CLASSIFICATION OF VIRGIN AND VIRGIN-RECYCLED FIBER BLEND HYGIENIC TISSUE PAPER BY MULTIVARIATE ANALYSIS

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This paper presents an application of multivariate analysis for classing virgin and non-virgin tissue paper products. The brightness, fluorescent whiteness, fiber fibrillation and effective residual ink concentration of commercial tissue paper products were measured according to ISO standard methods. Based on these parameters, the multivariate analysis techniques, i.e., principal component analysis (PCA) performed on the preliminary study of the data set structure, soft independent modeling of class analogy (SIMCA), and partial least square discriminant analysis (PLS-DA), were used to develop classification models. The results showed that the PLS-DA model provided better classification in the applications.

The present method is simple and accurate. It is suitable for use in quality control testing of tissue papers during the manufacturing, as well as in the analysis of point-of-sale samples from commercial markets.

Keywords: tissue paper, virgin fiber, recycled fiber, multivariate analysis

INTRODUCTION

Hygienic tissue paper refers to a class of soft, absorbent, disposable papers and is commonly used for facial tissue (paper handkerchiefs), napkins, bathroom tissue and household towels. This kind of tissue products can be made from 100% chemical pulp (virgin fiber) to 100% recycled fiber or a combination of the two. Typically, a chemical pulp with longer fiber length is introduced to improve the product strength. Although the utilization of recycled fiber can significantly reduce the use of raw material and energy in tissue paper production,[1] some toxic substances, such as mineral oils and heavy metals, remain in the recycled fibers and could contaminate the new products.[2-4] Another common practice amongst the paper mills is the addition of a fluorescent whitening agent (also toxic) in order to offset the effect of residual ink in recycled fiber on the paper brightness.[5,6] Therefore, the use of recycled fiber in the production of hygienic tissue paper poses a risk for users to potentially come in contact with these harmful substances. Both EU and US have established regulations around the limit of these harmful substances, such as organochlorine, formaldehyde, dyes, inks, and heavy metals.[7,8] The procedures involved in these tests are very complicated and time consuming. As a result, there is still a risk to use the recycled fiber added products because of the presence of many unidentified harmful substances. Therefore, some countries and districts[9] have resorted to establishing regulations that forbid the use of recycled fiber in the production of the tissue papers that are used for personal cleaning and hygienic purpose, typically facial tissue. In order to validate whether point-of-sales samples are following regulations, an effective method to identify the presence of recycled fiber used in these tissue products is needed.

Considering the features of recycled fiber,[1,10] there are several parameters, such as fibrillation,

ink content, brightness, fluorescent strength and others, that are widely used for checking if the products are made from recycled fibers. However, in many cases the portion of recycled fiber blended into the products is very small and as a result makes detection very difficult. There are also some minor contaminations because the labeled ink or fluorescent substances when using commercial pulp board or the process are different for different products. Therefore, based on the single parameter mentioned above, it is difficult to judge if the products are truly virgin fiber made or not. Moreover, it is also hard to develop a mathematical equation that can provide a quantitative relationship between the product types (i.e., made from virgin fiber or recycled fiber blend) and these tested parameters.

Compared with the traditional approaches, multivariate analysis (also called chemometrics) methods[11] have been found to be very useful for the classification analysis in many areas.[12-14] Multivariate analysis allows valuable information to be extracted from multivariate data arrays, which are difficult to handle using classical univariate statistical methods. They were successfully used in many complex case studies, such as in food classification, environmental monitoring and papermaking process,[15-17] in which there were multiple parameters whose interpretation is far from simple. Multivariate analysis methods provide tools for finding relationships between groups of analyzed samples and/or related variables or parameters.[18,19] Therefore, multivariate analysis should be capable to be used for the classification of virgin and virgin-recycled fiber blend hygienic tissue paper products.

The aim of the present study was to a develop multivariate analysis method for the classification of virgin and virgin-recycled fiber blend tissue paper products, based on the traditional parameters in the paper testing, including fluorescent strength, brightness, residual ink content, and so on. Multivariate analysis techniques were attempted in the classification investigation.

EXPERIMENTAL

Samples and the parameters tested

56 samples of tissue papers and relevant base papers and pulps from nine manufacturers (A to I) were obtained from different production sections and 11 samples were prepared in our laboratory according to a known recipe. The samples were divided into two groups (i.e., virgin fiber only and virgin-recycled fiber blend) and detailed information on the samples is provided in Table 1. The related parameters, i.e., fluorescence intensity, brightness, fluorescent whiteness, effective residual ink concentration (ERIC), and fiber fibrillation of the samples, were tested using standard methods.[20-23] The testing apparatus included a UV analyzer (ZF-1, SHANGHAI GUCUN OPTIC INSTRUMENT FACTORY, Shanghai, China), a Digital Whiteness meter (SE071, Lorentzen & Wettre, Shanghai, China) and a Fiber analyzer (XWY-V1, Huazhi Technology Co. Ltd., Zhuhai, China).

Methods in multivariate analysis

Principal components analysis (PCA)

In multivariate analysis, PCA (unsupervised pattern recognition) is often the first step of exploratory data analysis to detect groups in the measured data. PCA is also a very effective data reduction technique that can provide low-dimensional representations (using extracted orthogonal PCs) of complex datasets through a visually interpretable score plot and a loading plot.[24] The scores are the projections of the original data onto the new vector space, defined by PCs. The score plot shows that the observations cluster in different groups. Loadings are the weights to quantify how much of each of the original variables are used to define each PC, and with which original variables to form the scores. The loading plot is also able to show the correlation structure between the variables.

Soft independent modeling of class analogy (SIMCA)

SIMCA (supervised pattern recognition) is a commonly used class-modeling technique based on disjoint PCA modeling realized for each class in the calibration set. For unknown samples, they are compared to the class models and assigned to classes according to their analogy with the calibration samples.

In SIMCA, the model distance critical limit (D-Crit) is used for classing new samples and D-Crit is calculated using an inverse cumulative F-distribution function.[25] The normalized distances to model (DMod (Norm)) for samples in the calibration set (workset) or in the prediction set[26,27] are respectively calculated by the following equations, i.e.,

$$DModX = \frac{\sqrt{\frac{\sum_{k=1}^{K} e_{ik}^2}{K-A} \times \nu}}{\sqrt{\frac{\sum_{i=1}^{N}\sum_{k=1}^{K} e_{ik}^2}{(N-A-A_0)\times(K-A)}}}, \quad \nu = \frac{N}{N-A-1} \qquad (1)$$

and

$$DModXPS = \frac{\sqrt{\frac{\sum_{k=1}^{K} e_{ik}^2}{K-A}}}{\sqrt{\frac{\sum_{i=1}^{N}\sum_{k=1}^{K} e_{ik}^2}{(N-A-A_0)\times(K-A)}}} \quad (2)$$

where K = number of X variables; A = number of components in the model or the selected number of components; e_{ik} = X-residuals of sample i; v is a correction factor (function of the number of observations and the number of components) and is slightly larger than one; A_0 = 1 if model is centered, 0 otherwise; N = number of samples in the workset. The difference in the formula is obvious, in comparison with the calculation of DModX, the correction factor is not present in the calculation of DModXPS.

If the sample distance to the model was larger than the critical limit (D-Crit), this sample didn't belong to the corresponding class. The smaller the distance of the sample to the model, the higher the probability that the sample belonged to the corresponding class.

Partial least square discriminant analysis (PLS-DA)

PLS-DA, supervised pattern recognition, is a classification method based on partial least squares regression (PLS-R).[28,29] The objective of PLS-DA is to find models that allow the maximum separation among classes of samples. A dummy variable can be constructed, representing the sample properties (e.g., virgin fiber group = 1, virgin-recycled fiber blend group = 0), and then used as Y-variable. The prediction from a PLS-DA model is a value of nominally zero or one, not exactly equals to 0 or 1 but close to 0 or 1, which is justified by the natural variability of the sample constituents. A value close to 1 or 0 indicates that the new sample is in the modeled class or not. In practice, a threshold is determined, above or below which the sample is considered to be in the class or not.

Assessment of the methods

The percentage of correct classification (%CC) is the criterion used to compare classification results obtained by the multivariate analysis methods:

$$\%CC = \left(\frac{N_c}{N_c + N_{ic}}\right)\times 100 \quad (3)$$

where N_c and N_{ic} represent the numbers of correct classifications and incorrect classifications, respectively.[30]

Software

Principal component analysis (PCA), soft independent modeling of class analogy classification (SIMCA) and partial least square discriminant analysis (PLS-DA) were performed using commercial chemometrics software, i.e., SIMCA-P (UMETRICS AB, Sweden).

RESULTS AND DISCUSSION

Classification of virgin fiber and virgin-recycled fiber blend samples by a single parameter (variable)

Fluorescence intensity

Although it can only provide qualitative information, the fluorescence intensity test is a traditional way used for judging if the products use recycled fiber or not.[31] For the products with addition of recycled fiber, the fluorescence intensity test must be positive. Fig. 1 shows the results from the fluorescence intensity test for the samples. It is noticed that 7 samples from the virgin fiber group (among 39 samples), i.e., about 18% of the samples, are positive in the fluorescence intensity test. Therefore, fluorescence intensity cannot be used as a single parameter in the classification.

Brightness

For pulp and paper, brightness is a parameter that reflects the removal degree of chromophore species (e.g., residual lignin) from pulps in the bleaching process. However, from the application point of view, it is not necessary for tissue products to use pulp with high brightness. For recycled fibers, brightness is also a good indicator to judge the effectiveness of the deinking process. As can be noted from Fig. 2, the brightness of the tested samples was quite close regardless of whether they were made of virgin fiber or virgin-recycled fiber blend. Therefore, it can be concluded that brightness is not a reasonable parameter for classifying the products either.

Residual ink concentration

In theory, residual ink can be only found in the samples containing recycled fiber, due to the incompletion of the deinking process. However, from Fig. 3 it can be observed that amounts of residual ink (as ERIC) were detected even in the samples made wholly from virgin fibers, although the average value of ERIC in the virgin-recycled fiber blend group was higher than that of the virgin fiber group. We believe that this is explained by contamination during the manufacturing process, e.g., because of the labeling (contains ink and/or fluorescent substances) in the pulp board purchased from external sources, possibly from the ink remaining in the reused white water. If the samples

are blended with a small amount of recycled fiber or if the deinking process is very effective, the values of ERIC in the samples (e.g., samples 14-17) are basically the same as those for the virgin fibers. Thus, there is a risk to use ERIC for the classification.

Fiber fibrillation

Fibrillation is a parameter that reflects the degree of fiber damage, which is more significant in the recycled fibers.[1] As seen in Fig. 4, the samples made from virgin-recycled fiber blends have higher fibrillation values, however, the fibrillation values vary a lot among the virgin fiber samples. Moreover, for a number of virgin fiber samples, the fibrillation values are close to those of the virgin-recycled fiber blend samples, although the average value of fiber fibrillation in the virgin-recycled fiber blend samples is higher than that of the virgin fiber only ones. Therefore, fibrillation cannot be used as a distinguishing feature between the groups.

Fluorescent whiteness

As mentioned above, a fluorescent whitening agent is widely used in the paper mills using recycled fibers, since it is an economic way to compensate the brightness loss due to the residual ink in recycled fiber. As seen in Fig. 5, the values of fluorescent whiteness of the samples made from virgin-recycled fiber blend materials are much higher than those of the virgin fiber samples. However, there are exceptions in both groups, e.g., samples 31, 46, 63, and 65 in the virgin fiber group. Such exceptions in the samples made from virgin fiber are potentially the result of contamination in the manufacturing process, as mentioned above. Therefore, although fluorescent whiteness is a distinct parameter for the fiber group judgment, much better than ERIC and fiber fibrillation, it cannot perform the classification task on its own.

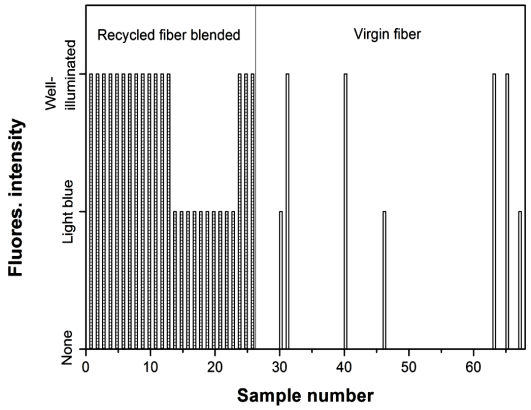


Figure 1: Fluorescence intensity of the samples

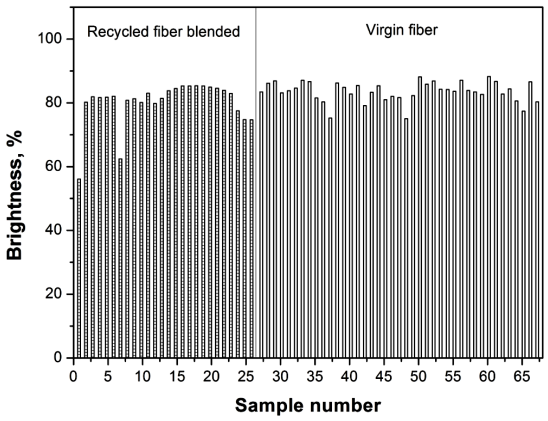


Figure 2: Brightness of the samples

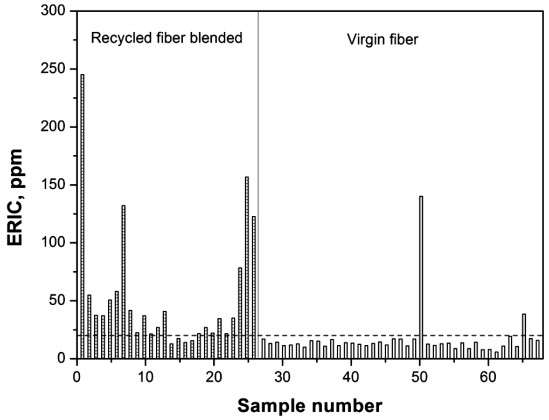


Figure 3: Effective residual ink concentration (ERIC) of the samples

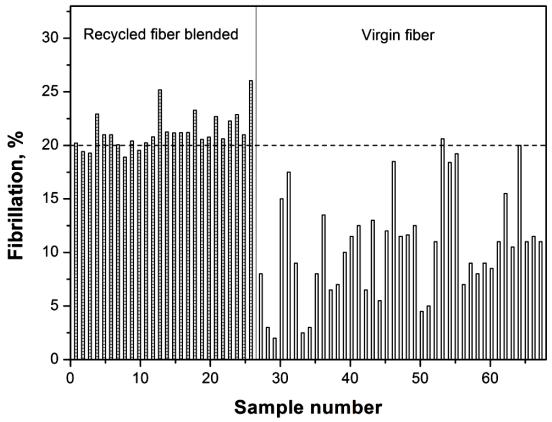


Figure 4: Fibrillation of the samples

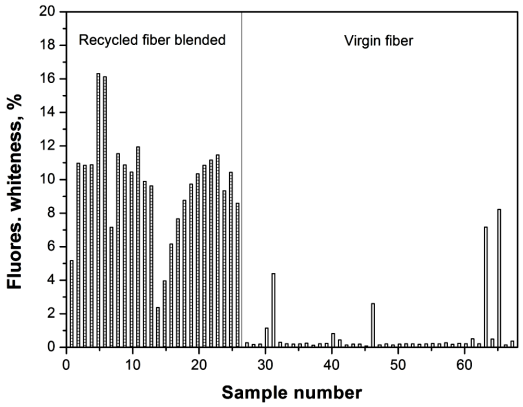
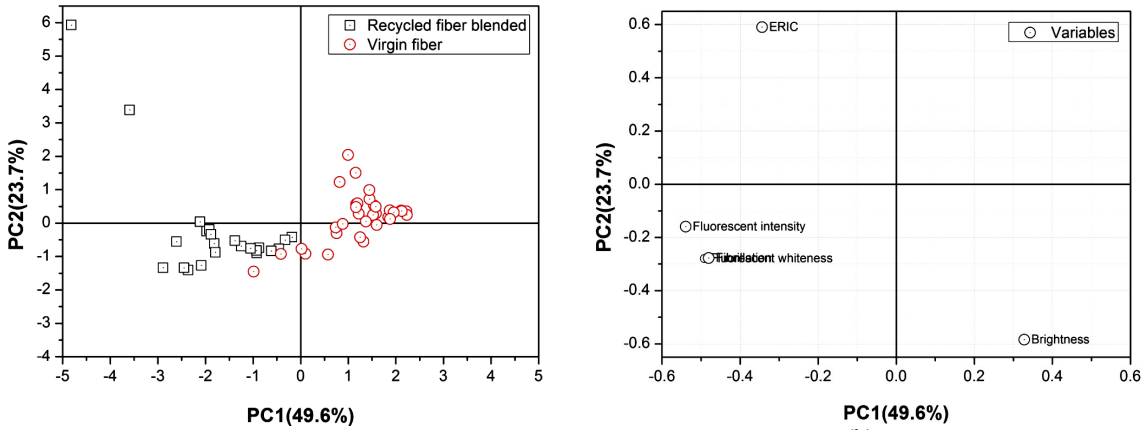


Figure 5: Fluorescent whiteness of the samples



(a) (b)

Figure 6: Score scatter plot (a) and loading plot (b) of the samples

In summary, none of the above test parameters can be used alone for distinguishing between the samples made from virgin fiber only and virgin-recycled fiber blends.

Multivariate analysis

As mentioned above, multivariate analysis is a capable tool to solve this problem in a complex system. In this study, we applied several multivariate analysis methods, i.e., PCA, SIMCA and PLS-DA, respectively, to perform the classification analysis for the tissue product samples listed in Table 1.

PCA

PCA is the first step in either SIMCA or PLS-DA in order to evaluate whether clustering exists in a dataset without using class membership information in calculation. Fig. 6 shows the score plot projection of the PCA performed on the parameters of the samples listed in Table 1. The significance of the extracted principal components (PC) was inferred by the explained sum of squares, in which PC1 and PC2 together explained 70.4% of the variance in the data. From Fig. 6, it is clear that the score vectors of the samples shown in Table 1 were basically distinguished into the virgin-recycled fiber blend and virgin fiber classes, which is also a prerequisite for a possible classification discriminant analysis.

PCA also provides values of the so-called loading vectors, showing how the variables were combined to form the scores. Loading vectors indicates which of the variables were important and correlative, and corresponded to the directions in the score plot. Fig. 6b shows the loading plot corresponding to the score plot (Fig. 6a) and it indicates that the variables, i.e., fluorescent whiteness, fluorescence intensity and fiber fibrillation, were the ones loading heavily (i.e., have a larger absolute value) in the first PC (shown in the horizontal direction), while the brightness

and ERIC, respectively far to the top and bottom, were the ones loading heavily in the second PC (shown in the vertical direction). Hence, it could be concluded that the clustering of samples was mainly reflected in the fluorescent whiteness, fluorescence intensity and fiber fibrillation variables. These three variables are closer to each other, indicating that there is a better correlation between them.

Table 1
Sample source and description

Sample No.	Description	Sample No.	Description
Virgin-recycled fiber blend		34	B-short fiber
1	A-before flotation	35	B-bagasse pulp
2	A-after flotation	36	B-base paper
3	A-base paper	37	C-bamboo pulp
4	A-roll paper	38	C-wood pulp
5	E-pulp	39	C-pulp board
6	E-base paper	40	C-base paper
7	G-not deinking	41	D-long fiber
8	G-after deinking	42	D-bamboo pulp
9	G-before defibrillation	43	D-Nourishing Sweet
10	G-after defibrillation	44	D-short fiber
11	G-after defibrillation+chemicals	45	D-wet bagasse
12	G-manufacture forbay	46	D-base paper
13	G-base paper	47	F-bamboo pulp
14	L-ratio 5%	48	F-Guitang Eucalyptus
15	L-ratio 10%	49	F-eucalyptus (two middle)
16	L-ratio 20%	50	F-eucalyptus (Brazil)
17	L-ratio 30%	51	F-Yingxing long fiber
18	L-ratio 40%	52	F-before defibrillation
19	L-ratio 50%	53	F-after defibrillation
20	L-ratio 60%	54	F-after defibrillation+additives
21	L-ratio 70%	55	F-base paper
22	L-ratio 80%	56	H-pulp board
23	L-ratio 90%	57	H-base paper
24	X2-roll paper	58	I-pulp board
25	X3-coiling towel	59	I-base paper
26	X8-towel	60	X1-roll paper
Virgin fiber		61	X4-roll paper
27	A-Jingfeng-long fiber	62	X5-roll paper
28	A-Dingfeng-short fiber	63	X6-roll paper
29	A-Yingwu-short fiber	64	X7-roll paper
30	A-base paper	65	X9-roll paper
31	A-roll paper	66	X10-roll paper
32	B-long fiber	67	X11-roll paper
33	B-mid fiber		

Table 2
Results for SIMCA classification

Sample	Calibration set		Prediction set	
	Number	%CC	Number	%CC
Virgin-recycled fiber blend	23	91.3	3	67
Virgin fiber	33	93.9	8	75

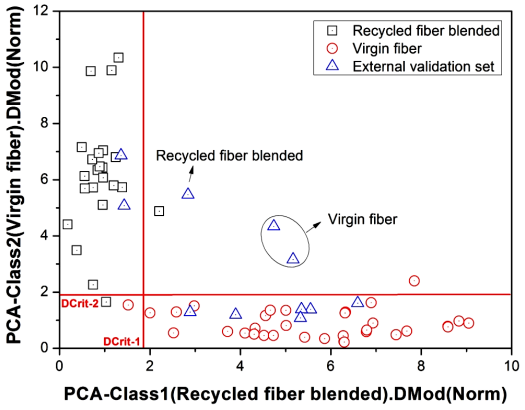


Figure 7: Cooman's plot of the samples

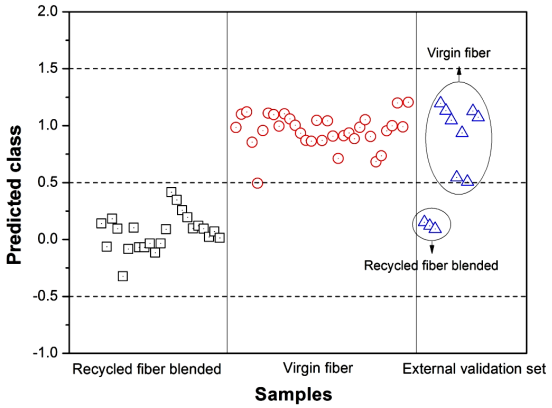


Figure 8: Predicted class scatter plot

SIMCA

Due to the promising results of unsupervised PCA shown above, the SIMCA classification (PCA supervised) was applied to the calibration dataset. Both the virgin-recycled fiber blend and the virgin fiber sample classes were respectively modeled using the PCA for all variables, and the critical distances (DCrit-1 and DCrit-2) corresponding to the two class models were calculated by an inverse cumulative F-distribution function. For each object in the calibration and prediction set, the distance to the two class models (DMod-1, DMod-2) was computed and plotted with the critical distance DCrit-1 and DCrit-2 to form Cooman's plot.[25] Fig. 7 is Cooman's plot (showing class separation) of the SIMCA model with the calibration sample set and the prediction sample set. There are four zones (i.e., I, II, III and V) divided by lines 1 and 2. The samples located in zones II and V belong to the virgin-recycled fiber blend class and the virgin fiber class, respectively. If the sample is located in zone I or zone III, it can not be classified. It can be seen from Fig. 7 that there are three samples in the prediction set that cannot be judged. Table 2 lists the results from SIMCA classification, which shows that the percentages of correct classification (%CC) for the predicted samples are below 75%, although they are higher than 90% for the calibration samples. Therefore, SIMCA is not suitable for the classification of the given tissue samples.

PLS-DA

Primary analysis

Compared with SIMCA, PLS-DA could provide a more accurate and reliable classification due to the partial least squares based regression. Fig. 8 shows the results obtained by PLS-DA, which include sample prediction from both the calibration set and the prediction set, based on the information listed in Table 1. The predicted Y values close to zero (between -0.5 and 0.5) indicate that the samples belong to the virgin-recycled fiber blend class, while the predicted Y values close to one (between 0.5 and 1.5) point that the samples belong to the virgin fiber class. If the predicted Y value is not located in the zone between -0.5 to 1.5, the sample cannot be identified. From Fig. 8, we found that although there are two samples located on the border line in the predicted set, the classification using PLS-DA is more accurate than that by SIMCA.

Table 3 lists the results for the percentages of correct classification (%CC) of the sample sets, which indicate that there is still some uncertainty regarding the virgin fiber set as classified by PLS-DA.

Table 3
Results of PLS-DA classification

Sample	Calibration set		Prediction set	
	Number	%CC	Number	%CC
Virgin-recycled fiber blend	23	100	3	100
Virgin fiber	33	97.0	8	100

Table 4
Results of optimized PLS-DA classification

Sample	Calibration set		Prediction set	
	Number	%CC	Number	%CC
Virgin-recycled fiber blend	23	100	3	100
Virgin fiber	33	100	8	100

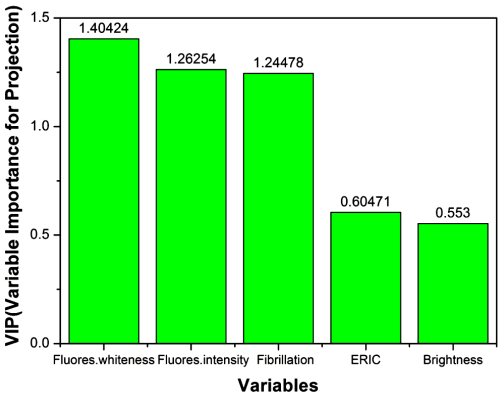


Figure 9: Plot of variable importance for the projection

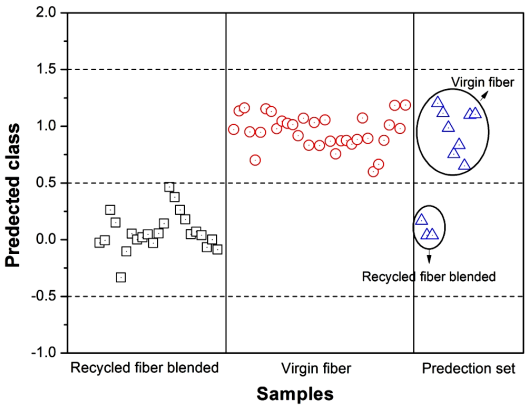


Figure 10: Predicted class scatter plot (fluorescence intensity and brightness variables removed)

Optimized analysis

In multivariate analysis, it is common practice to purposely select the variable number and/or variables for modeling in order to achieve good results.[32,33] The loading plot in PCA and variable importance for the projection (VIP) plot in PLA-DA provide a good guidance in selecting the variable. From the loading plot (Fig. 6b), we noted that there are good correlations between the variables, i.e., fluorescent whiteness, fluorescence intensity and fiber fibrillation. Fig. 9 shows the VIP plot in the classification, which indicates that the fluorescent whiteness, fluorescence intensity and fiber fibrillation variables were more important than the brightness and ERIC variables.

According to these results, we tried different modeling ways by removing either the less important variable(s) or the highly relevant variable(s) in the classification study based on PLS-DA. The results showed that the best classification could be performed when we excluded the brightness and fluorescence intensity from the variables for the modeling. Fig. 10 shows that the two class samples for both the calibration set and the prediction set can be clearly divided. The results shown in Table 4 also indicate that the percentages of correct classification (%CC) are 100% for both the calibration samples and the prediction samples. The reason is most likely due to the fact that fluorescence intensity is a variable relevant to fluorescent whiteness and only provides qualitative information. Clearly, the optimized PLS-DA method provided better results than those based on SIMCA analysis in the tissue sample classification.

CONCLUSION

We have demonstrated the methods for the classification of tissue paper products made from virgin-recycled fiber blends and virgin fiber only. It can be concluded that the multivariate analysis technique could provide a better judgment on the sample classes than using only a single variable. Amongst different multivariate analysis methods, the regression based PLS-DA technique with the fluorescent whiteness, effective residual ink concentration (ERIC), and fiber fibrillation variables provided the best results in sample classification. The presented method is suitable for use in the examination of point-of-sale tissue paper samples from commercial markets.

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