Studies on Surface Properties of Polymeric Coated Paper Material

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ABSTRACT: Surface properties of a polymeric coating system have a strong influence on its performance and service life. However, the surface of a polymer coating may have different chemical, physical, and mechanical properties from the bulk. Significant progress has been made during the last three decades in the improvement of coating on materials. It has been established that polymeric blends have great potential in replacing economically many conventional materials because of their high specific strength. It is needed today, constantly, to improve the surface finish of any material for efficiency and shiny appearance in the severity of working environment. In packaging, materials having longer service lives and those are less corrosive are highly used. The effect of polymer based coating on the paper material improves its mechanical properties and flame resistance. Effect of flame retardant polymer coating illuminates the surface of the sheet. Important application of the material sheets will be for corrosion receptivity and humidity resistance of this material will certainly improve. Blends of PMM/PVDF are mainly used to improve piezoelectric properties of PVDF. In the present study we report the measurement of surface properties of thin layer of polymer blend coated on the cardboard sheet substrate material. Polymer blend solutions of PMMA/PVDF was prepared at 90/10 (w/w) proportions in miscible solvent of toluene and DMF. Thin film was prepared on the surface of cardboard by dipping the cardboard material in the solution. Thickness of the dried polymer coated paper sheet was measured to see uniformity of coating and for different concentrations. Surface properties such as flexibility index, yellowness, and gloss reflectance were also measured. The study on these polymer coated paper will help in improving the surface property of paper as well as its use in packaging. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4167–4171, 2006

Key words: polymer blends coating; flexibility index; ferroelectric material

INTRODUCTION

Poly(vinylidene Fluoride) is a well-known flouro polymer used as coating material, having four different phase transformations before melting temperature.[1] At present, blending or alloying polymers constitutes one of the most attractive approaches to obtain new polymeric material with specific characteristics.[2] On the basis of PVDF a series of new materials have been developed, either through copolymerization or by blending PVDF with polymethacrylates or fluorinated polymers. The latter can be done by combining the superior barrier properties (chemical/flame resistant and toughness/flexibility) of PVDF[3–5] with hardness, rigidity, low smoke toxicity, and superior transmission/refractive properties of PMMA,[6–8] PMMA/PVDF blends are of considerable commercial relevance. It was observed that the blends were miscible, and it is checked by usual physical testing methods such as IR and X-ray diffraction. Both PMMA and PVDF exhibit several relaxations in DSC and DMA measurements. In DMA measurements the relaxation at highest temperature (called as α-relaxation) changes its location on the temperature scale gradually with composition. This indicates the miscibility of two polymers. When a material is mechanically contracted or rubbed with another material or exposed to certain radiation some charges appear on its surface.[9] In case of polarized dielectric material such as PVDF these surface charges can be observed persistently. This may be due to pyroelectricity and the effect produced can be retained for fairly long time.[10] Because of this electrostatic effect these materials are of great demand in electronic devices.

High performance coating in aeroscope, automotive, biomedical, and electronics application imply ever-increasing and quality-assurance demands on the component material and their processing. Today it is the interface that is demanding more and more attention rather than the bulk component of the coating and substrate materials. For a durable adhesion, a pretreatment of the substrate is inevitable. An extremely accurate and reliable characterization of the substrate surface at the nanometer scale is imperative. An in-

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depth understanding of structure–property relationship with regard to mixing ratio and cure mode of the coating materials is a prerequisite for their successful application and long-term durability. Most coatings are the results of the marriage between the two different materials—an organic inorganic substrate and a polymeric resin—that form adhesive bonds with each other.[11] An additional factor that complicates the prediction of coating performance and service life is that the polymer coatings are heterogeneous.[12] The quality and durability of coating is directly related to the nature of adhesion. Adhesion may be defined as the energy required to dismantle the interface between two materials. Physicists and engineers usually describe adhesion in terms of forces, with the force of adhesion being the maximum force, exerted when two adhered materials are separated.[13] There are many theories regarding the mechanism of adhesion, such as adsorption (van der Waals forces), electrostatics, diffusion, chemical bonding, mechanical interlocking etc. The energy required to separate the coating and substrate is a function of the adhesion level but it depend on the mechanical and viscoelastic properties of the material.[14] The properties of a coating material are strongly dependent upon the molecular weight of the resin. Normally low molecular weight, high functionality polymers are used to overcome the problems of low volatile organic compound and high solids. If the degradation of polymer is over ruled then demand of long life can be sustained. Looking into these parameters different polymers were studied for effects such as radiation, degradation, corrosion resistance, high electrical resistance, thereby improvement in external durability. When any external attack takes place, the polymer coating can be considered as the best outfit to the powder coating material.

Polymers having suitable required properties can be mixed to get both common enhancements in the properties as well as additional advantage. It is also observed that it is difficult to find coating system that would be able to resist all the factors on their own structural strength. It is not conceivable that only one additive would be able to take care of all the ill effects. One would need UV absorbers and antioxidants to take care of some of the problems. It is reported in many literature that PVDF coating is environmentally stable for many years.[15] The matrix component in the composite system is easily vulnerable to environmental conditions. Hence, most matrix-dominated properties, such as low compressive strength, are severely affected and are of greatest concern to the designer. The deterioration depends on the capability of the composite system to withstand the severity of the environmental conditions. In fact a combination of environmental conditions such as the moisture plus high temperature may worsen the situation and lead to faster degradation.[16,17] The status of polymer surface is important for many properties and applications, including chemical resistance, hydrophilic selective-permeability, adhesion, biocompatibility, etc. Surface properties are of special concern as they are affected by the interaction of polymeric surface with their environment.[18] These polymeric blends were characterized for various physical properties such as percentage nonvolatiles, viscosity, and IR compatibility with other substrate material, as well as their storage stability. These coated polymeric substrates were characterized for the coating properties such as adhesion, flexibility, scratch hardness, impact resistance, solvent, and chemical resistance. The results are very encouraging and for some of the compositions the film performance was quite stable and comparable to that of plastic coated sheet systems. Our interest was to study the adsorption of polymeric solution on the paper substrates, which are industrially important for the adhesion of polymer with paper and in providing stability for applications.

EXPERIMENTAL

Materials

Poly(vinylidene fluoride), received from kurary chemicals (Japan) in RG Granules form, was dissolved in Dimethyl formamide (DMF), and Poly(methylmethacrylate), received from IPCL, Baroda, India, was dissolved in toluene to prepare required concentration of two polymers in the blends. Blends of PVDF and other polymers are mainly used for coating of films and foils. PVDF normally exist in the amorphous form, i.e., α phase; under the influence of high electric field or by stretching, the polymer is brought in the form of polarizing phase, i.e., β phase. The dielectric relaxation, which is more prominent in case of PVDF, is also one of the tools to understand the compatibility of these polymers.

Blending and film preparation

In the process of polymerization, we use different monomers that have a definite structure. With this criteria, rather than polymerizing the polymer, polymer blends of two different polymers mixed in different concentration can be used as a coating material on the substrate. In recent years there has been considerable interest in polymer blends, in particular the subject of mutual compatibility of the component polymers.[19,20] One of the more fascinating polymer pairs that has been reported to be compatible over a range of composition in the solid state is PMMA and PVDF.[21–23] In recent times different miscible polymer blends can also be brought under polarizing form. With this interest PMMA/PVDF blends were prepared. Blends of two polymers with different propor-

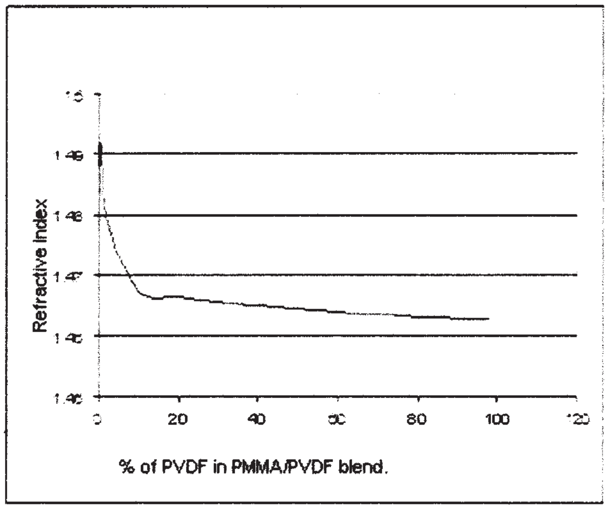

Figure 1 Refractive Index Variation for % variation of PMMA/PVDF blends.

tions, 98/02 (w/w), 90/10 (w/w), 80/20 (w/w), were prepared by solution casting from Dimethylformamide (DMF). Solutions of these compositions were mixed thoroughly and different proportions were spread on the cardboard substrate. The film was cast on the cardboard substrate, keeping the card board in the glass petri dish at 60°C. The sample curing was done at ambient temperature for 16 h. The films were postcured at 80°C for 2 h.

Measurements

IR Spectra of PMMA and PVDF blends were taken to study the proportion of two polymers by ATR–FTIR (Paragon 500 Model, PerkinElmer). Impact and flexibility index measurements were done using canonical mental test. Refractive Index measurements were carried out using Abbe's Refractometer for various different concentrations. % Gloss reflectance measurements were carried out using Gloss meter by directly placing the film coated cardboard sheet on the sample plate at room temperature. Thickness measurements for the entire sample were taken by micrometer screw gauge.

RESULTS AND DISCUSSION

Blend composition

Poly(methyl methacrylate) (PMMA) and Poly (vinylidene fluoride) (PVDF) blends are compatible and miscible blends. Most unambiguous criterion of these blends is the single glass transition temperature, which is around 70°C. Anomalous heterocharges are observed on the surface of this blend. The objective was to obtain the most suitable mixture of the two Components and to select the new material with desired properties. In our case, we have blended PMMA and PVDF with different Compositions.

Refractive index

Figure 1 shows refractive Index Variation of the two polymers solution and it was observed that as the content of the PVDF increases in the solution form of PMMA and PVDF the Refractive Index of the Compound Composition decreases gradually, becomes almost stable for the 80/20 (w/w) Composition and remains stable for further change in the Composition of both the polymer. Refractive Index differences between the pure component and the blend can alter the band shapes and lead to a shift in frequency to lower levels. In general the frequency shifts to lower levels.

Gloss reflectance measurements

Figure 2 shows the Gloss reflectance of the composite sample of polymer blend film on the cardboard substrate. It is seen that as the concentration of PVDF in the PMMA increases, there is a linear increase in the gloss reflectance value. Effect of repetitive annealing of the coated sheet shows increase in the gloss reflectance. The shiny appearance also improves the strength of the sheet as well as its durability. The maximum reflectance was observed for the 60/40 (w/w) composition of polymer blend. Some authors reported that the gloss of PVDF coatings increased by 15% over four years when a typical acrylic coating exhibited a 60% decrease in gloss over the same period.[24] Other disadvantages of PVDF coatings, such as inability to produce a glossy finish, high melt viscosity, inferior scratching and marring resistance and high cost, make it indispensable to introduce a sec-

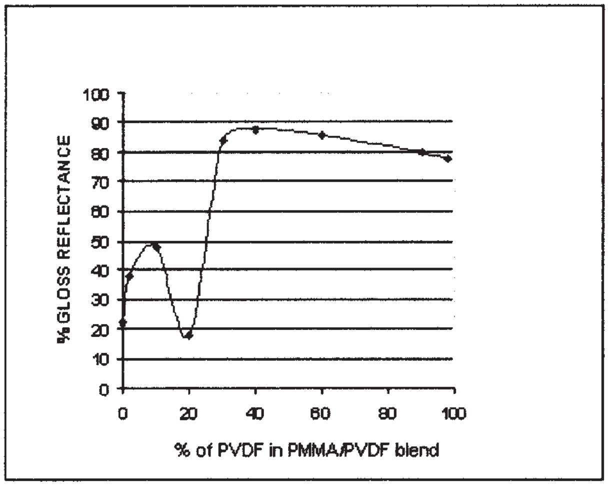

Figure 2 Variation of Gloss reflectance with respect to % variation in PMMA/PVDF blends.

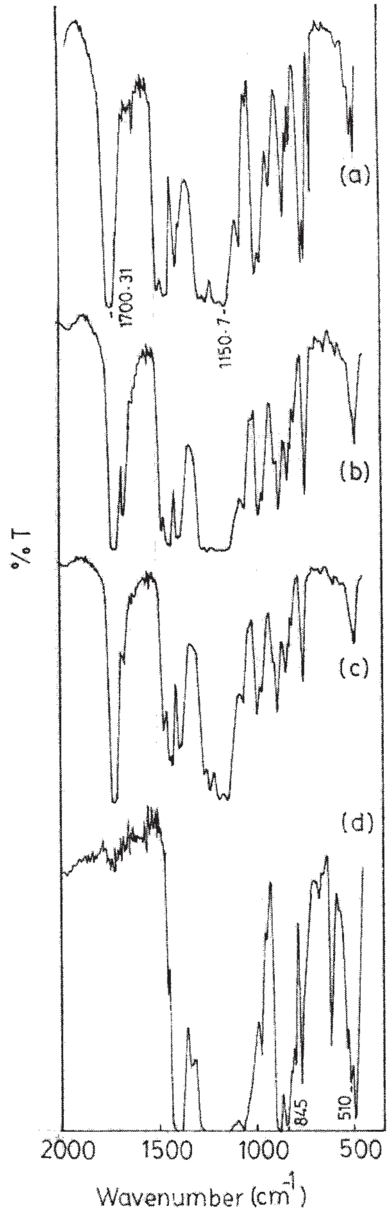

Figure 3 : Infrared spectrum for different proportion of PMMA / PVDF blends
a) Pure PMMA
b) 98 / 02, PMMA / PVDF
c) 90 / 10, PMMA / PVDF
d) Pure PVDF

Figure 3 Infrared spectrum for different proportion of PMMA/PVDF blends: (a) Pure PMMA, (b) 98/02, PMMA/PVDF, (c) 90/10, PMMA/PVDF, (d) Pure PVDF.

ondary polymer component to optimize the performance of PVDF material.[25]

Infrared spectroscopy

The infrared Spectra were taken for different proportions of polymers in the blend film. Figure 3(a) shows the spectrum of pure PMMA that presents the C═O absorption at 1700.31 cm^{-1} and the typical C—O—C absorption at 1150.7 cm^{-1}.[26] Figure 3(d) shows the IR spectrum of pure PVDF, providing more information about the crystalline phase of PVDF. Even though the CF bending at 510 cm^{-1} and the CH$_2$ bands at 845 cm^{-1} have been widely used to confirm the β structure, it would be more accurate to assign the 470 cm^{-1} band as a characteristic β form.[27,28] The spectra of the PVDF shows that a conformational change has been induced in the compatible blend but only a fraction of PVDF is involved in the conformational change, as shown in Table I. The energy gain with mixing between two polymers is partly attributed to the interactions between the PMMA carbonyl group and the electric moments of the PVDF monomer units and partly to hydrogen bonding between the PMMA carbonyl oxygen and the PVDF protons.[29,30] The study determines the effect of PMMA addition on the crystalline form of PVDF, crystallized from solution. The changes in the content of the two phases, due to addition of different concentrations of PMMA, were detected by IR spectroscopy.[31,32]

Impact ball test

Impact test and flexibility index by conical mental test were performed for all the samples. It was observed

TABLE I
Infrared Spectroscopic Peak Values for PMMA, PVDF, and Their Blends

Infrared frequencies for pure PVDF (cm^{-1})	Infrared frequencies for PMMA/PVDF blend (cm^{-1})	Infrared frequencies for pure PMMA (cm^{-1})
3017	2997.3	3547.5
2977	2952.4	3438.0
1420	2801.0	2996.1
1399	1850.1	2950.7
1290	1731.8	2842.7
1149	1620.8	2362.5
1056	1560.2	1956.9
976	1484.9	1728.0
873	1436.5	1604.3
853	1400.4	1560.2
612	1242.8	1449.2
489	1150.7	1387.2
410	989.4	1242.1
288	882.6	1149.8
208	841.9	1063.8
100	750.3	988.7
	489.6	912.5
		842.1
		826.8
		810.3
		749.8
		733.8
		696.9
		482.8

TABLE II
Measurements of Refractive Index and Thickness (*t*) of Coated PMMA/PVDF Blend Film with Different Proportion

Obs No.	PMMA/PVDF blends (w/w) with different proportions	Thickness of the film (cm)	Refractive index
1	98/02	0.014	1.4640
2	90/10	0.016	1.4675
3	80/20	0.013	1.4665
4	70/30	0.015	1.4658

that the sample withstands the weight of the ball of around 1 kg by different speed with longer distance. The sample adheres to the cardboard and was not affected because of the different impact stresses. It was observed that the substrate paper could not bear immediate impact and breaks with the highest stress given at a longer distance. This shows that the sample adheres well with the substrate, thereby increasing the mechanical strength of the paper substrate.

Thickness

Thickness of sample was measured by keeping the sample between the two jaws of micrometer screw gauge. It was observed that the sample is uniform throughout the surface of the film and less variation in the thickness was observed for different composites. The values are shown in Table II.

CONCLUSIONS

Strength and durability of coatings depends very much on the integrity of the interface and the dimensional stability of the polymeric coating substance after cure/crosslinking reactions. For high quality products, an accurate characterization of the substrate surface and cure mode of polymeric coating is of utmost importance. The nature of surface is extremely smooth, shiny, and uniform and adhesion of the polymer with the paper was very stable from all the surface properties tested at the R.T.P. The use of polymer blend has certainly improved the performance of polymer-coated surface. The type of polymers used for blend and fraction of it used for composition for coating over the area of substrate paper determines the overall property of the coated material.

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