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THE CURSE OF THE NYLON PEEL PLY

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ABSTRACT

A case is presented that most peel plies can be relied upon to ensure the creation of a surface on composite laminates on which it is *not* possible to produce a strong durable adhesive bond. The surface resin needs to be removed by grit blasting, to expose freshly fractured resin to which it is possible to bond reliably. This problem is particularly acute for nylon peel plies, which are usually coated with release agents because, if they are not, they *will* react chemically with epoxy laminating resins to make glue. With released peel plies, the adhesive bonds formed during manufacture cannot *stay* stuck. They may adhere well enough in the short term, albeit at a reduced strength, but give no hint of the complete interfacial failures which often follow as moisture is absorbed in service. With absolutely *clean* nylon peel plies, the peel ply cannot be removed without destroying the composite part in the process. Nonreleased polyester peel plies, on the other hand, do not *need* a release agent and can create microscopically smooth, but uncontaminated, replicates of the peel-ply surface. Bonds made to such surfaces tend not to deteriorate with time. Depending on the particular combination of laminating resin, peel ply, and adhesive, these bonds can either be weak or quite strong. Low-pressure grit blasting is the only surface treatment for composite bonding which can be advocated without reservations, but many organizations favor the use of nonreleased polyester peel plies without mechanical abrasion. The paper includes Energy Dissipative X-ray analysis (EDX) scans for contaminating materials on and transferred by peel plies, and photomicrographs of the surfaces of and left by stripping off various peel plies. Problems with released peel plies abound, and their use without *thorough* mechanical abrasion on parts to be bonded or painted should be discontinued. The incidence of problems attributed to nonreleased peel plies is greatest in actually using them, with relatively few service problems. What is still needed for composite bonding is a durability test equivalent to the wedge-crack test used for metal-bonded structures; otherwise, service problems with interfacial failures of composite structures will continue to occur.

KEY WORDS: Adhesives, Composites, Non-Destructive Evaluation, Surface Preparation

INTRODUCTION

In an earlier paper, Reference (1), the senior author described what he knew of the difficulties in making epoxy-type adhesives bond reliably to fiber-polymer composites made with similar

thermoset matrices. The paper focused particularly on known problems associated with using peel plies *without* any subsequent mechanical abrasion of the surface. Thorough abrasion is needed to remove release agents transferred from released peel plies, or to promote adhesion to the otherwise chemically inert surfaces created by curing against uncontaminated peel plies. The paper was enhanced by inputs from colleagues all around the world, particularly by the samples of different peel plies and resins cured at different temperatures which were supplied by the Oxford Brookes University in England. The fact that such procedures would result in weak bonds likely to fail prematurely in service at interfaces between the glue layer and the resin has been known for decades. With the help of colleagues at Douglas, after many years of effort, these practices had been banished from the approved Douglas Process Specifications in the middle 1980s, for reasons explained in Reference (2). Most of these failures occur in service *after* the aircraft have been delivered to the customers. The manufacturers and subcontractors are therefore not constantly reminded of them. So, there have since been pressures to revert to simply stripping off a peel ply as a supposedly adequate surface preparation for adhesive bonding. Obviously, under ideal conditions, no contamination will be *added* to the surface during the time interval between removal of the peel ply and bonding the structure together. Unfortunately, no amount of care during this stage of the process will guard against contamination which was introduced *before* the peel ply was stripped off, or *before* the peel plies were delivered to the factory of the user, in the form of release agents. If the peel plies are not (further) contaminated while in the custody of the user, the user cannot *see* them being contaminated. This has been misinterpreted by some as justifying not making tests to *find out* whether or not there were any contaminants which could transfer to the bonding (or painting) surface on the finished part. The problem is compounded by the omission of durability tests to establish whether or not adhesive which appears to adhere in the short term will actually stay stuck throughout the life of the component. A possible significant clue in this regard may be found in the experiences of one subcontractor. In meeting unusually stringent hot-wet test requirements for bonded composite joints, imposed by their customer, found that it was necessary to co-cure a surfacing ply of adhesive in the laminates in the area to be bonded, *and* grit blast that surface as well.

Because most of the failures have not occurred immediately, the difficulty of making durable bonded joints to contaminated composite surfaces is not well understood. There are many bonded composite structures for which it is impossible to ensure that they will either fail or not fail in service. There can be no doubt however that, impact damage aside, the only in-service bond failures of composite structures have been interfacial, with *all* of the adhesive on one side and *all* of the resin on the other. There *is* no doubt that bonding directly to the surface left by stripping off released, and even nonreleased, peel plies degrades even the short-term strength of bonded composite joints. Specified lap-shear test requirements have been reduced to less than half the bond strength measured using exactly the same adhesive on the same laminate, but with a thoroughly abraded bonding surface. This reduction is “justified” by the logic that, for thin structures, the lower strengths are “adequate,” totally overlooking the point that the *real* reason for the test *should* have been to validate that the bonding *process* had been completed properly. This assessment *cannot* be made without applying sufficient load to fail a *properly* processed bond.

A prime intent in preparing Reference (1) was to elicit help in resolving the issue of making durable composite bonds, before even more suspect panels were manufactured and before the problem grew in magnitude to the size of the corresponding older problem with metal bonding [see Reference (3)]. Discussions with colleagues elsewhere in the McDonnell Douglas Corporation and throughout the aerospace industry around the world have revealed many failures similar to the one which inspired Reference (1). This is a truly world-wide concern, not an isolated problem. Far more information is available now as to why easily released "peel" plies do *not* create a surface suitable for bonding, and even strongly adhering "tear" plies *cannot* be relied upon to create a freshly fractured resin surface to which adhesives could be guaranteed to stick permanently. The pooling of information has even permitted *other* similar problems to be resolved, elsewhere. It has definitely stiffened the resolve of those who *already* knew that it was *necessary* to thoroughly abrade composite surfaces for bonding not to allow their suppliers to switch to peel-ply removal alone. Low-pressure grit blasting is the *ONLY* surface treatment so reliable that there have been *NO* bond failures. Unfortunately, manufacturers and subcontractors unwilling to use thorough mechanical abrasion have continued to use peel plies alone, whether released or not.

Conversely, one manufacturer of composite panels who was having trouble making *paint* adhere to peel-ply surfaces, bought a low-pressure grit-blast machine to save the cost of the hand sanding previously needed. The machine paid for itself in less than three months and was so easy to use that the previous resistance to grit-blasting for adhesive bonding is beginning to erode.

This new article reports on the considerable volume of additional useful information on this subject, emphasizing the invaluable contributions by the members of the Royal Australian Air Force, who provided all of the data reported here. The presence of silicone release agent all over the typical released nylon peel ply examined here, and the absence of contamination on the nonreleased polyester peel ply, go a long way towards explaining the very different results achieved in service by these two different surface treatments. There are also released polyester peel plies which are far easier to remove but which *should* require thorough mechanical abrasion if the surfaces left by their removal are to be painted or bonded. Presumably, the nonreleased polyester peel plies grip too tenaciously to be used on thin laminates or on those composite materials with an even weaker than normal bond between the fibers and the matrix. It is well known that tenaciously adhering peel plies must be stripped off laminates made from unidirectional tape by peeling *parallel* to the surface fibers. Stripping tear plies off *across* unidirectional tape surface plies results in delaminations. Some manufacturing and repair centers have found it *impossible* to remove some nylon peel plies when they really were *absolutely* clean and have had to switch to the corresponding product from a different supplier which did not adhere quite so tenaciously. McDonnell Douglas has found *one* nylon peel ply which is not released but which is coated with a proprietary sizing agent which permits the peel ply to be removed without damaging the laminate or contaminating the bonding surface. If there is absolutely no barrier between nylon peel plies and epoxy resins being cured against them, the reactive nylon will combine chemically with the epoxy and eliminate the interface completely, denying the possibility of breaking it apart to remove the peel ply. (There may be a few exceptions, depending on the catalyst and hardener in the resin, but the statement is true most of the time.) This problem is more acute for resins curing at 350°F (180°C), but is still significant

for those cured at 250°F (120°C).

There is an inherent problem with removing really tenaciously adhering plies from the surface of carbon-epoxy panels. The problem is that the bond between the carbon fibers and the epoxy matrix is so weak that if the bond between the epoxy matrix and any truly clean peel ply is too great, removing the peel ply will strip off *all* of the surface resin and expose large areas of bare fibers to which it is virtually impossible to bond. By definition, therefore, if the fibers are *not* exposed, the adhesion between the peel ply and the resin must be *even weaker* than that between the resin and the fibers. This may totally undermine the whole concept of a tear ply capable of creating a freshly fractured surface of resin with which it is possible for an adhesive to form a bond anywhere near as strong and durable as that created by grit blasting the surface. (Significantly, it is so difficult to strip off the peel plies which appear *not* to contaminate the bonding surface that some of the opponents of grit blasting may yet conclude that they would rather abrade instead. The senior author has even heard of the need to *grind* one tear ply off because it grips so well that it breaks frequently while it is being removed.)

Heat-scouring employed during manufacture of certain “nonreleased” peel plies would not even be needed if it were not for the fact that the nylon filaments had *already* been coated with lubricants or sizing during the extrusion of the fiber and the weaving of the fabric. This is done both to minimize wear on the machinery and to prevent the fiber surface from fraying. The description “nonreleased” merely means that the peel-ply manufacturer did not put the release agent on himself. This is in no way meant to imply that no effort is made to control the surface of nonreleased peel plies. Most and sometimes all of this residual contamination *is* removed and surface treatments applied to tread the very fine line between making it too easy to remove the peel ply, which would inevitably decrease the strength of the bond, and too difficult to remove the peel ply, which could damage the laminate. Most problems with peel plies may be more appropriately blamed on *unrealistic expectations of the users*, some of whom *expect* to be able to bond directly to the surface left after even released peel plies have been removed, with no abrasion at all or only ineffectual scuff sanding. The position of the RAAF in this regard (with which the senior author heartily concurs) is that the *only* function of the peel ply is to protect against gross external contamination and to provide a good base from which to start the grit-blasting operation to ensure that the adhesive will stick and remain stuck. (Obviously, the use of peel plies on composite components for entirely mechanically fastened structures which are not painted is another matter.)

One of the largest aircraft manufacturers now tests for contaminants before accepting shipments of peel plies, and many organizations within that corporation now prohibit the use of nylon peel plies and tightly control the use of the few polyester fabrics which *are* permitted. One can only hope that this enlightened practice will spread throughout the remainder of the industry.

As some of the authors’ colleagues have said, “since any peel and tear plies are cured *with* the composite parts, they need to be subjected to just as stringent purchasing, quality, and handling requirements as the portion of the cured laminate which is *not* discarded. Otherwise, contaminants *will* be transferred to the laminates.” It seems utterly incongruous that such care is taken in preparing bonding and lay-up tools in a *separate* area outside the clean room to protect

against the *very same contaminants* that are often applied over the *entire opposite surface* of the part whenever released peel plies are the final layers included inside the vacuum bag. Peel plies and bagging films may be consumables, but this in no way diminishes the effects they can have on the composite parts cured against them.

WHY NYLON PEEL PLIES CAN VIRTUALLY NEVER WORK

Nylon peel plies can never create a surface suitable for epoxy bonding for one very simple reason – surface contamination. In the absence of any release agent or coating on the nylon fibers, the active thermoset polymer would combine chemically with the epoxy resin, as it was being cured, to make one of the toughest adhesives known to man. About two thirds of the Shell 951 and American Cyanamid FM-1000 nylon-epoxy adhesives are nylon. By definition, then, any nylon peel ply which *can* be removed from an epoxy laminate *must* have been coated with a release agent or sizing, whether it was applied during the creation of the peel ply, the weaving of the fabric, or the initial drawing of the filaments. Proof of this statement can be deduced indirectly from the experience of one user of a heat-scoured fine-weave nylon peel ply who had to switch to another product because he simply could not get the first one off. The only difference between most “nonreleased” and released nylon peel plies would seem to be in the *amount* of the coating and *who* applied it. Released peel plies are copiously coated by the manufacturer of the peel plies, while nonreleased peel plies are cleaned at that stage. If *too good* a job is done cleaning the nonreleased peel plies, they cannot be removed. (While McDonnell Aircraft uses one particular polyester peel ply as surface preparation for composite laminates, there are a few applications with one particular nonreleased nylon peel ply coated in a proprietary sizing. In either case, however, thorough sanding is called for in all areas to be bonded.)

There are those who are convinced that, even if peel plies are coated with release agents, *none* of it will transfer to the laminate and that it is therefore unnecessary to abrade such surfaces before painting or adhesive bonding. It is hoped that Figures 1 to 17 will cause them to question their beliefs. These figures report on tests made by the RAAF at Amberley on a popular released nylon peel ply. Concern had been raised by bonded repairs to F/A-18 aircraft using pre-cured patches, made and applied according to the manufacturer’s specifications of the day, which were falling off in a relatively short time. (Fortunately, as a result of these incidents, the peel plies now specified for the manufacture of these pre-cured patches are of the non-released variety.)

Figure 1 shows how silicon has been detected by an Energy Dissipative X-ray analysis (EDX) test made on the released peel ply itself *after* it had been stripped off the surface of the laminate forming the precured patch. The carbon and oxygen are present in the nylon fibers. The silicon is in the residue of the silicone oil applied as a release agent to the peel ply. There is a microscopic trace of sulphur, the significance of which is explained later in relation to the very much larger signal from a sample of the resin in the composite laminate.

Figure 2 is a photomicrograph of this surface, showing how clearly each fiber in the peel ply is defined, just as was reported in Reference (1). Figure 3 is an enlargement of the boxed area in Figure 2, showing the small area of fractured resin where the peel-ply fiber direction changes. This is about all the bondable surface that is created, since the individual fibers away from these

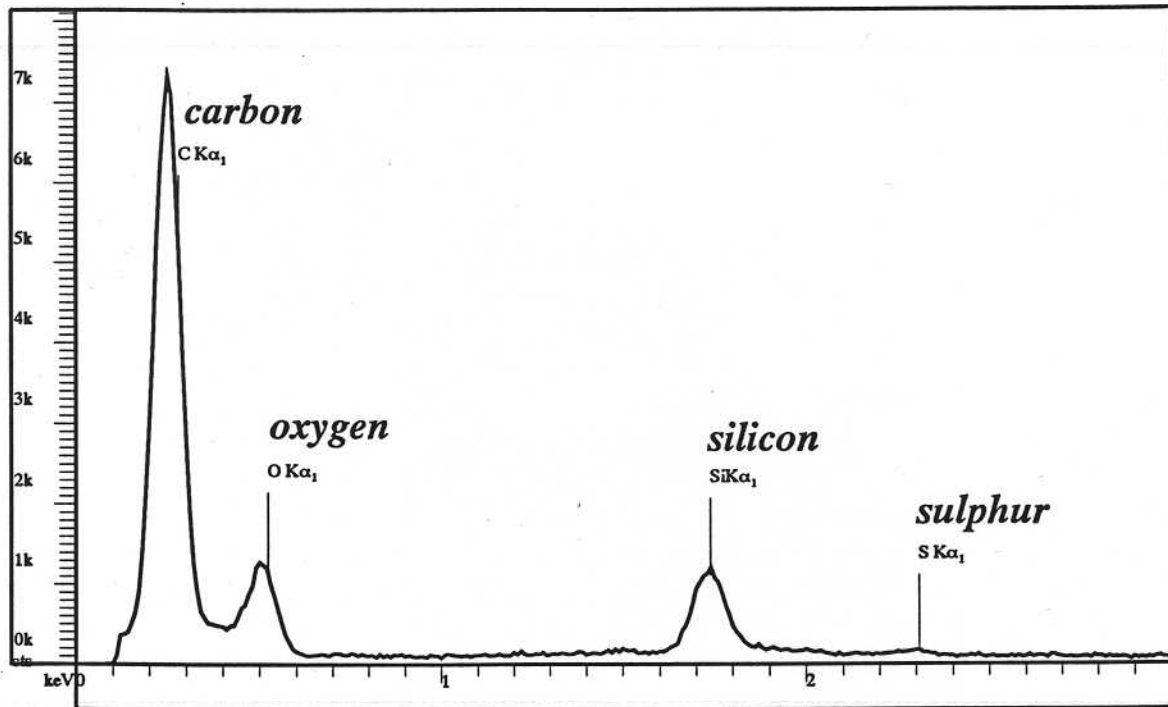


Fig. 1 EDX Analysis Spectrum Scan of Surface of Used Release-Coated Peel Ply

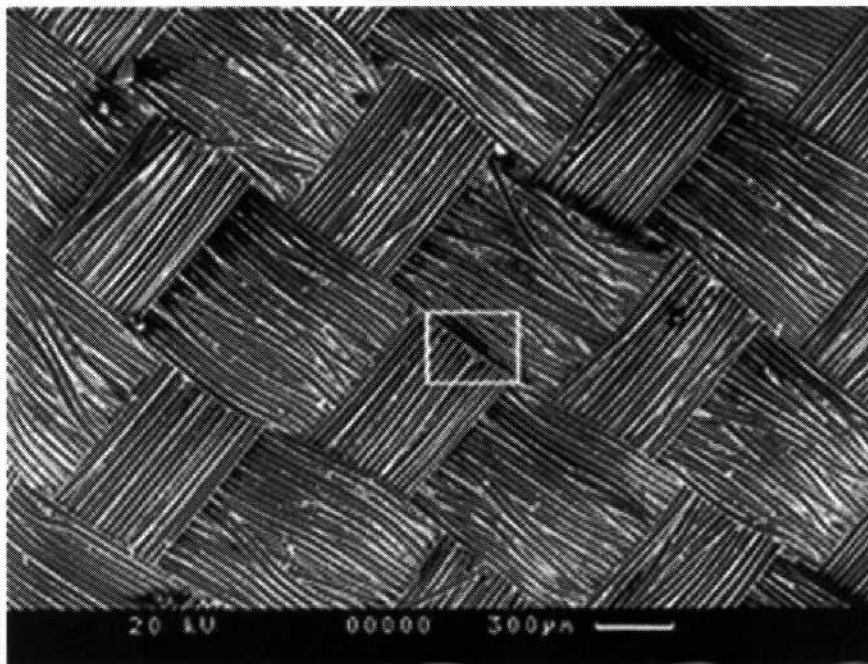


Fig. 2 Low-Magnification SEM Video Print of Used Released Nylon Peel Ply, Showing Clearly Defined Individual Fibers

crossovers are almost bare. Only microscopic flecks of the adhesive adhered to the fibers, indicating how little freshly fractured resin surface is created by removing the peel ply.

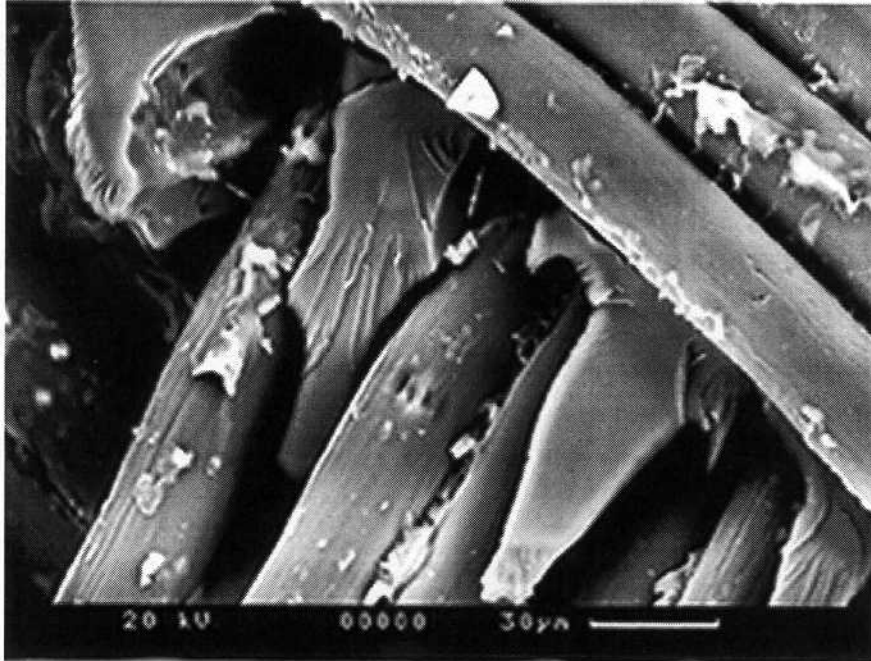


Fig. 3 Enlarged SEM Video Print of Used Nylon Peel Ply, Showing Fractured Resin Only at Fiber-Bundle Crossovers, With Virtually No Resin Adhering to Nylon Fibers

Figure 4 presents an EDX assessment of the opposite side of this interface, the surface of the *laminata* (pre-cured patch) created by stripping off the peel ply, showing less silicon on this

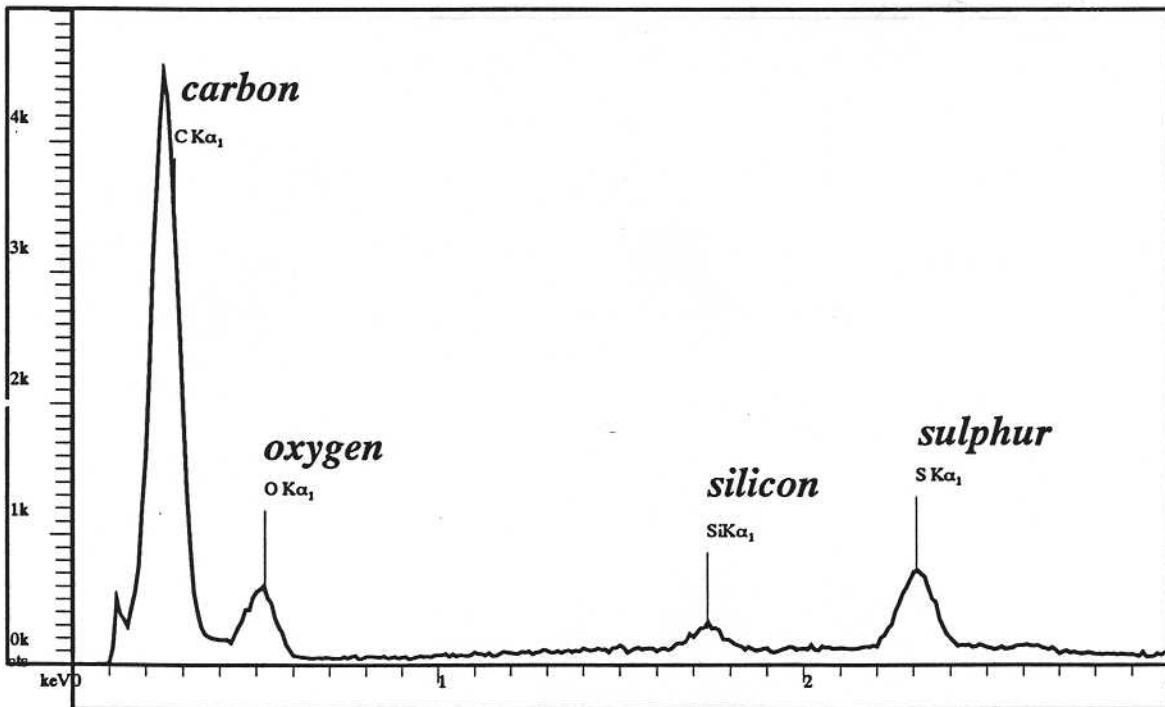


Fig. 4 EDX Scan of Laminata Surface Created by Stripping Off Released Nylon Peel Ply, Showing Silicon Transferred From Peel Ply and Sulphur from Within Epoxy Resin

surface than on the fibers of the peel ply, which is consistent with the fact that it transferred *from* the peel ply *to* the patch, and not vice versa. The many tests to exclude possible origins of the release agent on the bonding surface of the composite laminates may seem to be redundant to those who already know that it is transferred from the peel plies. However, the *complete* matrix of possibilities is included to convince those who sincerely believe that release agents do *not* transfer, and therefore do not need removing, that this is simply not so! The strong sulphur signal in Figure 4 is associated with the hardener in the resin. The significance of this sulphur is profound. Figure 1 shows virtually no trace of sulphur. This proves conclusively that the stripping off of the released nylon peel ply does *NOT* remove resin from the actual *surface* to be bonded, which explains why adhesives will not adhere to this surface. If removing the peel ply created the kind of freshly fractured resin surface it has commonly been *believed* it would, there would be unmistakable evidence of sulphur in Figure 1, just as strongly as in Figure 4. This peel-ply created surface is quite unsuitable for bonding.

Figure 5 shows the impression left on the surface of this patch, after removing the peel ply. The distinct pattern left by each individual fiber in the peel ply is quite evident, Figure 6 is an enlargement of the boxed area in Figure 5. The smooth furrows were caused by the fibers in the peel ply. Most of the bondable fractured resin is confined to the crossovers between fiber bundles. Figure 7 is an-other enlargement of the impression left by the peel ply, showing very little fractured resin other than the thin strands between adjacent fibers. Overall, except for some porosity (the result of vacuum-bag curing of the laminate), the furrow surfaces are relatively smooth and have not been fractured during removal of the peel ply. This surface would be just as unbondable as those illustrated in Reference (1), which is confirmed by the number of these such

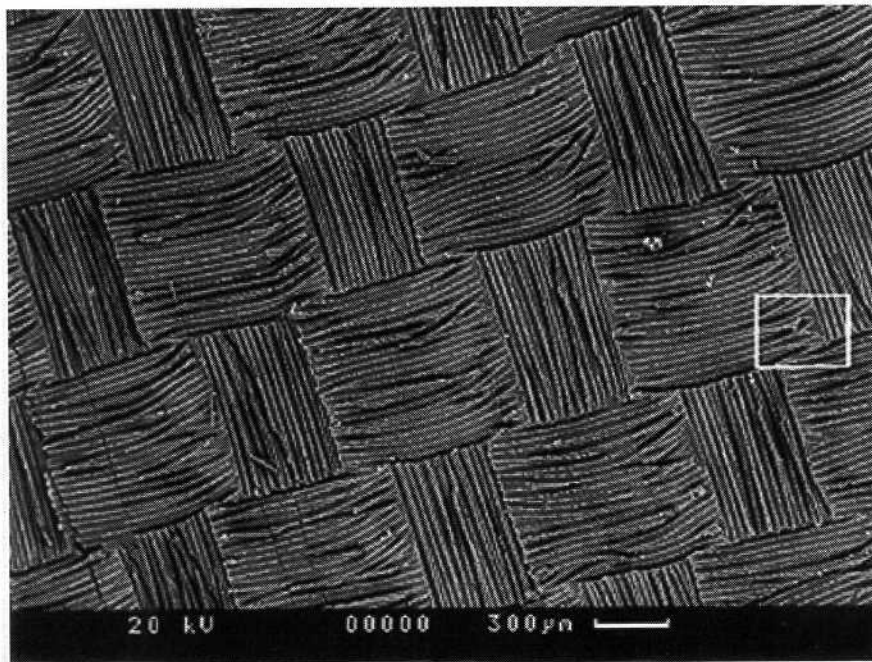


Fig. 5 Resin Surface of Carbon-Epoxy Patch, Showing Clear Impression of Released Nylon Peel Ply

patches which departed the aircraft.

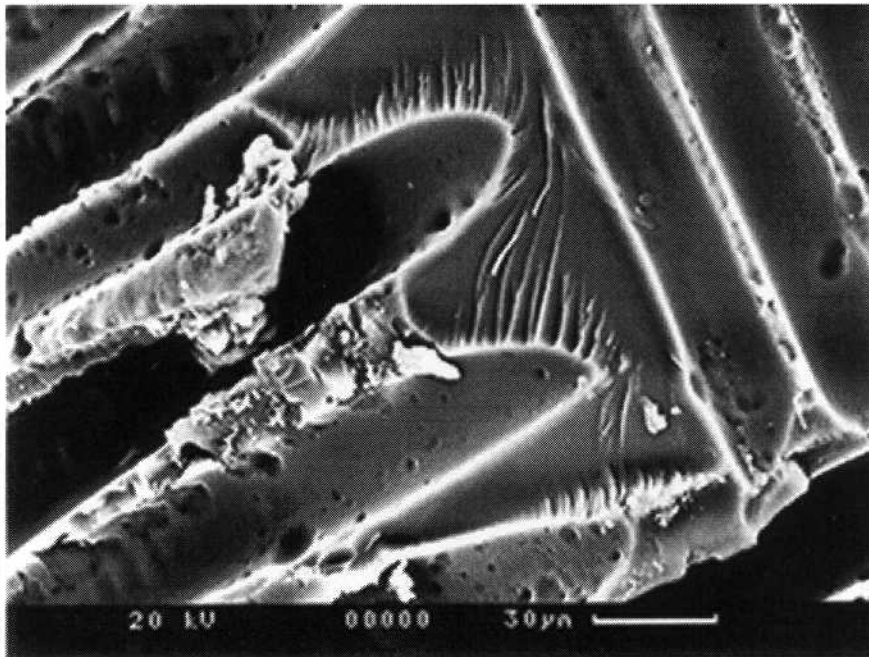


Fig. 6 Enlargement of Laminate Surface, Showing Fractured Resin at Fiber-Bundle Crossovers in Peel Ply

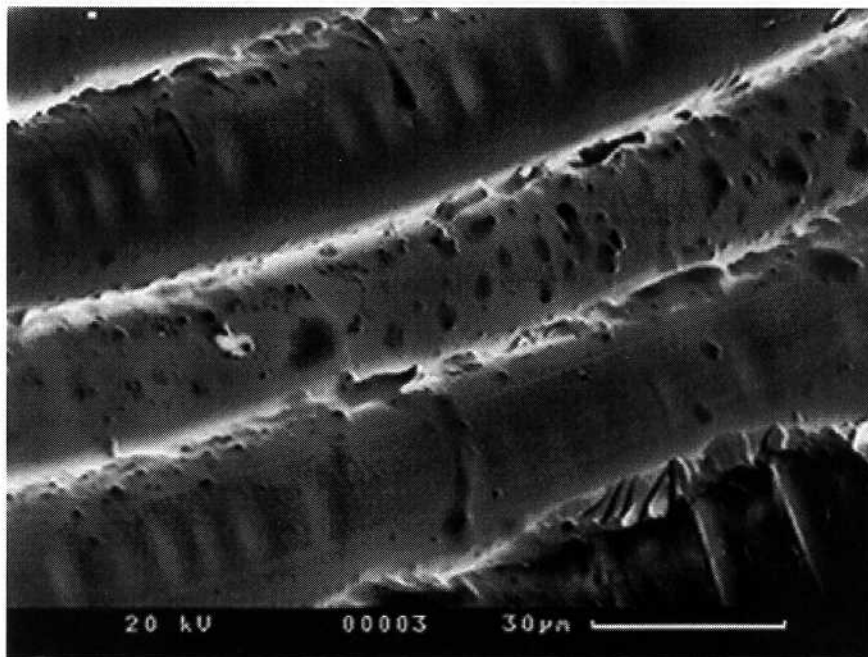


Fig. 7 Additional Enlargement of Laminate Surface Showing Smooth Furrows Left by Released Nylon Fibers. (Porosity Caused by Vacuum-Bag Cure of Laminate)

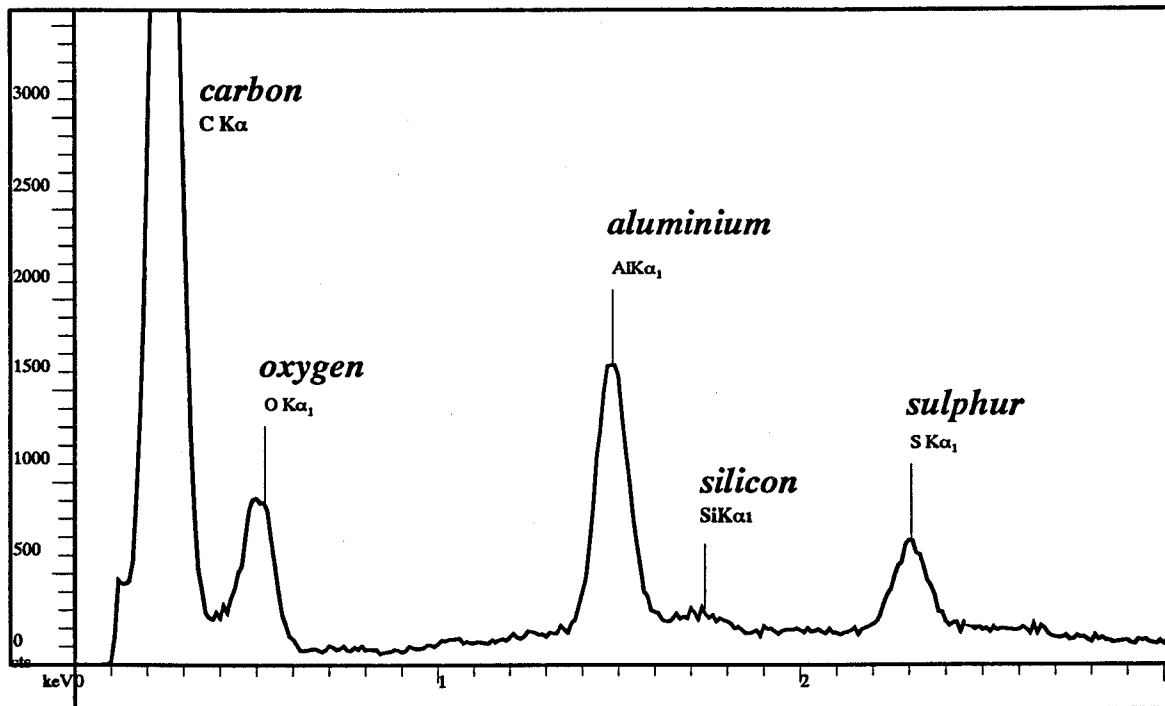


Fig. 8 EDX Scan of Carbon-Epoxy Patch After Light Grit Blasting has Removed Silicone Contamination Transferred from Released Nylon Peel Ply. (Aluminum from Residual Aluminum Oxide Grit-Blast Material)

Proof that the silicon came from the peel ply and not from the interior of the laminate is provided in Figure 8. This EDX assessment of the surface of the patch, *after* it had been lightly grit blasted, shows that the silicon has been virtually totally eliminated. (Note that this picture is drawn to an enlarged vertical scale, with respect to the earlier two diagrams.) The aluminum comes from residual aluminum oxide grit-blast material.

Figure 9 shows the corresponding EDX scan after further grit blasting of the surface. A comparison with Figure 8 shows that only light grit blasting is sufficient to remove the silicon contaminant, since further grit blasting did not reduce the residual signal significantly.

Figure 10 shows the surface of a patch after grit blasting more severely than is desirable. The fibers visible in Figure 10 are individual carbon fibers, which are almost as difficult to bond to as nonactivated resin surfaces. [As a point of comparison, Figures 9 and 10 in Reference (1) show that the surface *can* be thoroughly roughened without even removing the texture of the peel ply.]

Two further EDX scans were run to pinpoint the origin of the silicon contaminant. Figure 11 shows that, even with further expansion of the vertical scale, there is no trace of silicon in a piece of epoxy cut from the interior of the laminate. (The sulphur trace, on the other hand, is distinct, confirming that it did *not* come from the peel ply.)

Figure 12 shows the result of an assessment of a piece of nylon cut from the *interior* of an individual nylon filament removed from the peel ply. Even at the expanded vertical scale, there is no trace of silicon, proving that it was added at the weaving stage, or later.

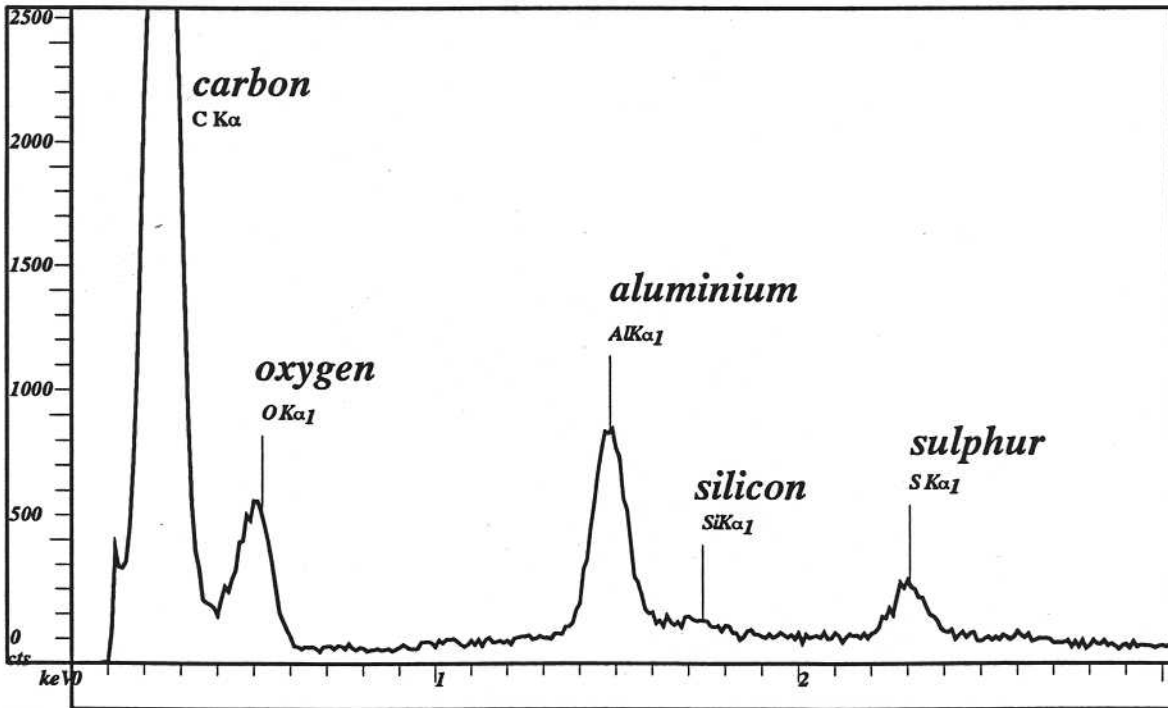


Fig. 9 EDX Analysis Spectrum of Patch Surface After Further Grit Blasting, Which is Shown to be Unnecessary

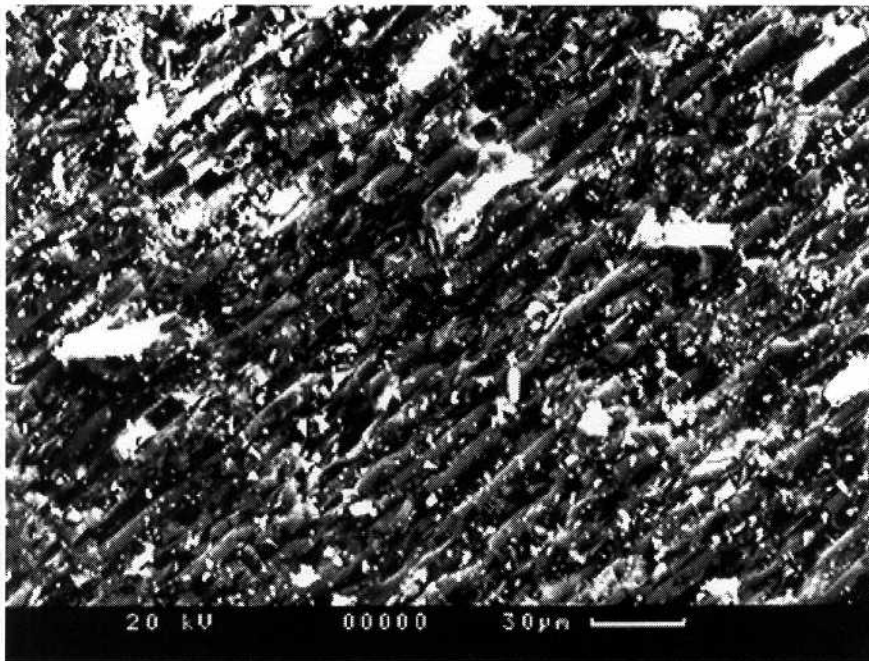


Fig. 10 Surface of Carbon-Epoxy Patch After Excessive Grit Blasting which, While It Has Not Damaged Fibers, Has Exposed Too Many of Them for Bonding

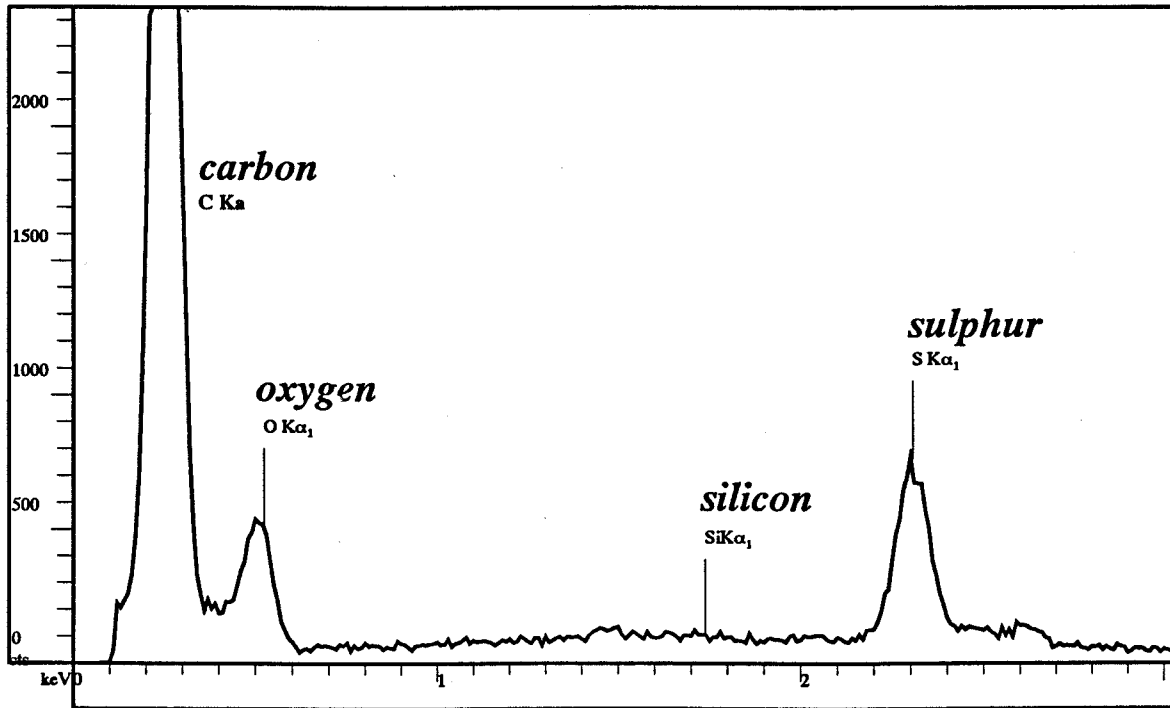


Fig. 11 EDX Scan of Epoxy Sample from Interior of Laminate, Showing No Trace of Silicon, Proving Surface Contamination was Transferred from Nylon Peel Ply

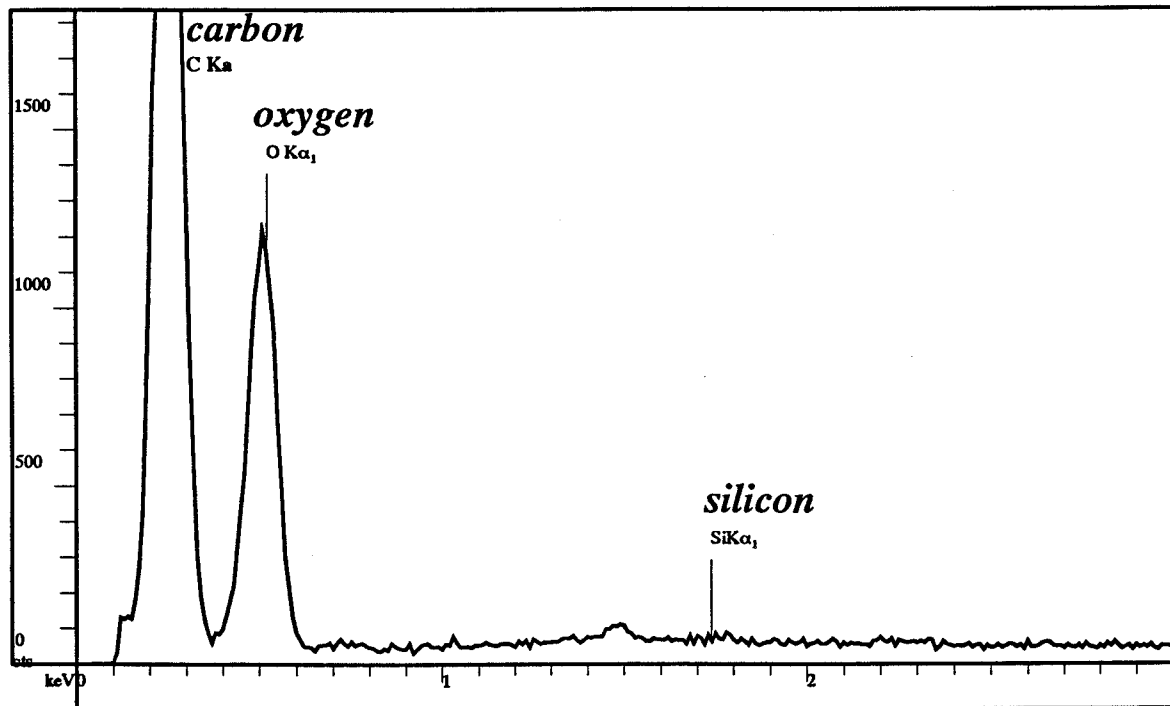
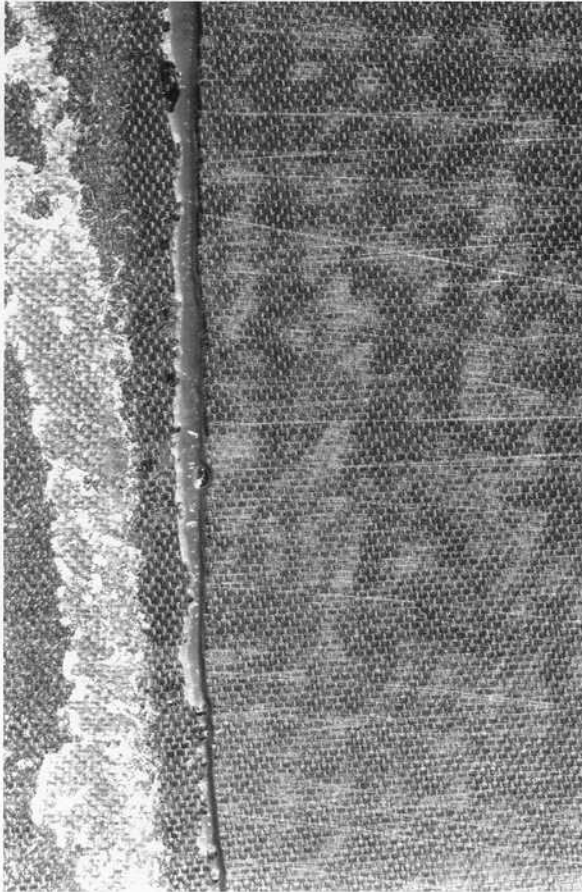


Fig. 12 EDX Scan of Sample of Nylon Cut from Interior of Fiber in Peel Ply, Confirming that the Nylon Itself Was Not The Source of Contamination of Bonding Surface



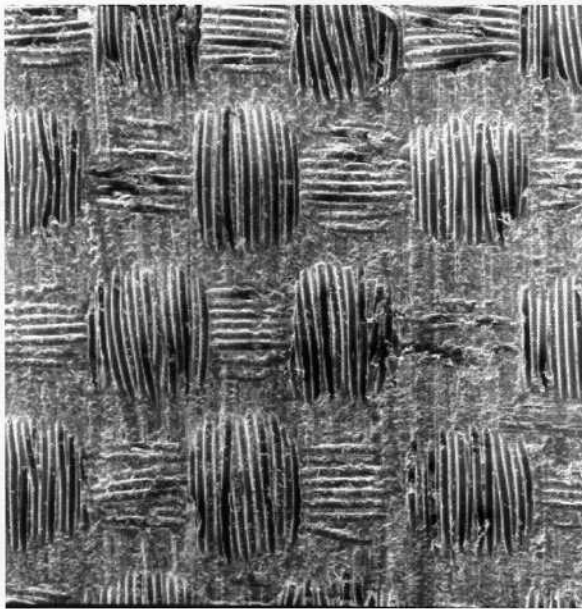
10X

Figure 18. Inadequate Roughening Achieved by (Scuff) Sanding



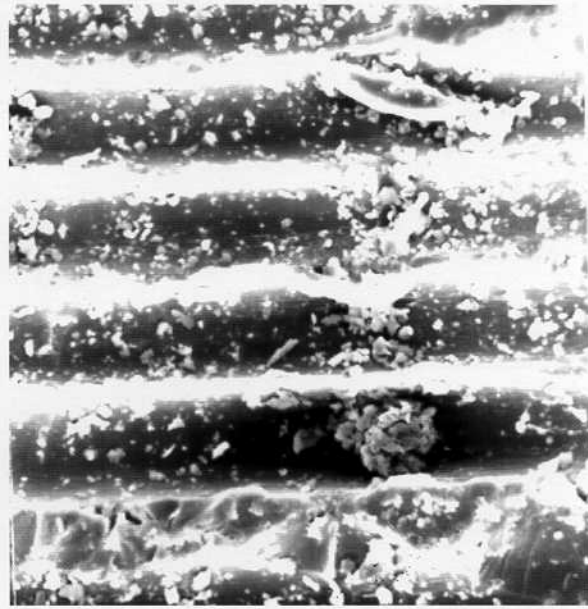
750X

Figure 19. Slight Fiber Damage Caused by Thorough Sanding of Unidirectional Carbon-Epoxy Laminate



100X

Figure 20. Surface of Woven Composite Laminate, Showing How Moderate Sanding Does Not Abrade the Entire Peel-Ply Imprint



1,000X

Figure 21. Highly Magnified Hand-Sanded Surface, Showing How Most of the Peel-Ply Imprint Remains

Figure 15 is the EDX analysis spectrum obtained on the general area of the virgin sample of peel ply shown in Figure 1. The carbon and oxygen occur naturally in the nylon fibers in the peel ply, but the silicon is present as contamination of the peel-ply surface (i.e. from the silicone release agents). The concentration of silicon is even higher than was revealed by examination of the peel ply *after* it had been stripped from the composite patch (see Figure 1).

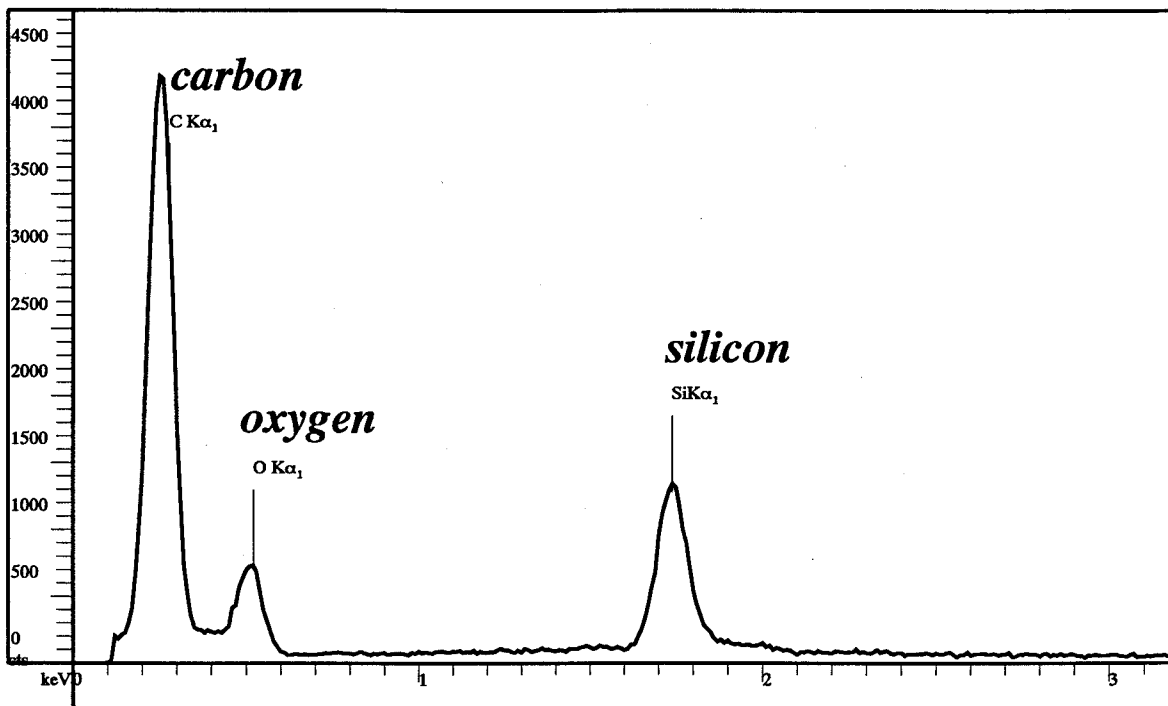


Fig. 15 EDX Scan Obtained on General Area of Virgin Nylon Peel Ply, Showing Strong Silicon Signal from Silicone Release Agent

Figure 16 shows the EDX analysis spectrum obtained from the surface of the nylon fiber in the sample of virgin peel ply at location A in Figure 14. This area was selected for examination because, under the microscope, the fiber was locally visibly *bare*, with no trace of coating. There is virtually no silicon signal at *this* location, confirming that the silicone was added by the peel-ply manufacturer, not at the fiber or fabric stage. Figure 17, in the other hand, records the EDX analysis spectrum when focused on the blob of silicone detected visually in Figure 14 (at point B). This silicon reading is higher, by a factor of 6 than the worst in any earlier examination. Can there still be any doubt about why bonding directly to the surface created by stripping off such a released nylon peel ply and bond *directly* to this surface instead of grit blasting it first is so unreliable as to have forced several aerospace manufacturers to ban this process? What more evidence can remaining manufacturers and subcontractors demand before they cease this practice, too?

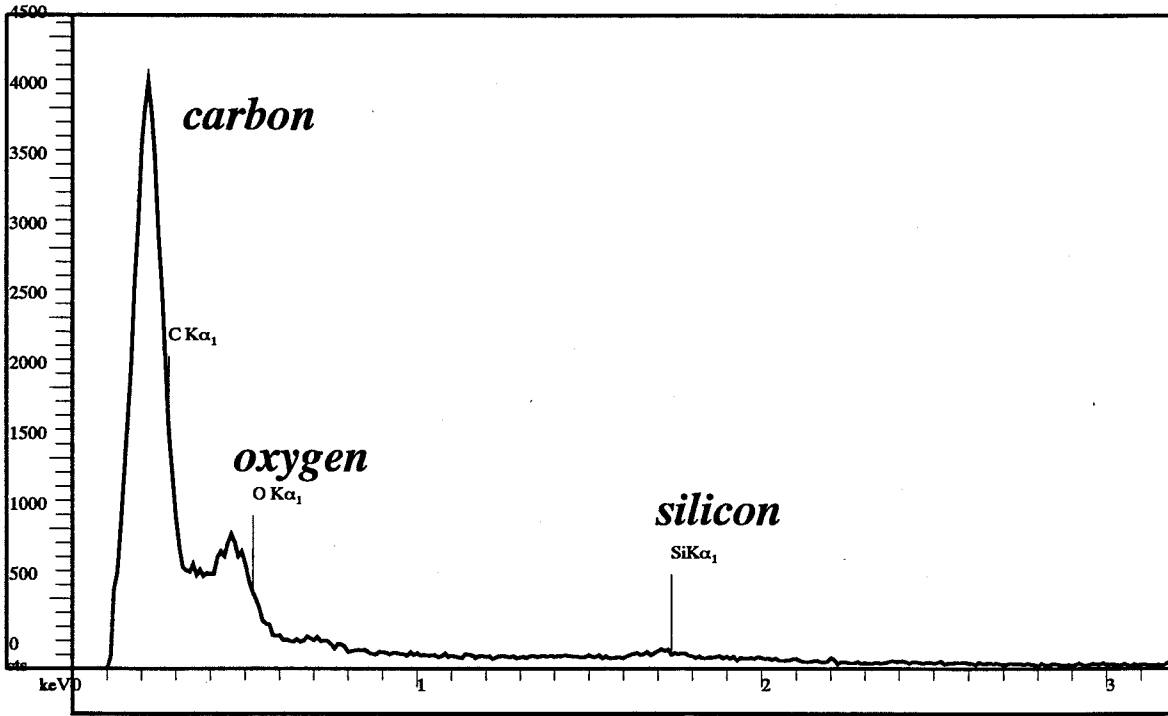


Fig. 16 EDX Analysis Spectrum of Locally Bare Section of Nylon Fiber in Virgin Peel Ply

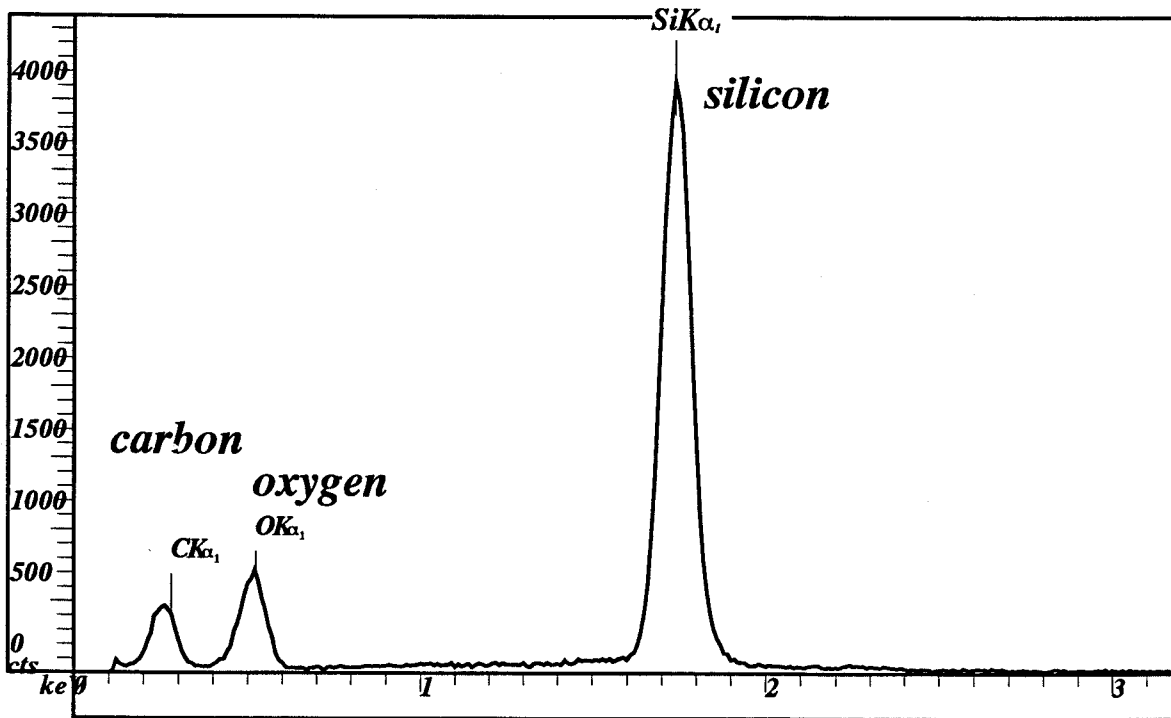


Fig. 17 EDX Scan of Deposit on Virgin Nylon Peel Ply, Showing Extremely High Concentration of Silicon from Blob of Silicone Release Agent

INPUTS ON NYLON PEEL PLIES FROM OTHER SOURCES

Despite the presence of silicone over most of the bonding surface, the very thin strands of fractured resin *between* the grooves left by the peel ply (see Figures 6 and 7) are sufficient to create a bond with an initial strength greater than zero. Indeed, it appears that the epoxy resin and adhesive on each side of the layer of silicone can combine chemically with this contaminant. The strength of such weak interfacial bonds is far less than the cohesive bond strength or the interlaminar strength of the composite itself. Nevertheless, it is sufficiently high to create the illusion of an adequate strength for thin parts whenever only short-term tests are performed. However, whereas the cohesive and interlaminar strengths do not diminish with time, this kind of interfacial strength decreases steadily, until the parts simply fall apart. The most credible explanation given to the senior author by polymer chemists about the dominant mechanism for loss of strength appears to be very similar to that which degrades the interfacial strength of poorly prepared metal bonds. This is the absorption of water, the hydroxyl groups of which break the chemical bonds between silicone and epoxies. Another of the mechanisms for this progressive loss of strength is thermal cycling, since the silicone and epoxy have very different thermal coefficients of expansion. There are also many more mechanisms of failure contributing to the breakdown of the interface. In short, just as for metal-bonded structures, processes which lead to interfacial failures cannot be tolerated. Only when the interface is *not* the weak link can a durable bond be relied upon.

Proving by test that the interface is not the weak link is not all that easy if the tests being run are aimed only at validating the adequacy of a specific design. For instance, if a composite part is quite thin, as many are, the laminate may not be strong enough to apply even 50 percent of the load needed to fail the bond cohesively before the laminate itself fails. Such a joint may be representative of the structure, but it is quite inappropriate for comparing different surface treatments, or even whether or not the adhesive had been cured properly. Likewise, if a laminate is made from woven fabric rather than unidirectional tape, shear transfer through a bonded joint has the potential of splitting the 90° bundles of fibers interlaminarly long before the adjacent 0° fibers in the fabric or the 0° fibers in the tape laminate would fail. (This is why, in stepped-lap bonded joints, designers strive *not* to locate a 90° ply on any of the steps.) Assessing different surface treatments for bonding composites, and whether or not there is a durability issue, *requires* that the coupons be unidirectional tape and that they be thick enough to fail a properly cured adhesive layer at the same stress as developed in metal-bond coupons. Qualification tests by one of Douglas Aircraft Company's subcontractors *confirmed* that this level of strength *can* be attained. Only *after* the unsatisfactory processes and material combinations have been excluded by *this* kind of testing should there be tests with specific woven fabrics to account for the phenomena associated with the fiber dispersion in the laminate rather than the bonded joint. Otherwise, the effects of different surface treatments and the like are *masked* by premature interlaminar failures because of the low shear-transfer capability of bundles of 90° fibers.

The authors are indebted to a colleague at Dupont for an explanation of the minute strands of nylon filament adhering to the grooves in the resin surface shown in Figures 16 and 17 of Reference (1). More expensive nylons have a very small range of molecular weights in the polymer. Less expensive ones contain a large range of ingredients with quite different molecular

weights (chain lengths). It appears that those oligamers of the shortest length will react with the epoxy resin as it cures and that this is the origin of the streaks in the aforementioned Figure 17. Far from a barrier to bonding, as the senior author had previously suspected, *this* form of nylon left on the bonding surface may represent the *most bondable* fraction of the total area of the furrows. However, the generation of this feature is inconsistent and cannot be relied on.

EDX tests like those reported here, or Auger spectrometer measurements, were performed on every mold-release spray considered for use during the construction of the Lear Fan all-composite aircraft. It was found that words like “silicone-free” and “nontransferring” on the labels of these products could not necessarily be taken at face value. Tests by which the presence or absence of known surface contaminants can be established have been easy to perform for many years now. One must wonder *WHY* such tests have not been a standard part of the qualification for all peel plies for many a long year. Relying on *visual* inspections to ensure the absence of contamination makes no more sense than using ultrasonic inspections which can tell *nothing* about how well glue is stuck to overrule the rejection of a bonded panel because of a visually observed failure to adhere to the *processing* specifications.

Silicone contamination has also adversely affected fibrous composite construction in other ways. One example concerns the manufacture of a conical carbon-carbon adaptor ring for a spacecraft many years ago. The perimeter was segmented, to maintain the correct fiber orientations, and stepped-lap joints were created between the segments, by staggering the positions of each ply. Each segment was consolidated under a nylon vacuum bag before they were positioned correctly and co-cured as a single assembly on the lay-up tool. The resin was successfully carbonized in the next step. Unfortunately, when the cone was tested, it failed prematurely at the stepped-lap joints. Examination revealed 100 percent coverage of these interfaces with silicon. It was eventually established that it had come from the nylon bagging material in the form of a continuous sheet of silicone which did *not* dissolve into the resin, but remained as a thin film. It had transferred under only vacuum pressure at the modest temperature used for consolidation. Far more would transfer under autoclave pressure at 350°F.

Widespread disbonds have also been found in carbon-epoxy honeycomb-sandwich panels which were co-cured in a single shot, apparently giving no opportunity for the introduction of the silicone contamination which caused the failures. The origin of the silicone release agent, which affected only one face sheet on the panel, was traced to the core having been stabilized on that side by a layer of film adhesive cured on it in the unrecognized step *prior* to the “*single-stage*” cure. The peel ply used to prevent this glue septum from sticking to the bleeder stack was the same one as had caused the disbonds noted in Reference (1). Since the facing on the core could not be sanded because of the telegraphed shape between the cell walls, and could not be grit blasted because the glue layer was too thin, no attempt was made to prepare *this* cured glue surface to make the *next* layer stick. This generic problem is important because, had a tenacious tear ply been used instead, to prevent the transfer of contaminant, its removal would have taken the glue septum with it. One must, therefore, question the wisdom of this manufacturing technique for stabilizing cores.

WHY POLYESTER PEEL PLIES WORK AT LEAST *SOME* OF THE TIME

In contrast with chemically reactive nylon *thermoplastic* peel plies, similar fabrics made from *thermoset* polyester fibers are so inert, because they are already fully cross-linked, that they do not *need* to be coated with a release agent to facilitate their removal. On that basis, they *must* be better than nylon peel plies. Nevertheless, this same inertness ensures that the cured epoxy surface created alongside the polyester fibers is *also* inert, making it very difficult for glue to adhere during the following cure cycle, unless the surface to be bonded is thoroughly abraded first.

As Mahoney has explained in Reference (4), whether or not an adhesive will adhere to a substrate is a function of the surface tension at the interface during cure. There is no universal peel ply which could create a bondable surface for all adhesives on all laminating resins. This is confirmed by the suppliers of peel plies, who explain the wide variety of available peel-ply materials and surface treatments as being *necessary* to accommodate all the needs of their customers. Unfortunately, this wisdom is not shared by the major aircraft manufacturers who, in the interests of apparent economy, do not test *every* combination of adhesives, laminates, and peel plies which they approve. Some even allow substitutions of materials to limit costs through purchasing from multiple sources, without testing the *combination* of materials. It is difficult within a factory to even separate those highly released peel plies intended only for use on thin-walled or thin-faced composite parts which would be neither bonded nor painted from the very different tear plies which should be specified for areas in which structural bonds will be made.

The importance of not substituting one material for another is well illustrated by experiences in England. What is believed to be the successful use of a particular polyester peel ply, when used in conjunction with a high-temperature-curing film adhesive, had been interpreted as an indication of suitability for using the same peel ply with a paste adhesive. This was found not to be the case. The hot bond attained a very low minimum viscosity during cure and was able to wet the surface, while the cold bond had such a high minimum viscosity that the paste adhesive never wet the bonding surface. The paste adhesive never stuck, although there were no gaps and the joint passed ultrasonic NDI inspection. A sample of the paste adhesive off a test structure made this way contains a perfect imprint of the peel ply looking for all the world like Figures 2 and 3 here and the many similar photographs in Reference (1). Yet, hot bonds applied to carbon-epoxy composite surfaces prepared using the same polyester peel ply have been made successfully for years, both in England and in Australia, since the same peel ply had been selected as standard for the RAAF whenever they had the authority to choose. (It should be noted, however, that the RAAF procedures call for grit blasting or thorough sanding after even this noncontaminating peel ply has been used. Grit blasting has the added benefit of exposing active bond sites in the composite matrix.)

Figure 18 is an EDX analysis spectrum of the surface of a virgin nonreleased polyester peel ply, of the type currently used by the RAAF for their *own* repairs. There is no silicon in the spectrum which confirms that there is no silicone deposit on the surface. One may reasonably infer, therefore, that *this* peel ply would not contaminate the bonding surface on the laminate with which it would be cured. Figure 19 is a SEM video print of this same polyester peel ply. The

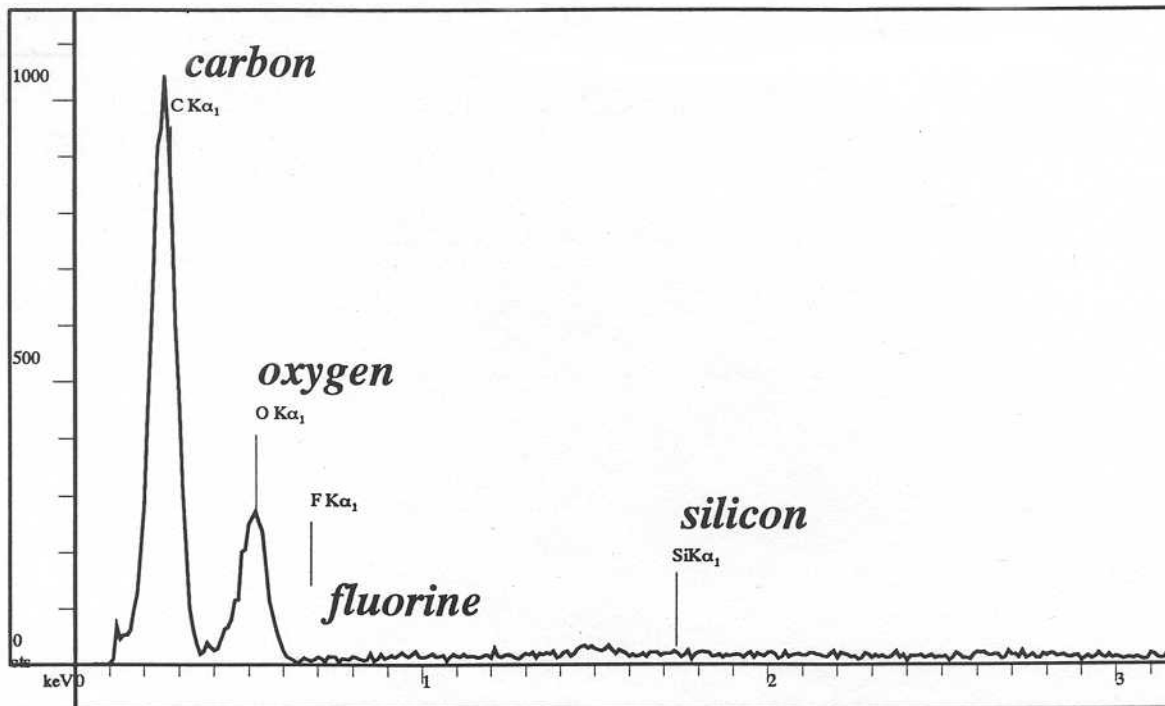


Fig. 18 EDX Scan of Nonreleased Polyester Peel Ply, Showing No Trace of Surface Contaminants

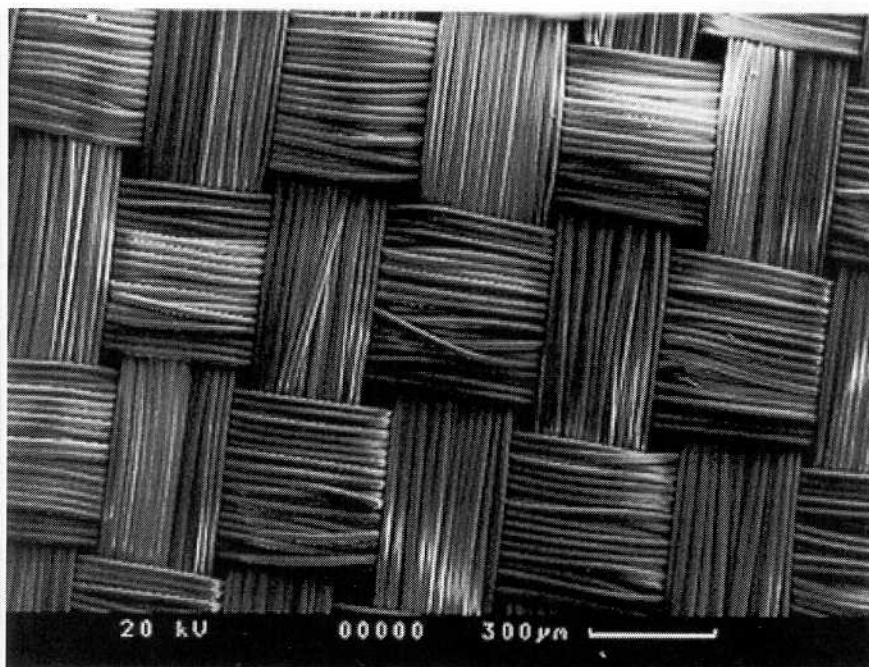


Fig. 19 SEM Video Print Showing Individual Nonreleased Polyester Fibers with Visibly Clean Surface Free from Contamination Seen on Released Nylon Peel Ply

fibers appear to be fairly “clean” and free from obvious contamination, unlike the released nylon fibers in Figures 14 and 15. Figure 20 is a more highly magnified print of the same polyester peel ply, further confirming the absence of contaminants.

Figure 21 shows the absence of any contamination on the surface left by stripping off this polyester peel ply. Checks were made for both silicon, from silicone, and fluorine, from Teflon.

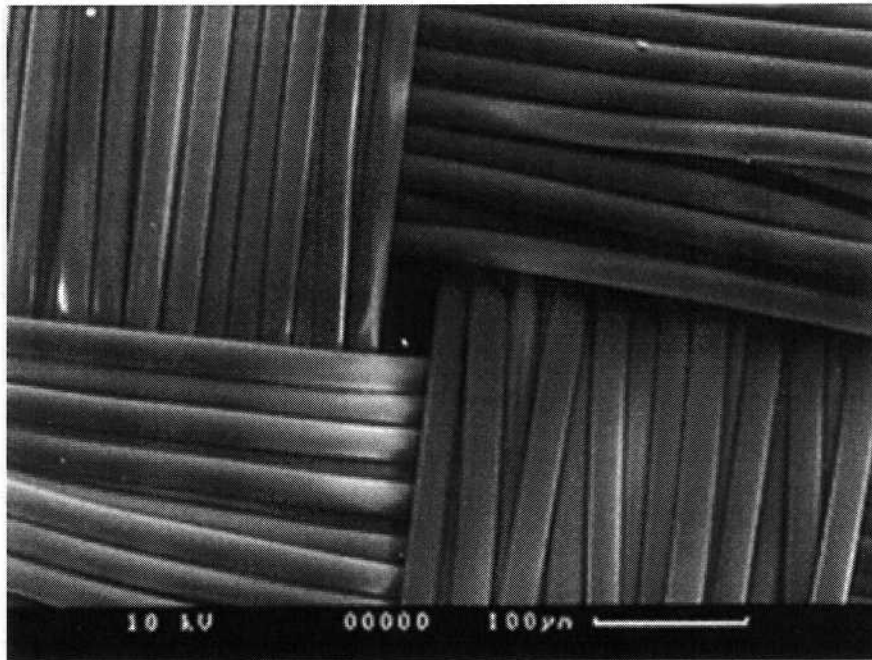


Fig. 20 Enlarged SEM Video Print of Surface of Virgin Nonreleased Polyester Peel Ply, Confirming Absence of Release Agents

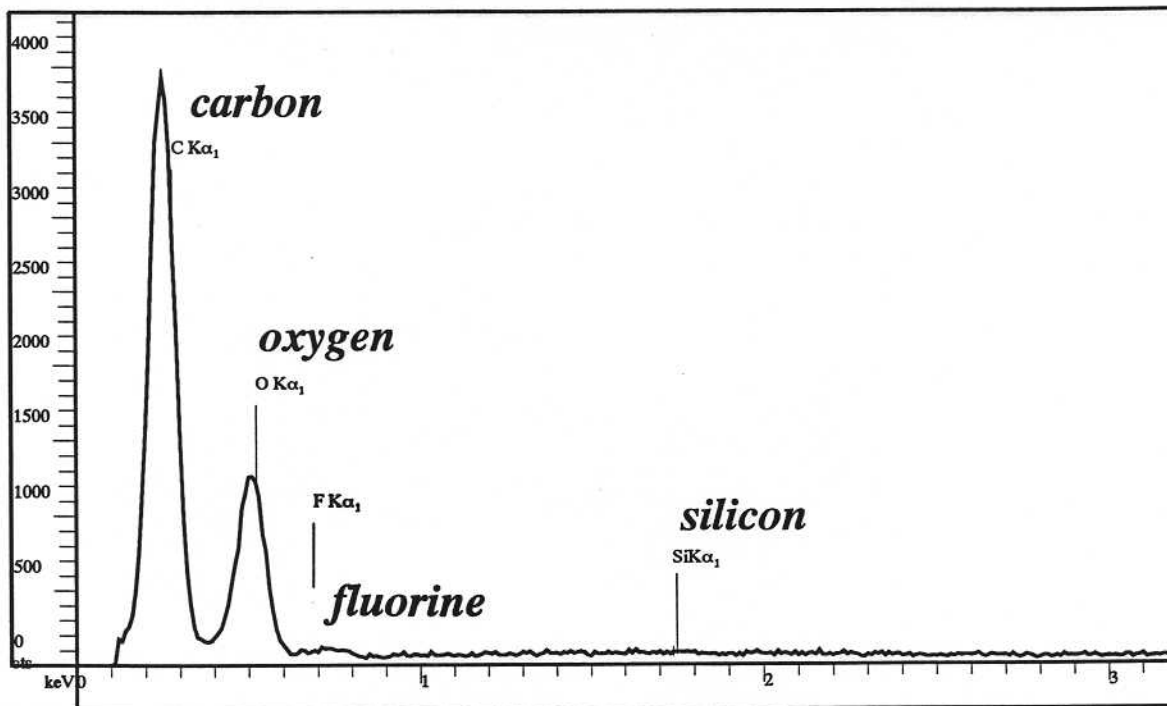


Fig. 21 EDX Scan of Laminate Surface Left by Stripping Off Nonreleased Polyester Peel Ply, Showing No Contamination by Either Silicon (from Silicone) or Fluorine (from Teflon)

No trace of either was found. This would imply that whatever bond strength *is* attained will *not* deteriorate in service. This is a strong message of encouragement for the use of *uncoated* polyester peel plies, despite the preference of some shop personnel for released nylon peel plies because they are so much easier to remove. The absence of contamination transferred from *truly* unreleased peel plies suggests that stripping off such a peel ply is probably an adequate surface treatment for painting and is even possibly sufficient for lightly loaded adhesives bonds such as those between face sheets and honeycomb cores.

It has long been a common belief that the greater difficulty in removing polyester peel plies was associated with actually creating a surface of freshly fractured resin to which a strong durable bond could be formed. However, Figures 22 and 23, at progressively higher magnifications, show that the furrows are just as slick as those left by removing a released nylon peel ply.

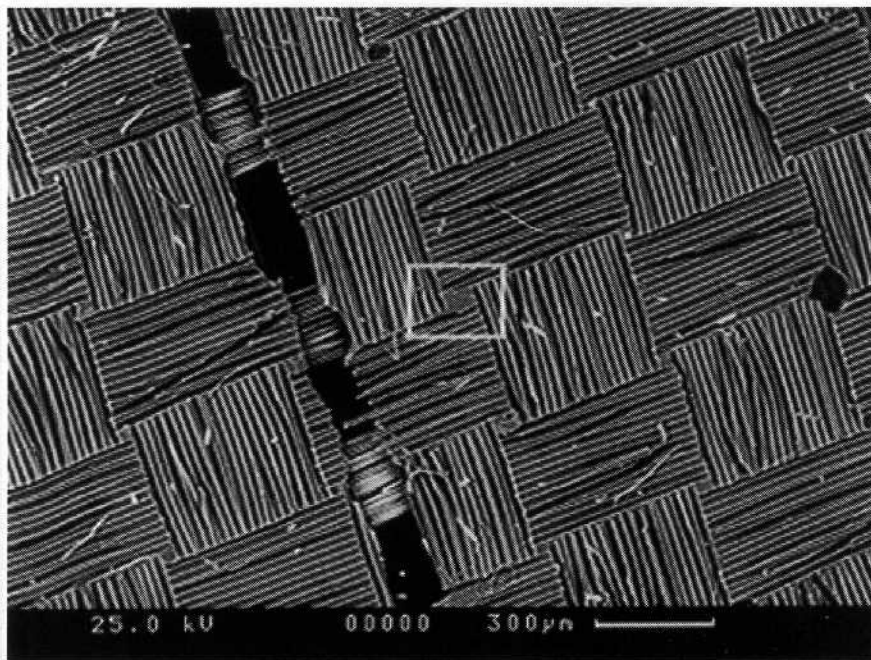


Fig. 22 SEM Video Print of Laminate Surface Created by Removal of Nonreleased Polyester Peel Ply, Showing Clearly Defined Imprint of Peel Ply

Figures 22 to 24 in Reference (1) confirm this absence of widespread fractured surfaces, although there is evidence of some adhesion between the laminating resin and the polyester fibers in the form of strands stuck to the epoxy surface which would presumably, in turn, adhere tenaciously to a subsequently applied adhesive layer. As with the released nylon peel ply, Figure 23 shows most of the fractured resin surface confined to the crossover points in the weave of the peel ply.

What can be stated with certainty about using nonreleased polyester peel plies to create bonding surfaces in composite structures is that it provides an infinitely better starting point for subsequent mechanical abrasion than released nylon peel plies. To be fair, one should add that even without the abrasion, there is no overwhelming evidence of widespread problems of the

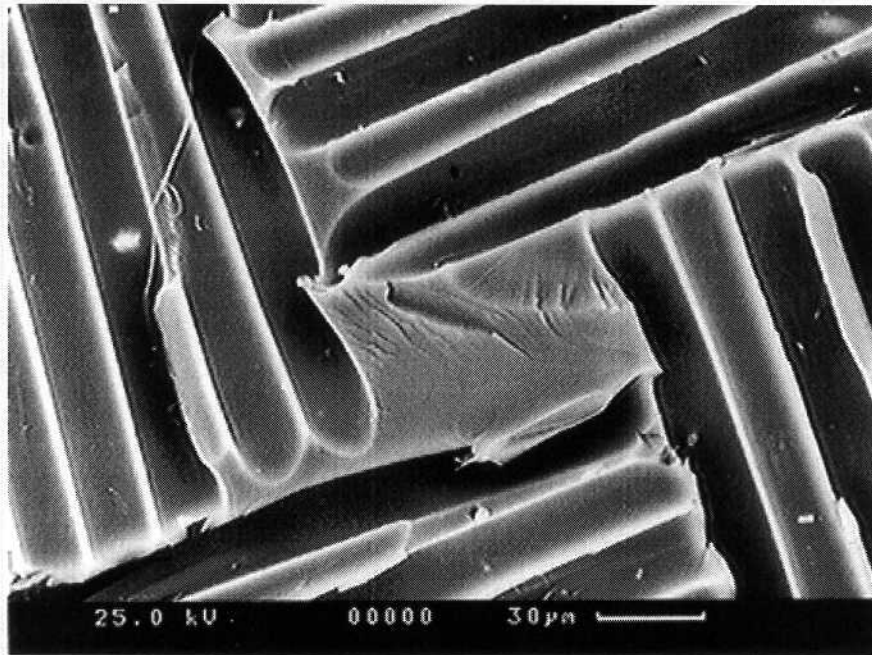


Fig. 23 Enlarged SEM Video Print of Composite Surface Left by Stripping Off Nonreleased Polyester Peel Ply, Showing Smooth Furrows Left by Individual Fibers, as well as Fractured Resin at Fiber-Bundle Cross-Over Points

kind encountered regularly with nylon peel plies. Nevertheless, since the bond is eventually made to an inert surface rather than to the more active surface created by grit blasting, no guarantee can yet be made that the mechanical abrasion is unnecessary. Also, it must be more difficult for an adhesive to wet this peel-ply surface than a grit-blasted one. This is evident from lower short-term lap-shear test results. Even so, all three authors strongly advise anyone still using nylon peel plies alone, who is unwilling to switch to grit blasting, to immediately switch to nonreleased polyester peel plies, as many other organizations have already done.

All three authors also have a strong preference for light grit blasting of composite surfaces to be bonded, no matter what previous treatment may have been applied, because there are *no* reports of failures with this technique. Also, it may well be easier to perform reliably than stripping off nonreleased polyester peel plies, particularly from thin laminates which are prone to delamination. Indeed, the former Space Division of British Aerospace used tenacious peel plies on their robust laminates and grit blasted those too thin and fragile for such treatment. So much for the myth that grit blasting is likely to do severe damage to the parts! The key to not doing so is simply to reduce the blast pressure to about 20 psi, instead of cranking it up to 100 psi, to finish the job more quickly.

While it is reasonable to expect that adhesives are far less likely to fail to adhere to uncontaminated surfaces created by stripping nonreleased polyester peel plies from the surface of a laminate than is the case with released nylon peel plies, there is no automatic guarantee of success, either. Each combination of materials and processes must be validated separately. The proof of this statement can be found in the experiences of a number of companies which

currently *favor* the use of polyester peel plies even though each acknowledged privately that, at some time in the past, it had suffered through a major disaster caused by having the adhesive fail to stick reliably to the surface created by some peel ply or another. One such company is now confident that all of its problems are behind it because they have recently switched to a *new* polyester peel ply – the very *same* peel ply that a sister company in the same corporation has just *abandoned* because of all of the problems it had caused *them*!

This uncertainty is the Achilles heel of even those peel plies known to really *not* be contaminated by release agents. What is needed is commonly referred to today as a *robust* system, one which is very forgiving of minor processing and surface-preparation variations.

Despite these legitimate doubts when the removal of a polyester peel ply is *not* followed by thorough mechanical abrasion, it should be acknowledged that polyester-peel-ply-removal alone is the preferred surface treatment throughout much of the aerospace and automotive racing industries in the United Kingdom. Their faith in these procedures is backed by extensive testing, by both industry and universities – testing which also exposed so many problems with nylon peel plies that these are definitely *not* recommended there.

CONCLUDING REMARKS

This article, and Reference (1), should serve as constant reminders to never again underestimate the importance of properly preparing the surfaces for bonding (or even painting) in fiber-polymer composite structures. The Utopian goal of being able to simply strip off a peel ply to create a near-100% surface of freshly fractured resin, to which any adhesive could form strong chemical bonds, may simply not be achievable. It has certainly not been attained so far.

Although they do develop some strength in the short term, bonds made directly to the surfaces created by removing *released* peel plies cannot be relied upon to last in service. Such surfaces *need* to be lightly grit blasted to remove the transferred contamination, even for paint to adhere in the long term.

The issue in regard to tenacious *nonreleased* peel plies is not so clear. On the one hand, some are impossible to remove, thereby proving beyond doubt that they were *not* contaminated! On the other hand, in the virtual absence of contamination on the inert bonding surfaces, there may be no mechanism whereby those chemical bonds which *do* form would deteriorate in service. It is clear, however, that these bonds are to microscopically *smooth* furrows in the imprint of the peel ply and *NOT* to freshly fractured resin as has often been believed to be the case in the past. Even so, there are many lightly loaded composite structures for which such a bond may yet be shown to be adequate after many years of service. In addition, certain adhesives can solvate the smooth clean laminate surface sufficiently to form strong chemical bonds which *are* durable. The difficulty is that these situations must be validated on an *individual* basis, for each combination of peel ply, adhesive and resin.

The strongest and most durable bonds are those made to lightly grit blasted surfaces. Those manufacturing organizations in favor of such processes, such as the RAAF, are able to perform

them no more expensively than those who favor peel-ply removal alone.

The wide variety of available peel and tear plies is testimony to the fact that there is *no* universal peel ply suitable for all laminating resins and all adhesives, a position adopted by the distributors of peel plies. Since the adhesion of both paint and adhesive to composite laminates is a function of the surface tension generated while the peel ply is being cured with the laminate and while the adhesive cured against the imprint left by removing the peel ply, different composite materials will achieve different strengths when used with the same peel ply, and vice versa. This requires that every *combination* of resin matrix, peel ply, and adhesive be checked for bond strength and durability before substitutions are permitted.

The incidence of bond failures caused by the use of *released* peel plies with no subsequent mechanical abrasion, the occasional scratch left by scuff sanding being totally inadequate, is sufficiently high to question the wisdom of allowing some such peel plies *anywhere* inside a factory unless one of two conditions is met. *ALL* composite surfaces to be bonded or painted *will be* grit blasted, *regardless* of what surface protection was applied prior to that point, or that *absolutely no composite structures built at that factory will ever be assembled by any means other than bolts and rivets*. Otherwise, there will continue to be instances of substitution of some easier-to-use released peel ply for the specified non-released peel ply by someone who does not understand *why* the more difficult peel ply was called for in the first place.

Absence of service problems in bonded, co-bonded and co-cured composite structures can be assured only by effective durability testing which can be completed in the short term, both at the start of a program, to select materials, and as a quality-control test during production. What is still missing from the composites world is a test equivalent to the wedge-crack test for metal-bonded structures.

Acknowledgment: Even during the preparation of Reference (1), which included a request for help, the senior author had received considerable assistance from colleagues around the world. Special recognition is due to Oxford Brookes University, England, for those samples made differently from the Douglas parts "bonded" with a nylon peel ply on a 350°F-cured epoxy resin laminate. Since then, many organizations have shared their experiences and offered encouragement, which is why this new article is able to include so much additional information. These include Airtech, Boeing, British Aerospace, Dupont, Fokker, Hawker de Havilland, McDonnell Aircraft, McDonnell Douglas Astronautics, McDonnell Douglas Helicopter Systems, the RAE (now DRA) Farnborough, the NADEP on North Island at San Diego, and the USAF Materials Laboratory in Dayton. The level of support given in the form of what would normally be regarded as competitive or sensitive information is some indication of the concern felt by those who *do* know what care is needed to prepare composite surfaces for adhesive bonding or painting about the bad reputation created for this technology by those who, quite frankly, don't. Only the difficulty of crediting the advice in such a way as not to identify where certain problems arose (including some at Long Beach) prevents the senior author from properly identifying all the other sources of information. Nevertheless, in expressing his thanks, he trusts that all who have helped will ultimately benefit from improvements to this technology that their assistance must surely bring.

Disclaimer: Although the results of tests on only two peel plies are presented here, there is no reason to believe that the results would have been any different had they be performed on the corresponding competitive products. Indeed, inputs from colleagues around the world have confirmed this. The intent of the article is *not* to criticize any specific products or suppliers; it is to *avoid repeating* mistakes which have already been made enough times to give this technology an undeserved bad image. Three points are very clear; (1) one *cannot* create a durable bond on the surface left after stripping off a *released* peel ply, no matter what the fabric is made of, (2) the only *universally* reliable surface preparation for bonding is low-pressure grit blasting, and (3) those instances in which *nonreleased* peel plies have been found to work are associated with *specific* combinations of resin, peel ply, and adhesive. Each combination must be validated separately, and only subtle changes in even one ingredient have invalidated the effectiveness of such bonds. Not enough is known about those peel plies coated with proprietary sizings, rather than release agents, to make any comment other than to refer to category (3) above. There is no universal peel ply. Fiberglass peel plies have not been mentioned separately because they fall into one of the categories discussed here; released plies which create surfaces which do not permit the adhesive to stay stuck, and fibers treated with sizing to *promote* adhesion and possibly even create a bondable surface of fractured resin. Unfortunately, as the senior author can attest, *these* tear plies are all but impossible to remove without breaking either the fibers or the laminate.

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