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The Thermal and Mechanical Performance of uPVC/Styrenic Copolymer Blends

W.C. Yap[1], K. Halliwell[1], I.F.M. Major[2], G.M. McNally[2] and W.R. Murphy[2]
[1]K2 Conservatory Roof Systems, The Burnden Group, Bolton, England
[2]Polymer Processing Research Centre, The Queen's University Belfast,
Stranmillis Road, Belfast BT9 5AH, Northern Ireland, UK

Abstract

uPVC profiles laminated with woodgrain foils occasionally deform in direct sunlight due to solar energy gain. Blending ASA copolymer and ABS copolymer resins with uPVC increased the heat deflection temperature of the uPVC, therefore reducing the potential for deformation. This paper reports on the thermal and mechanical performance of these blends.

Introduction

Unplasticized Polyvinyl Chloride (uPVC) is commonly used in the USA and Western Europe to produce a wide range of building materials including conservatory doors and window frames. The material is cheap and is considered to be robust being stiff and strong with good acid and alkali resistance, flame-retardancy and UV resistance [1]. However, a major challenge to uPVC processors is to try and combat the deformation of uPVC profiles by direct sunlight due to solar energy gain [2]. One way of achieving this is to increase the heat deflection temperature of the uPVC by blending it with another resin that has a higher glass transition temperature. Styrenic copolymer resins have been considered suitable for such a purpose. These include acrylonitrile-butadiene-styrene (ABS) copolymer and acrylonitrile-styrene-acrylic (ASA) copolymer [3].

ABS is a two phase polymer consisting of a glassy matrix of a copolymer of styrene and acrylonitrile and the synthetic rubber copolymer of styrene and butadiene [4]. Several different grades, being rubbery or brittle and hard, can be made by varying the conditions of the forming process and the proportion of the three ingredients. The butadiene groups impart good impact strength; the acrylonitrile group provides heat resistance, while the stryene units give good rigidity. A 'typical' composition of ABS could contain 20-30% acrylonitrile, 20-30% butadiene and 40-60% stryene. ABS is typically used for interior and exterior automotive parts, domestic appliance housing, telephone casing or generally for applications that require good impact strength but little chemical resistance.

ASA copolymer is closely related to ABS copolymer, as a graft rubber is dispersed with a styrene acrylonitrile (SAN) phase - but contains an acrylic ester instead of butadiene as a constituent rubber phase [5]. There are a number of differences between these two rubber phases that should provide for divergent properties between each resin. The acrylic ester rubber does not contain any C-C double bonds while the butadiene rubber contains many and therefore will lead to differences in chemical resistance. The butadiene rubber is also less heat resistant, more vulnerable to environmental conditions but provides for greater low temperature resistance.

The aim of this programme of work was to examine how effective styrenic copolymers are at increasing the heat deflection temperature of uPVC by conducting dynamic mechanical thermal analysis of injection moulded uPVC/styrenic copolymer blends. The storage modulus of each blend is an indication of the heat deflection temperature. Two different types of styrenic copolymer were used for comparative purposes. Mechanical analysis highlighted how, firstly, addition of these copolymers affects the properties of uPVC and also how each type of styrenic copolymer compares to the other.

Experimental

Materials - The materials used in this investigation were an acrylonitrile-butadiene-styrene (ABS) copolymer which goes under the trade name of Terluran® HH and an acrylonitrile-styrene-acrylic (ASA) copolymer which has a trade name of Luran® S. Both resins are produced by BASF. Terluran has an MFI of 2.94 g/10min and density 1.02gcm^{-3} and Luran has an MFI of 4 g/10 min and density 1.07gcm^{-3}. The uPVC formulation is produced by the PVC Group UK Ltd and has a K-value of 65.

Preparation of samples – The blends were compounded prior to injection moulding on a Killion (Davis Standard) 38mm diameter, 25/1 L/D single screw extruder. Temperature profile was 170°C, 180°C, 190°C and 200°C. The blends were tumble mixed prior to being feed into the hopper. Tensile, impact and flexural specimens were manufactured from the uPVC/styrenic copolymer blends using an Arburg 320S Allrounder 500-350 injection molding machine with a clamping force of 500kN. This machine has a general-purpose screw of diameter 45mm and L/D ratio of 18. The barrel temperature profile was maintained at 170, 180, 190, 195 and 200°C during the manufacture of the various samples, with a mould cooling temperature of 40°C.

Tensile analysis - The tensile properties of the various samples were tested according to ASTM 638-

96. These tests were performed using an Instron 4411 Universal Tester with a load cell of 5kN and a constant crosshead speed of 100mm/min. A minimum of ten specimens were tested for each blend. The tensile modulus, break strength and % elongation were recorded and averaged for at least 10 specimens.

Flexural analysis – The flexural modulus of the samples were determined according to ASTM D790 using an Instron 4411 Universal Tester with a compression load cell of 5kN and constant crosshead speed of 5.1mm/min. A minimum of 8 samples were tested for each blend.

Impact analysis – The impact performance of the samples was determined using a CEAST automatic fractovis free falling dart impact tester, fitted with a data acquisition system. The sampling time was 8 seconds and data were obtained every 2 milliseconds resulting in a graph of force versus time. The peak force (N), peak energy (J), total energy (J) and impact strength (J/mm) was also recorded.

DMTA analysis - Dynamic mechanical thermal analysis of the samples was performed using a Polymer Lab MARK II dynamic mechanical thermal analyser. The samples of dimensions 46x13x3 mm were mounted in the DMTA in the dual cantilever mode. The samples were scanned over the temperature range 0 to140°C at a scan of 3degC per minute and at frequency of 1 Hz. A heat deflection temperature can be derived from the storage modulus thermogram.

Results and Discussion

Tensile Analysis - The effect of increasing ABS copolymer and ASA copolymer concentration on the tensile modulus of the uPVC/styrenic copolymer blends is shown in Figure 1. Pure ABS copolymer resin had a slightly lower tensile modulus compared with virgin uPVC. Blending of the ABS copolymer in lower concentrations with uPVC caused a slight decrease in the tensile modulus of the uPVC but increased as the level of ABS copolymer increased. These results suggest that the addition of this ABS copolymer can affect the stiffness of the uPVC even though both have similar tensile modulii. This may be related to how each polymer interacts with the other when blended.

The tensile modulus of ASA copolymer was significantly lower than that of the uPVC. Blending ASA copolymer with uPVC caused a progressive decrease in tensile modulus with increasing ASA copolymer concentration up to 50%. Pure ASA copolymer had higher tensile modulus than the 30-50% blends; this suggests that the lower tensile modulus of the ASA copolymer begins to affect the stiffness of the uPVC as the concentration increased. Since, the tensile modulus of the blended samples was lower than the pure ASA copolymer resin it can be suggested that polymer interaction further effects tensile performance. Comparing the tensile modulii of ASA copolymer and

ABS copolymer in Figure 1 it can clearly be seen that ABS copolymer had the higher tensile modulus of the two. Blends of uPVC/ABS copolymer also showed higher tensile modulii than the blends of uPVC/ASA copolymer.

The effect of increasing ABS copolymer and ASA copolymer concentration on the break strength of the uPVC/styrenic copolymer blends is shown in Figure 2. ABS copolymer resin had far greater break strength than uPVC. Addition of ABS copolymer to virgin uPVC caused a large progressive increase in break strength but the break strength for each blend, including the highest concentrations of ABS copolymer, were significantly lower than the pure ABS copolymer. The ASA copolymer resin also exhibited higher break strength than the uPVC. Blending of the ASA copolymer with the uPVC provided a progressive increase in break strength but with the break strength of the blends still much lower than the pure ASA copolymer samples. Clearly the ASA copolymer provides the uPVC with improved break strength. Comparing both styrenic copolymers shows that ABS copolymer has slightly higher break strength than the ASA copolymer but there was very little difference between either when blended with the uPVC.

The effect of increasing ABS copolymer and ASA copolymer concentration on the % elongation of the uPVC/styrenic copolymer blends is shown in Figure 3. uPVC had a slightly higher elongation-at-break than the pure ABS copolymer. Blending the ABS copolymer with uPVC provided a significant increase in the elongation-at-break up to 40% concentration of ABS copolymer. Beyond this level of ABS copolymer, the blend showed a decrease in elongation-at-break but the 50% sample still exhibited higher elongation than the pure ABS copolymer sample. This suggests that up to a certain optimum level of ABS copolymer the uPVC/ABS copolymer blends provide for increased stretching of the sample when compared to either of the virgin samples. The interaction of the polymers with each other offers the necessary conditions for increased elongation.

Pure ASA copolymer and virgin uPVC had identical elongation-at-break values, when blended together there was a large increase in elongation. The largest elongation-at-break was observed for the 10% ASA copolymer concentration. Increasing ASA copolymer concentration led to a steady decrease in elongation-at-break. Clearly, small ASA copolymer concentrations increase the elongation-at-break of the uPVC but additional ASA copolymer begins to hinder this elongation. Comparing the two styrenic copolymers reveals that ASA copolymer had higher elongation than the ABS copolymer, both in pure form and at lower concentrations when blended with uPVC. The ABS copolymer did show higher elongation-at-break when in higher concentrations.

Flexural Modulus - The effect of increasing ABS copolymer and ASA copolymer concentration on the

flexural modulus of uPVC is shown in Figure 4. Virgin uPVC showed greater flexural modulus than pure ABS copolymer. When blended together, ABS copolymer increased the flexural modulus of uPVC up to 30% concentration. Beyond this point, additional ABS copolymer decreased flexibilty of the blend. All blends had greater flexibility than pure ABS copolymer. Pure ASA copolymer was less flexible than uPVC. Blending lower concentrations of this ASA copolymer with uPVC led to a sizable increase in flexural modulus. Higher concentrations of ASA copolymer led to a large decrease in flexural modulus, even to levels below hhat of pure ASA copolymer. Clearly the presence of ASA copolymer in higher concentrations in uPVC led to an increase in sample flexibility. Pure ASA copolymer had higher flexural modulus than pure ABS copolymer but when blended with uPVC the ABS copolymer tended to provide for the higher flexural modulus.

Impact Performance – The effect of increasing ABS copolymer and ASA copolymer concentration on the flexural modulus of the uPVC is shown in Figure 5. Pure ABS copolymer had higher impact strength than uPVC. When the ABS copolymer was blended with the uPVC it provided for substantially improved impact performance, the impact strength of the 10-40% uPVC/ ABS copolymer blends was almost double that of the virgin uPVC. Beyond 40% ABS copolymer concentration the impact strength decreased. Clearly the structure provided by the blending of the ABS copolymer with the uPVC gave an improved impact performance, although excessive ABS copolymer hinders this impact improvement. Pure ASA copolymer had higher impact strength than the virgin uPVC. Blending the ASA copolymer with uPVC, like the ABS copolymer, provided for a substantial increase in impact performance. The highest impact strength was recorded for the lowest ASA copolymer concentrations. Additional ASA copolymer caused a progressive decline in impact performance. ASA copolymer tended to exhibit better impact properties than the ABS copolymer both in virgin form and as blends with uPVC.

DMTA – Table 1 shows the heat deflection temperatures derived from the storage modulus thermograms in shown in Figure 6 and 7. With increasing ABS copolymer and ASA copolymer concentration in the uPVC/ABS copolymer blends there was an increase in the HDT. ABS copolymer provided for the highest HDT among the blends even though ASA copolymer has the highest HDT. However, ASA copolymer did produce higher HDTs at lower concentrations.

Storage modulus is very closely linked to tensile modulus as both are a measure of part stiffness. The storage modulii recorded in Figures 6 and 7 correlates well with the tensile modulii in Figure 1. In the working range (0-30°C), virgin uPVC exhibited higher E' values than both the blends and pure ASA copolymer. The thermogram also highlighted, just as Figure 1 did, that the higher ASA copolymer concentration blends were less stiff. The thermograms showed that ABS copolymer gives slight fluctuations in stiffness and no set trend when blended with uPVC, although all gave similar values within the working range.

Loss modulus is a measure of the energy that is dissipated by the part during deformation. It is a measure of viscous flow in which portions of the polymer will flow under conditions of stress in the form of stress relaxation. An increase in loss modulus indicates an increase in the structural mobility of the polymer. The glass transition temperature of a polymer (or a blend) can be noted directly from a loss modulus thermogram. The Tg of uPVC can be seen clearly in Figures 8 and 9 to increase significantly when blended with both ASA copolymer and ABS copolymer. There was a step increase in Tg with increasing styrenic copolymer concentration. There was also an increase in the value of the E" with increasing concentration indicating an increase in structural mobility within the part. This may explain the decrease in tensile modulus and increase in elongation-at-break with increasing styrenic copolymer in the blends.

Tan δ is a measure of viscoelastic response at different temperatures. Higher tan δ values indicate an increase structural mobility and a greater tendency for viscous flow – resulting in an increase in ductile behaviour. The lower the tan δ, the more brittle the part. The tan δ of each styrenic copolymer, shown in Figures 10 and 11, behaves quite differently with increasing concentration in the uPVC blends. Increasing ASA copolymer concentration caused a large decrease in the tan δ value, while increasing ABS copolymer increases the value of tan δ.

Conclusion

This work has clearly shown that styrenic copolymers can greatly increase the heat deflection temperature of uPVC, without affecting the mechanical properties of that polymer. The copolymer was able to achieve the highest increase in heat deflection temperature but the ASA copolymer achieved a higher heat deflection temperature at the lower concentrations. The mechanical properties of the two styrenic copolymers were similar, although there was slight divergence at certain concentrations in the blends. The styrenic copolymers did improve the mechanical performance of the uPVC, particularly the impact strength. Clearly, styrenic copolymers have been shown themselves to be an important component in uPVC profile extrusion.

References
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3. DeArmitt, C. "Raising the softening point of PVC", Plastics Additives & Compounding July 2004, p.32-34
4. Nelson, G., "Styrenic Specialities:Terluran", BASF
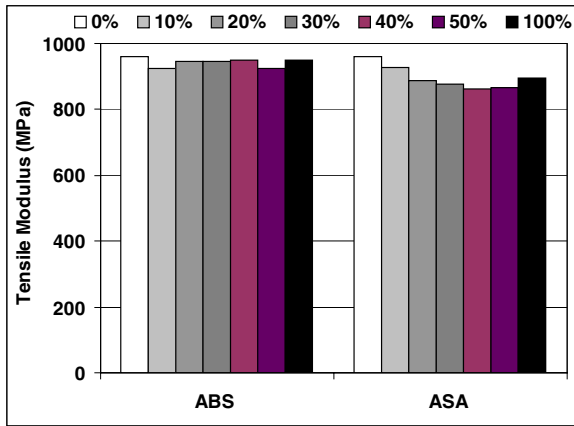5. Nelson, G., "Styrenic Specialities:Luran", BASF

Figure 1 - The effect of increasing ABS copolymer and ASA copolymer concentration on the tensile modulus of uPVC
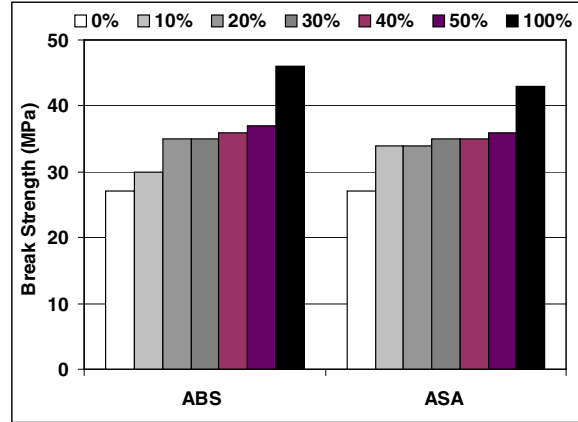

Figure 2 - The effect of increasing ABS copolymer and ASA copolymer concentration on the break strength of uPVC
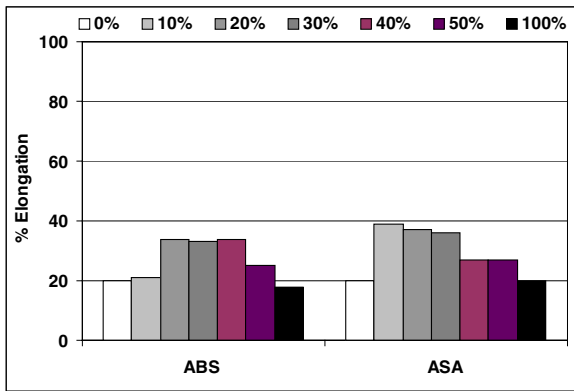

Figure 3 - The effect of increasing ABS copolymer and ASA copolymer concentration on the % elongation of uPVC
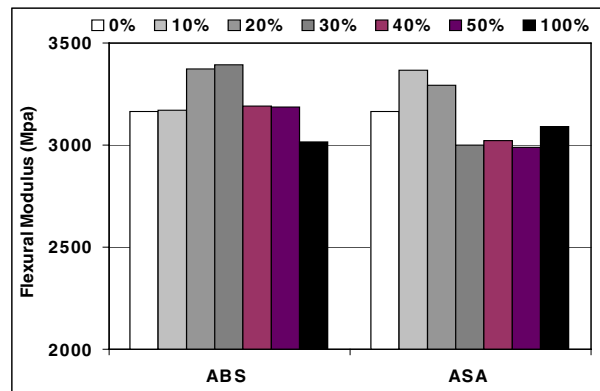

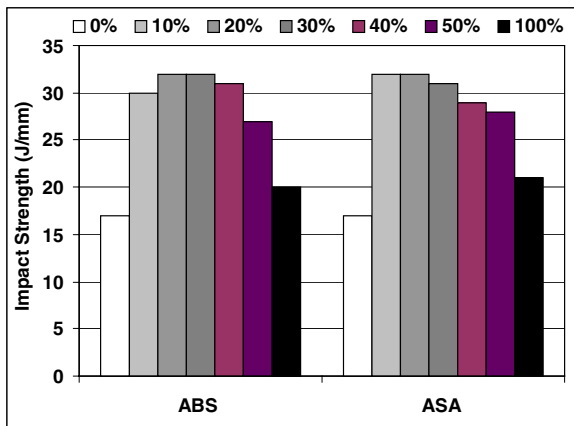Figure 4 - The effect of increasing ABS copolymer and ASA copolymer concentration on the flexural modulus of uPVC

Figure 5 - The effect of increasing ABS copolymer and ASA copolymer concentration on the impact strength of uPVC

	Heat Deflection Temperature (°C)	
	Luran	Terluran
0%	65	65
10%	72	69
20%	73	71
30%	75	77
40%	76	80
50%	77	81
100%	97	94

Table 1 - The effect of increasing ABS copolymer and ASA copolymer concentration on the heat deflection temperature of uPVC
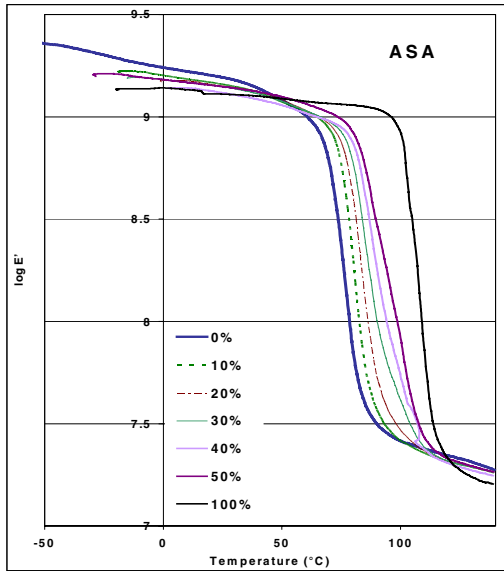
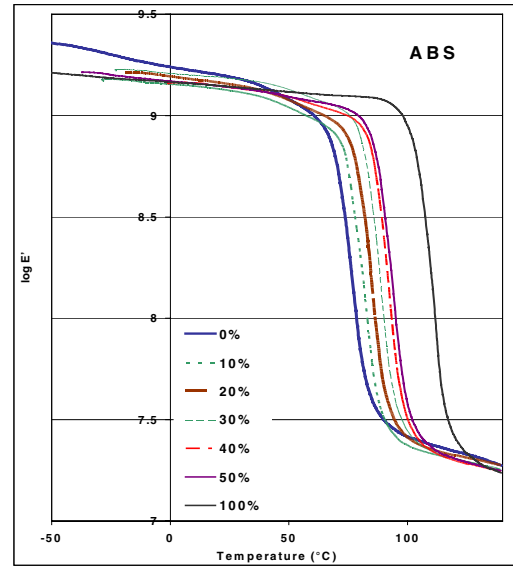Figure 6 – Storage Modulus of uPVC/ASA
copolymer blends

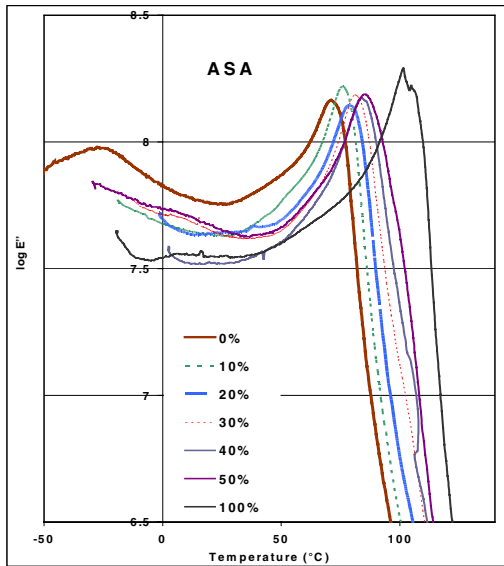Figure 7 - Storage Modulus of uPVC/ABS
copolymer blends

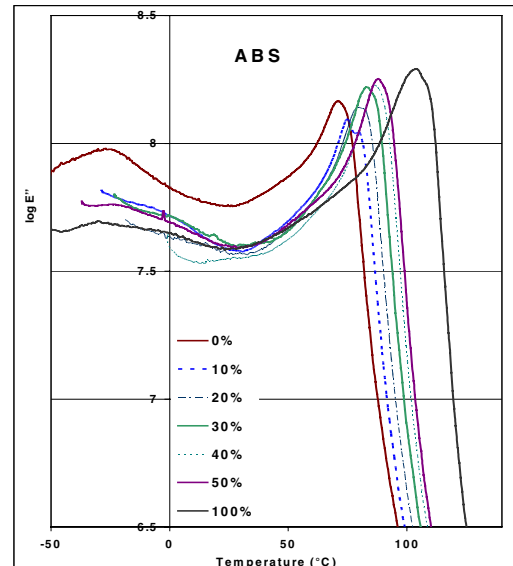Figure 8 – Loss Modulus of uPVC/ASA
copolymer blends

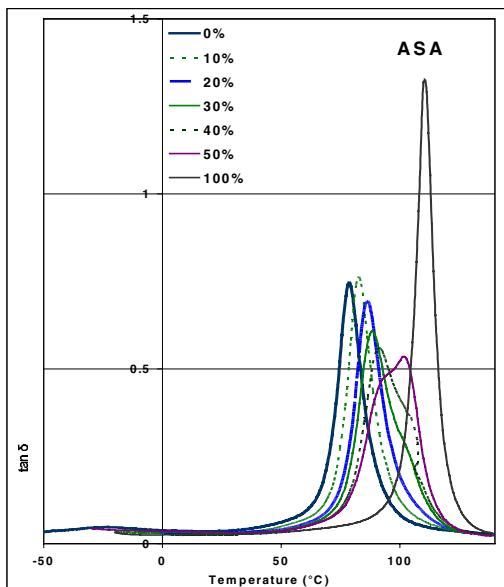Figure 9 - Loss Modulus of uPVC/ABS
copolymer blends

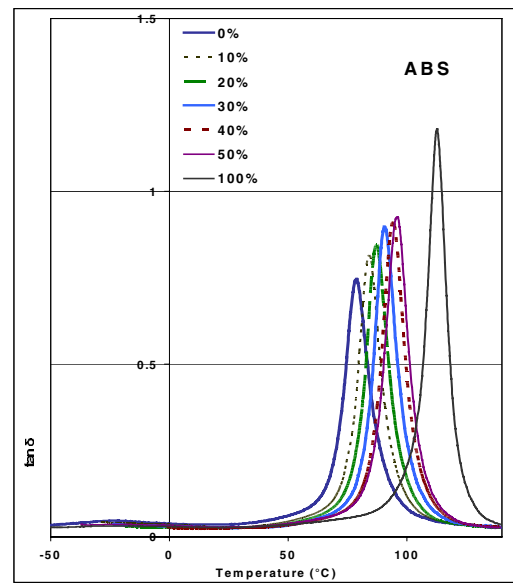Figure 10 – Tan δ of uPVC/ASA copolymer
blends

Figure 11 - Tan δ of uPVC/ABS copolymer
blends