Gas Plasma Treatment of Kevlar® and Spectra® Fabrics for Advanced Composites

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The engineering properties, (strength, stiffness, weight and heat tolerance) of fiber and the fabrics made thereof are the primary reason for its selection. However, secondary characteristics such as surface properties are assuming more critical importance. For example, if a polyethylene fabric is to become the reinforcement in a composite structure, the surface of the fiber needs to be altered to promote the adhesion of a matrix polymer to the fiber, preventing an otherwise weak composite structure.
A cold gas plasma process is shown to provide a dramatic increase of the flexural strength of Kevlar® and Spectra® composites. With plasma processing, the surface of the material is cleaned and modified by just a few angstroms in an economical and environmentally safe method. A plasma system capable of economical treatment of composite reinforcement fabrics up to 60" in width is available and is being used commercially.

Background

Any process which changes the polymer must not change the bulk properties or the polymer may lose its primary physical and chemical characteristics. Prior to gas plasma treatment, various techniques have been used for fabric treatment such as chemical and/or solvent etch, flame treatment, and corona discharge. However, these treatment techniques have significant drawbacks.

Wet chemical and solvent treatment, if effective, often add numerous additional processing steps such as neutralization, washing and rinsing and drying. These solvents and chemicals are usually hazardous or designated hazardous, constituting a toxic waste disposal problem and cost.

Corona and flame treatment while a very cost efficient treatment method is often not effective on many non-woven and fabric substrates. Because of the potential for rapid high heat generation, treatment is conducted at high speeds, thus the residence times are insufficient to permit penetration of the active species that effect change into the fiber bundles or interstices of non-woven webs and fabrics. Since corona discharge systems depend on ionizing free air, the process may not produce consistent results from day to day, season to season and location to location. Further, electrostatic discharge produces ozone as an effluent, which must be properly processed before venting to the atmosphere, thus adding to the cost of the treatment process.

Cold Gas Plasma for Re-engineering Polymer Surfaces

Over the past quarter-century the technique of re-engineering polymer surface properties through exposure to a gas plasma has been extended to virtually all polymers. A variety of results can be easily obtained, specific to the polymer and the gas species employed. Producible effects run the gamut from highly wettable surfaces exhibiting superior adhesion characteristics and chemical reactivity to completely unwettable, inert surfaces. More sophisticated plasma processes permit dissimilar polymers to be "grafted" onto the bulk polymer chain, or the deposition in-situ of a micro-thin coating via plasma polymerization.

The effect of a plasma on a given material is determined by the chemistry of the reactions between the surface and the reactive species present in the plasma. At the low exposure energies typically present in glow-discharge plasma systems the interactions occur only in the top few molecular layers. The majority of plasma activation processes are related to preparing the surface for subsequent operations such as printing or altering the surface wetting characteristics.

Gases, or mixtures of gases, used for cold plasma treatment of polymers include air, nitrogen, argon, oxygen, nitrous oxide, helium, tetrafluoromethane, water vapor, carbon dioxide, methane, and ammonia. Each gas produces a unique plasma composition and results in different polymer surface properties. For example, the surface energy which is analogous to wettability and chemical reactivity can be increased very quickly and effectively by plasma-induced oxidation, nitration, hydrolyzation or amination. Conversely, plasma-induced fluorination depresses surface energy, producing an inert and non-wettable surface.

Gas Plasma Equipment

The reactor is a vacuum chamber equipped with vacuum pump, purge plumbing, process gas sources and regulators, a source of electromagnetic energy and a system controller to orchestrate the process.

The equipment operation cycle is carefully monitored and controlled by the electronics package, which operates the valves, pressure/vacuum flow gates and the RF source. In the 4th State system the roll product to be treated (up to 60" width and 19" package diameter) is loaded in the payoff chamber and threaded through the chamber to the take-up reel. The plasma treatment operation is then initiated and entirely controlled by the push of a single button. The process steps are: 1) pump down to predetermined vacuum pressure (base pressure), 2) introduce process gas and allow to stabilize at a desired process pressure, 3) initiation of plasma by providing rf energy, 4) transport product through the system and 5) after treating the desired length, shutting rf power and process gas delivery, 6) pump down to base pressure to eliminate residual process gas(es), 7) vent to atmosphere and 8) remove treated product.

Discussion and Results

Typical composite results for plasma treated and untreated (as received) fabric are presented in Tables I & II. These fibers are as dissimilar as one could ever anticipate in synthetic polymers. Spectra is ostensibly only carbon and hydrogen, an analog of wax but a polymer of extremely high molecular weight and orientation (30:1 draw ratio). Kevlar is a polyaramid with a variety of chemical elements and groups and is primarily aromatic in structure. By the judicious selection of process gas the fiber surface of either fiber is reengineered to make it compatible with and, if desired, reactive to the resin matrix of choice. The improvements in flexural strength and modulus are the result of an increase in interlaminar shear strength which in the case of the Kevlar was measured only for the plasma treated fabric composites.

As is readily seen a plasma treatment provides significant improvements over untreated material, 200 to 300% and more is not uncommon. Since there is a myriad of fabric styles in use, as well as different grades of both Spectra and Kevlar, the above data is presented as representative of typical improvement obtained across a broad matrix of fabric styles and fiber grades. Because the construction of the fabrics are different one should not compare the properties of these different composites, but that similar improvements are realized with all constructions.

Conclusion

The outstanding specific strength and modulus characteristics of advanced fibers can now be more effectively realized in reinforced composites with plasma surface treatment. The plasma treatment process can be readily tailored by the judicious selection of the process gas and process parameters to permit the "reengineering" of the top molecules of the fiber to a specific surface energy, chemical compatibility or reactivity to specific resin matrices. In addition, for fibers such as Kevlar where moisture absorption is known to have deteriorating effects, the plasma process is inherently an effective drying process providing further benefits.

4th State's plasma system shown has the capability of treating 60" wide products and roll diameters to 19.5". It is available to conduct development trials or toll treatment. Consider your product possibilities by reengineering the reinforcement fiber.

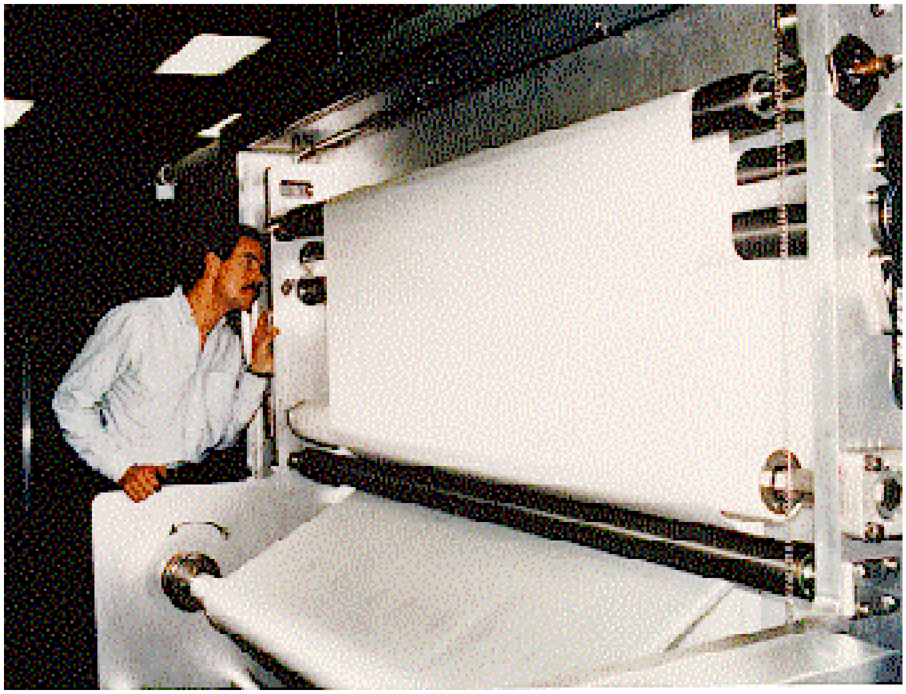
Table I
Kevlar 49 Composites
Style 120
normalized to 60% fiber volume

Lot	**Fabric Treatment**	**Flexural Strength MPa**	**Flexural Modulus GPa**	**Interlaminar Shear Strength MPa**
1	none	131.6	17.5	
2	none	88.5	19.8	
3	none	130.8	36.1	
4	none	167.3	25.4	
Mean		**129.6**	**24.7**	
Std. Dev.		**32.2**	**8.3**	

Lot	**Fabric Treatme**	**Flexural Strength MPa**	**Flexural Modulus GPa**	**Interlaminar Shear Strength MPa**
5	plasma treated	389.6	32.4	47.6
6	plasma treated	393.7	34.5	28.3
7	plasma treated	356.5	33.1	31.7
8	plasma treated	366.1	33.8	31.7
Mean		**389.6**	**32.4**	**34.8**
Std. Dev.		**18.1**	**0.9**	**2.7**

Table II
Properties of Spectra 900 / Epoxy Composites1
Fabric: 8 Harness Satin

Property	**Plasma**	**Untreated**
Fiber Volume (%)	70	67
Flexural Strength (MPa)	153	47
Flexural Modulus (GPa)	21	3
Interlaminar Shear Strength (MPa)	13	4



Plasma Fabric Treater
60" width capacity

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References

1. Kaplan, S.L., Rose, P.W., Nguyen, H.X. and Chang, H.W., Gas Plasma Treatment of Spectra Fiber, SAMPE Quarterly, Vol. 19, No. 4, July 1988

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