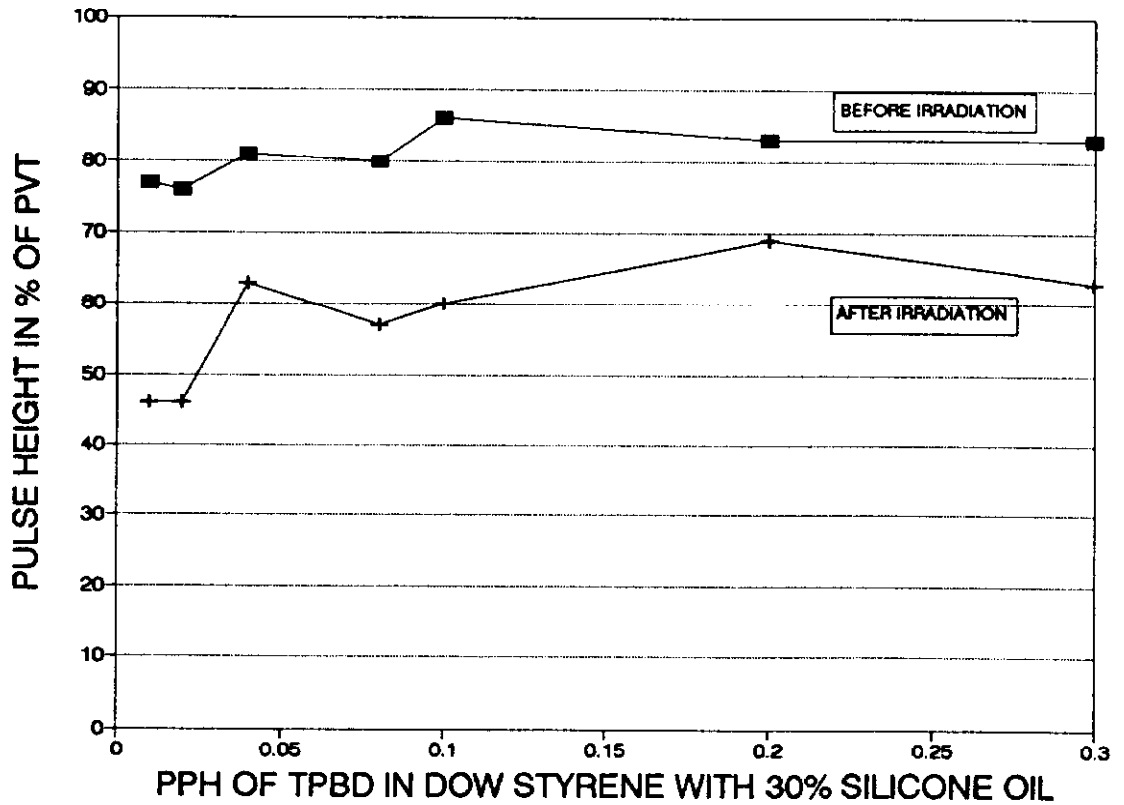


Fig. 17. Effect of TPBD concentration with 30% DC705

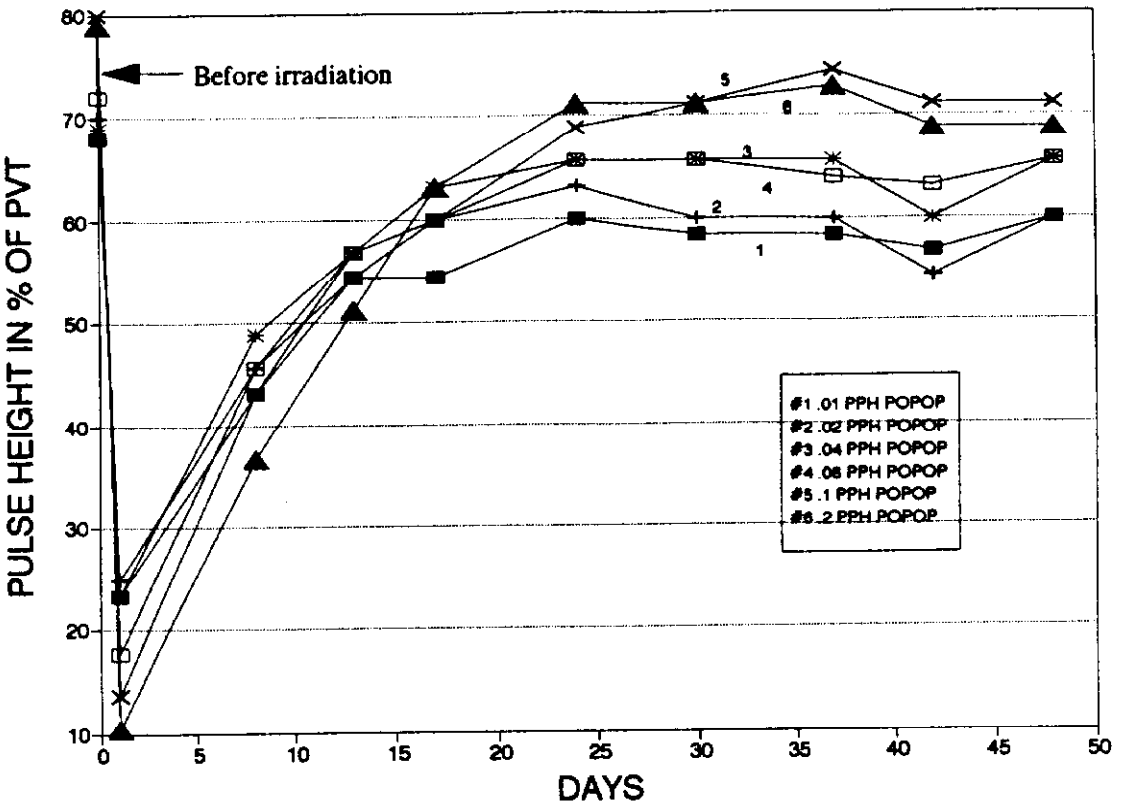


Fig. 18. Anneal rate of TPBD with 30% DC705

DEPTH ANNEALING

Figure 19 shows a representative sample of a depth annealing curve. It happens to be for a sample made from an injection molding scintillator compound made by Kuraray. Figure 20 is the same data except that it is the square of the anneal depth that is plotted on the ordinate. The result is a straight line which is compatible with the idea that this visual annealing is caused by a diffusion of oxygen into the sample where it combines with the radiation-formed color centers to give a colorless compound.

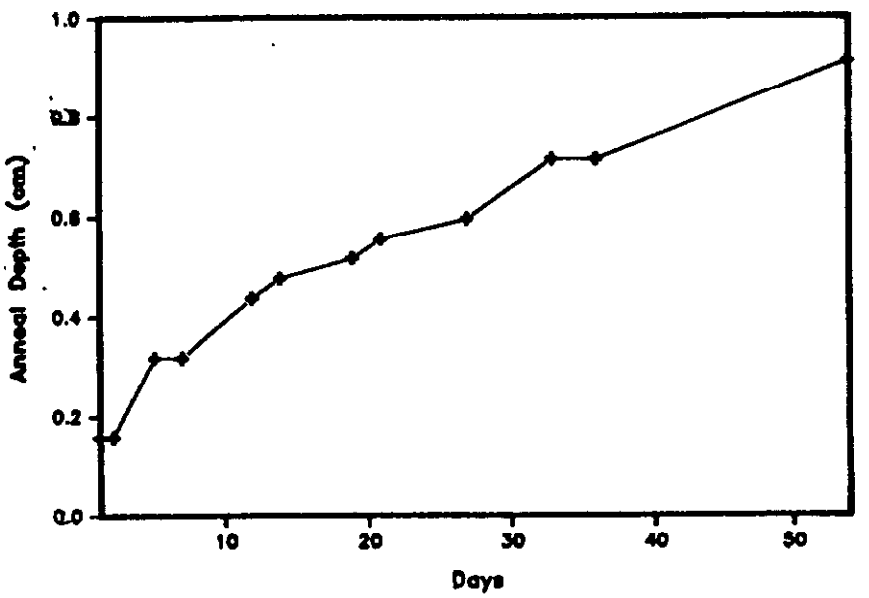


Fig. 19. Typical depth anneal curve

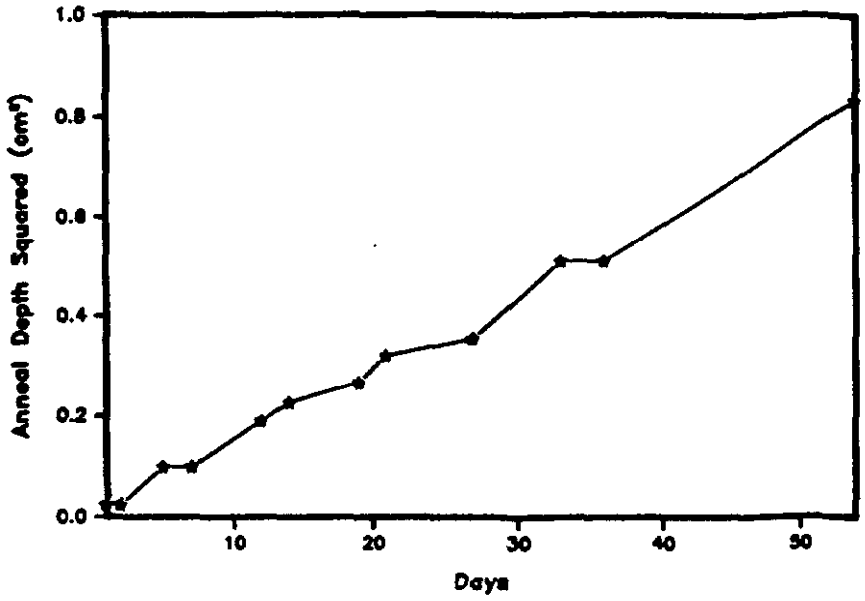


Fig. 20. Depth annealing curve plotted with the depth squared

That the visual depth annealing process can be very complicated is shown by Fig. 21. This is a photograph of an irradiated cylinder of polymethylmethacrylate containing 2 pbw of p-terphenyl and 0.2 pbw of POPOP in 100 parts of the polymer. The photograph is taken looking along the axis of the 2.5 cm long cylinder which is illuminated from the bottom and is surrounded by a piece of black paper. Immediately after irradiation the sample was uniformly dark in color but can now be seen to have 3 different color zones.

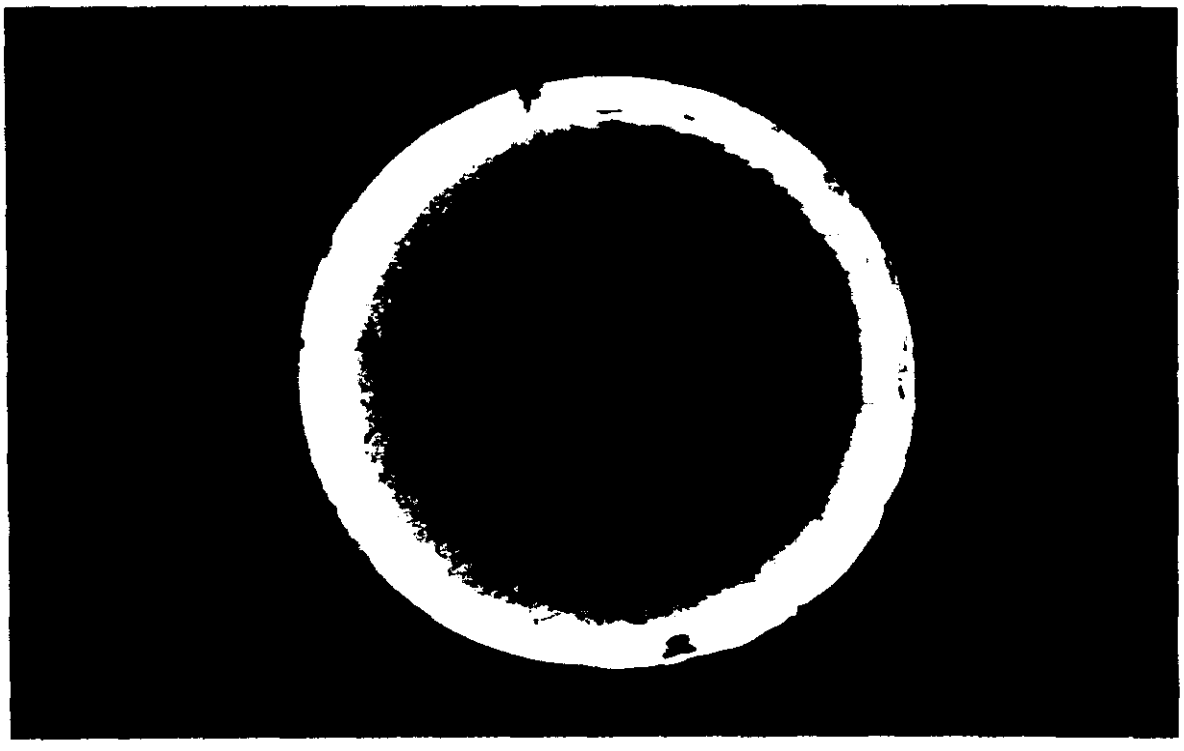


Fig. 21. Anneal rings in irradiated polymethylmethacrylate

LIGHT TRANSMISSION

Figure 22 is an example of the change in light transmission caused by irradiation. It presents light transmission data for a sample consisting of 65 pbw of Dow polystyrene, 35 pbw of DC705, 2 pbw of p-terphenyl, and 0.2 pbw of POPOP. The upper curve is the transmission spectrum of the sample with respect to air. The slightly lower curve is the same thing after the 10 Mrads irradiation. Both have been normalized to be 100% at the red end of the spectrum. The lowest curve is the difference between the two and represents the transmission loss caused by the radiation.

UNCONVENTIONAL PLASTICS

Figure 23 is a listing of the plastics that have been considered for scintillator bases. Most of them have had their light transmission measured before and after receiving 10 Mrads of radiation. Many of them have been formulated with shifters and had their pulse heights measured before and after irradiation. None have shown as much promise as the styrene family of plastics. Figure 24 gives the chemical structures of the members of this family.

One plastic has been found to yellow less than polystyrene when exposed to 10 Mrads. It is the polymer of ethyleneglycoldiallylcarbonate made by the Pittsburgh Plate Glass Co. as polymer CR39. It is frequently used to make lenses for eyeglasses. It is a crosslinked polymer so shifters must be added to the monomer. It is best polymerized with a PPG peroxide that is potentially explosive. It is also completely aliphatic and therefore is probably not a good scintillator, but it may be made usable in the same way that polymethylmethacrylate has been made usable by the addition of naphthalene or a similar compound. Figure 25 is the light transmission spectrum of a sample of CR39 from PPG after 10 Mrads of gamma irradiation and referenced to an unirradiated sample. It has been normalized to 100% at the red end. It is the best found during these tests, and shows no visually detectable yellowing. Both the PPG company and J. Harmon of the University of Florida are pursuing this material as a rad hard scintillator.

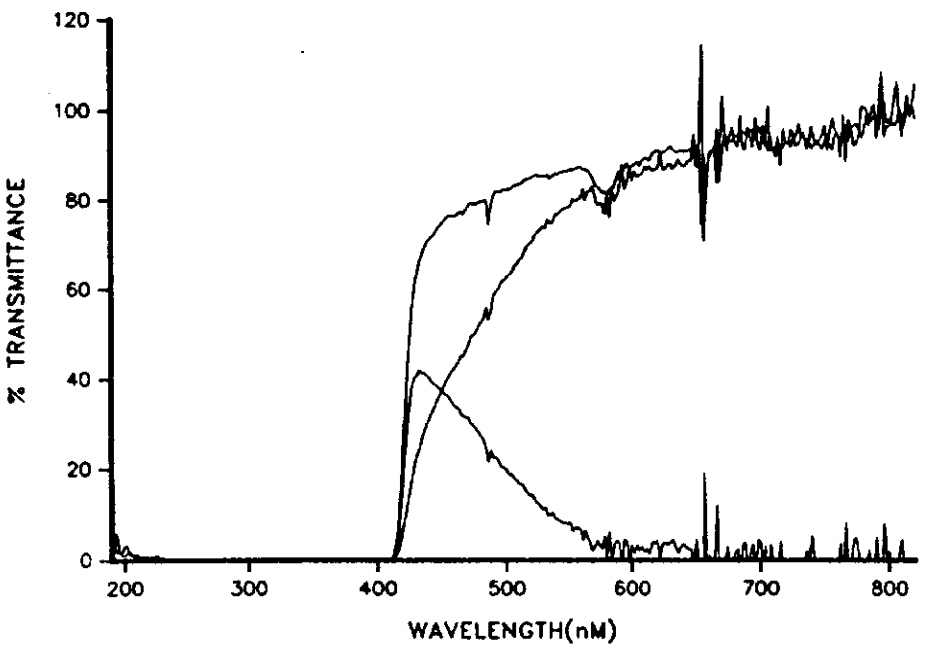


Fig. 22. Typical light transmission curves

polyalphamethylstyrene, polyarylate, polyarylsulfone, polycarbonate, epoxy, polyethyleneglycoldiallylcarbonate, polyethylenemethacrylicacid, polyethylenevinylacetate, polyethyleneteraphthalate, polymethylmethacrylate, polyphenylsulfone, polystyrene, polystyreneacrylonitrile, polystyrenemethacrylate, polysulfone, polyvinyltoluene, celluloseacetateproprionate, polyetherimid, fluorinatedethylenepropylene, polystyreneacrylicacid, polymethylpentene, polyvinylbutaral, polyvinylidenefluoride, polyvinylpyrolidone

Fig. 23. Plastics investigated

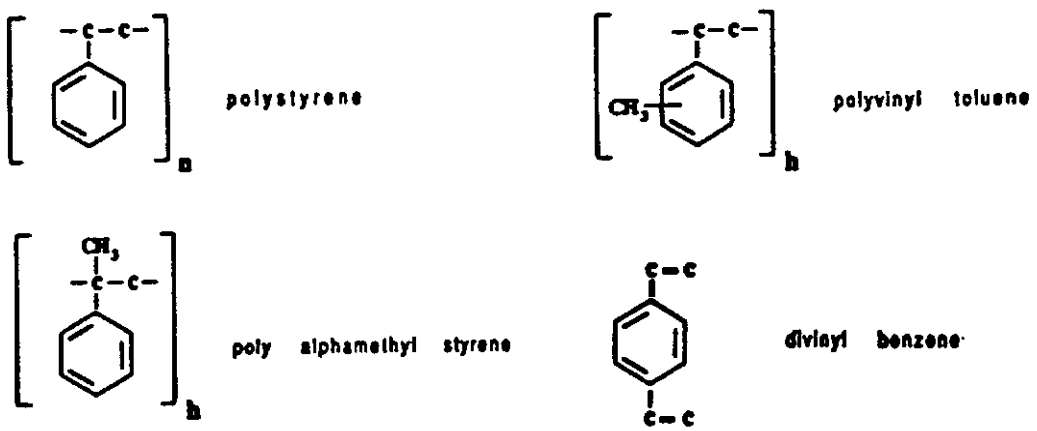


Fig. 24. Chemical structure of styrenes

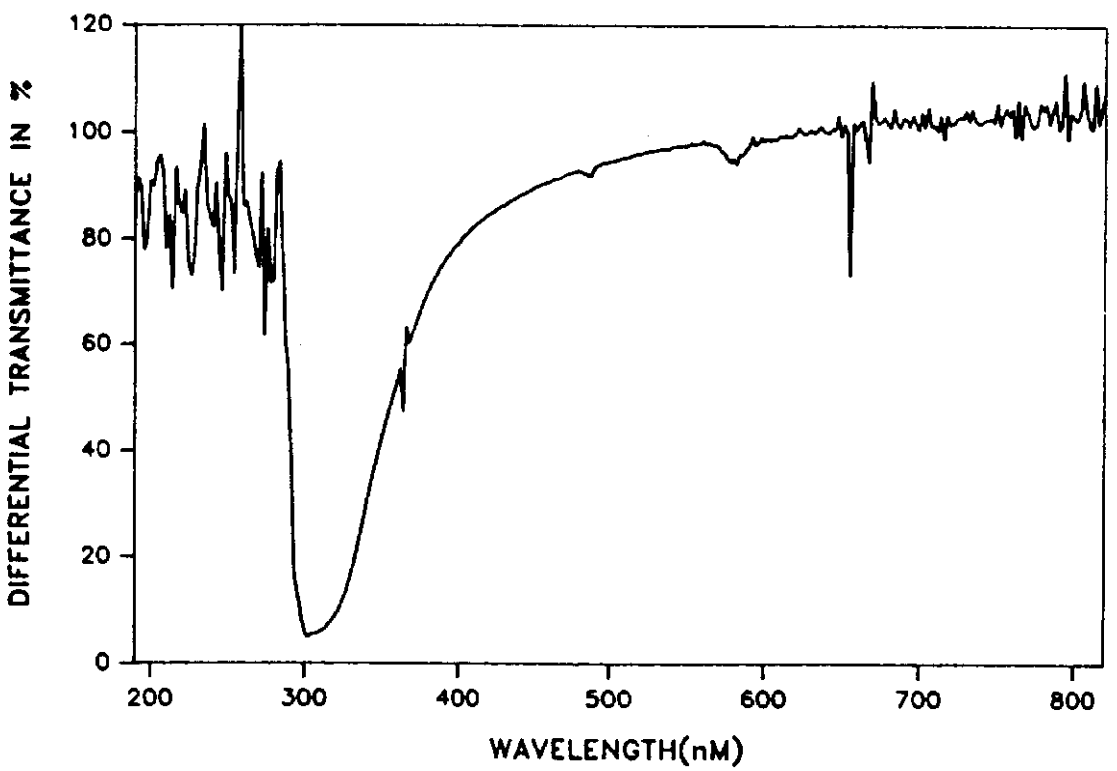


Fig. 25. CR39 light transmission loss after 10 Mrads

Epoxy resins (diglycidylether of bisphenol A type) such as Dow DER 332 have also been found of potential interest. Good scintillators have been made by dissolving the shifters in the DER 332 at about 120°C then cooling to 75°C before adding 6 pbw of trimethoxyboroxine (TMBOX) to 100 pbw of the DER 332. The TMBOX is added under nitrogen to prevent reaction between the TMBOX and the moisture in the air. The sample is then quickly vacuum degassed to remove air bubbles and cured overnight at 75°C. The resultant scintillators have light outputs of about 70% of PVT. They may be good general purpose scintillators since they are crosslinked and therefore solvent and heat resistant. They are also easily cast into any desired shape. The radiation hardness is not as good as polystyrene, as they yellow more and anneal slowly. However it may be possible to formulate them with diffusion enhancers and antirads to improve their rad hardness. They have been made with 70 pbw of epoxy to 30 pbw of the DC705 oil. However, unlike the polystyrene and oil combination, they show a tendency for the oil to diffuse out of the epoxy. The major advantage, for radiation hardness, of an epoxy system is that the crosslinking may mean that larger amounts of diffusion enhancers may be added without making the scintillator too soft. Figure 26 shows the results for two identical samples with and without the antirad AM 340. The antirad appears to increase light output before irradiation and decrease it after. The samples consisted of 70 pbw of DER 332, 30 pbw of DC705, 2 pbw of p-terphenyl, and .2 pbw of BMSB (bismethylstyrylbenzene). BMSB and TPBD have both been successfully used as secondary shifters, but POPOP cannot be used because it reacts with the epoxy to make an opaque compound. Other diffusion enhancers are now being investigated as are different curing agents.

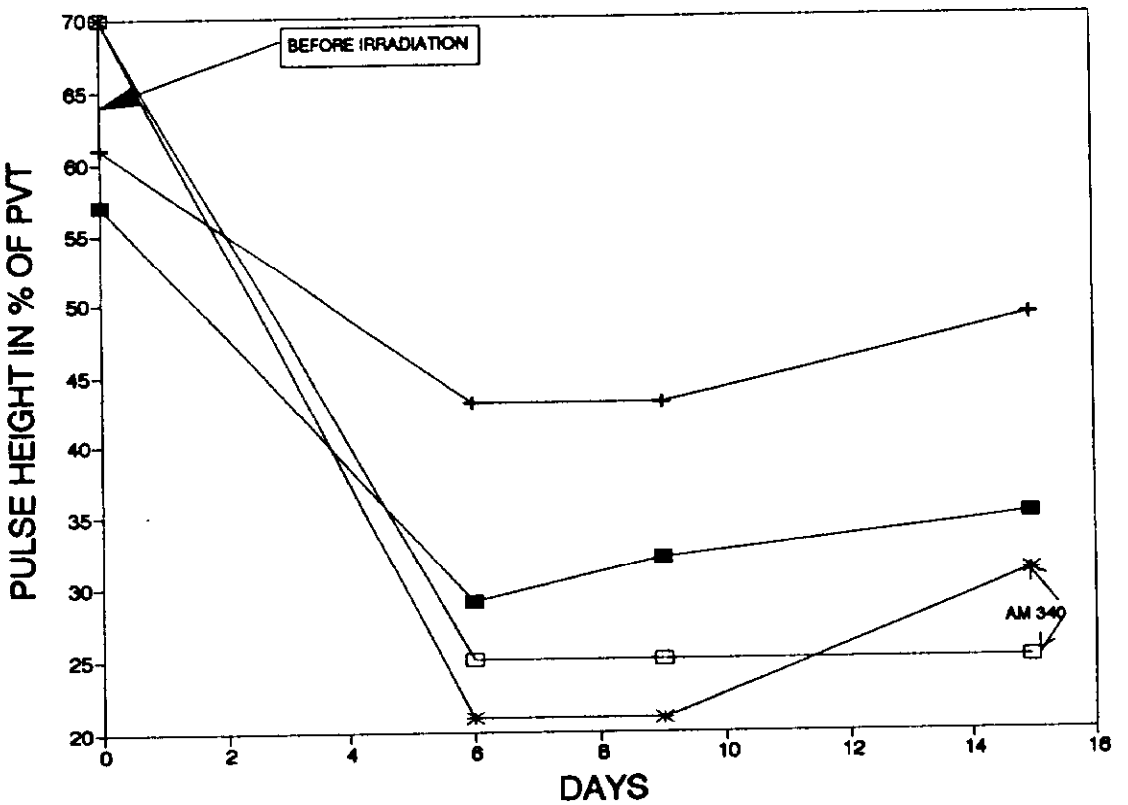


Fig. 26. Pulse height anneal data for epoxy with 30% DC705

FUTURE PLANS

An ambitious program of continued research is planned. Since it has been determined that many of the components of the scintillators interact in unpredictable ways, simple concentration studies will become problems in n-variable space. A program of studies of scintillators made from the monomers has also been started. It will be very interesting to try using the oil and antirads in vinyltoluene to get more light output. Polyvinyltoluene is not readily available, but a small amount has been obtained from Bicron so it will be possible to try PVT samples made from polymer as well as from monomer. It will be particularly interesting to try both styrene and vinyltoluene with DC705 oil and divinylbenzene crosslinking agent. The crosslinking may give better mechanical properties with the same amount of oil. The ideal structure would appear to be a three dimensional group of crosslinked cells filled with a comparatively fluid medium containing the shifters and antirads. Work is planned to measure the mechanical properties of promising formulations. It must be determined that they are dimensionally stable and not subject to surface crazing or to diffusion out of any of the components. It is interesting to speculate that the DC705 oil might actually change the stress crazing tendencies of polyvinyltoluene for the better. It is also planned to continue looking for less expensive diffusion enhancers than the DC705. Obviously the radiation doses will be increased toward a 60 Mrad goal.

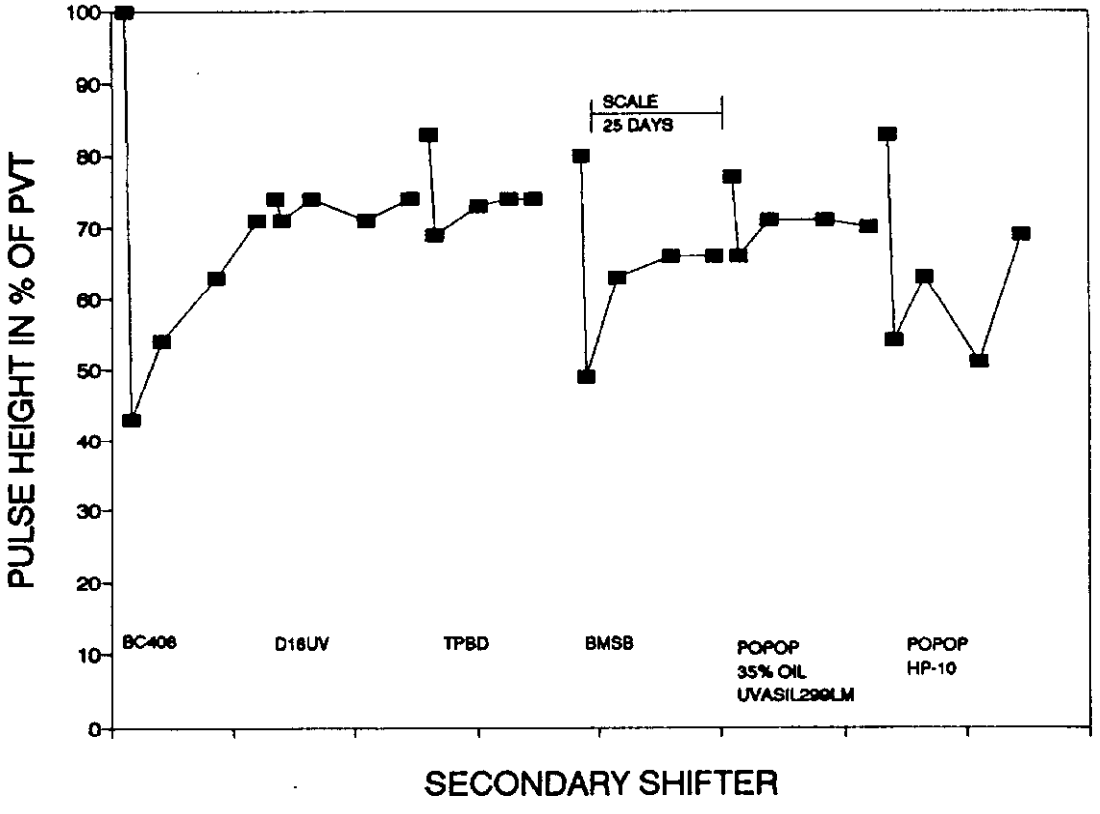


Fig. 27. Anneal rates for "best" samples 3-12-92
(30% oil except as noted)

SUMMARY AND CONCLUSIONS

Figure 27 summarizes the data for several of the most promising systems. D18UV is the sample discussed in the abstract. All samples (except the BC408 control from Bicron) are 70 pbw of Dow polystyrene, 30 pbw of DC705, 2 pbw p-terphenyl, .2 pbw of secondary shifter, and .5 pbw of antirad when present. It has been demonstrated that DC705 oil is effective in increasing the annealing rate of polystyrene scintillators. It has also been shown to be effective in activating antirad agents. It is theorized that the major reason for the improvements is the increased mobility of reactive species. The DC705 used alone increases the permanent radiation damage, but that is negated by the antirads. Useful plates of scintillator have been made and are being tested with shifter fibers before and after radiation. Improved scintillators have been produced from polymers and it has been proven that they can be injection molded. A scintillator that decreases its light output by only 4% after 10 Mrads has been developed.

ACKNOWLEDGMENTS

We would like to acknowledge the hard work and good advice received from many people. Ge Zhang from IHEP, Beijing, PRC is visiting Fermilab and was responsible for the measurement of the decay times. Many of the epoxy samples were made by Janna Flint. M. Davidson, B. Herdt, W. McCaw, B. Sizemore, S. Bastion and J. Poces of the Materials Development Laboratory of Fermilab all made significant contributions. C. Witt, K. Kobliska, E. Nehrlich, E. Campbell, R. Zarko and J. Keller assisted in the laboratory. The work as presented was performed at Fermi National Accelerator Laboratory, which is operated by Universities Research Association, Inc. under contract with the U.S. Department of Energy.

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