

# DISCRETE RELAXATION SPECTRUM AND K-BKZ CONSTITUTIVE EQUATION FOR PVC, NBR AND THEIR BLENDS

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## ABSTRACT:

Frequency sweep experiments were performed on poly(vinyl chloride) (PVC) and acrylonitrile butadiene rubber (NBR) as well as their miscible blends PVC/NBR (70/30), PVC/NBR (50/50), and PVC/NBR (30/70) in oscillatory shear. The samples were prepared by mechanical blending at 160°C. In order to investigate the validity of time temperature superposition (TTS) principle the loss angle  $\delta$  versus the logarithm of the absolute value of the complex modulus,  $G^*$ , were plotted. It was shown that the TTS principle is not valid for the above-mentioned polymer materials and therefore they are not thermorheologically simple. Master curves of PVC, NBR, and PVC/NBR (50/50) blend were therefore obtained approximately. Using a nonlinear regression method, discrete relaxation spectra were determined for PVC, NBR, and PVC/NBR (50/50). To study non-linear viscoelasticity behavior, the experiments of steady shear, start up steady shear, and step strain were carried out. The damping function was determined by the step strain experiments. Using K-BKZ constitutive equation, the shear viscosity and the shear stress growth function were calculated from the discrete relaxation spectra and the damping function and then compared to experimental data. The K-BKZ constitutive equation provides very good prediction over the entire range of experimental results.

## ZUSAMMENFASSUNG:

Frequenz-Sweep Experimente wurden an Polyvinylchlorid (PVC) und Acrylonitrilbutadiengummi (NBR) und an deren mischbaren Abmischungen PVC/NBR (70/30), PVC/NBR (50/50) und PVC/NBR (30/70) in oszillatorischer Scherströmung durchgeführt. Die Proben wurden durch mechanische Abmischung bei 160°C hergestellt. Um die Gültigkeit des Zeit-Temperatur-Superpositionsprinzips (TTS-Prinzip) zu untersuchen, wurde der Verlustwinkel  $\delta$  gegen den Logarithmus des Absolutbetrages des komplexen Moduls,  $G^*$ , aufgetragen. Es wurde gezeigt, dass das TTS Prinzip für die oben erwähnten Polymerwerkstoffe nicht gültig ist, und dass diese deshalb nicht thermorheologisch einfach sind. Masterkurven für PVC, NBR und PVC/NBR (50/50) wurden deshalb approximativ erhalten. Unter Benutzung einer nicht-linearen Regressionsmethode wurden diskrete Relaxationsspektren für PVC, NBR, und PVC/NBR (50/50) bestimmt. Um nicht-linear viskoelastisches Verhalten zu untersuchen, wurden stationäre Scheruntersuchungen, Scheranlaufversuche, und sog. Step/Strain Experimente durchgeführt. Unter Benutzung eines K-BKZ konstitutiven Gleichung, wurden die Scherviskosität und das Anwachsen der Schubspannung aus dem diskreten Relaxationszeitspektrum und der Gedächtnisfunktion berechnet und dann mit experimentellen Daten verglichen. Die K-BKZ Gleichung liefert eine sehr gute Vorhersage über den gesamten Bereich der experimentellen Daten.

## RÉSUMÉ:

Des expériences de cisaillement oscillatoire en balayage de fréquence ont été effectuées sur du PVC et du caoutchouc de butadiène acrylonitrile (NBR), de même que sur leurs mélanges miscibles PVC/NBR (70/30), PVC/NBR (50/50) et PVC/NBR (30/70). Les échantillons furent préparés par mélange mécanique à 160°C. Dans le but d'étudier la validité du principe de superposition temps température (TTS), on a utilisé la représentation graphique suivant: l'angle de perte  $\delta$  en fonction du logarithme de la valeur absolue du module complexe  $G^*$ . On a montré que le principe TTS n'est pas valide pour les matériaux mentionnés ci-dessus, et donc qu'ils ne sont pas thermorhéologiquement simples. Les courbes maîtresses du PVC, du NBR et du mélange PVC/NBR (50/50) ont donc été construites de manière approximative. En utilisant une méthode de régression non linéaire, des spectres de relaxation discrets ont été déterminés pour le PVC, le NBR et le PVC/NBR (50/50). Afin d'étudier le comportement viscoélastique non linéaire, des expériences de cisaillement établi, d'application instantanée de déformation et de cisaillement établi ont été menées. En utilisant l'équation constitutive de type K-BKZ, les fonctions de viscosité de cisaillement et de montée en contrainte de cisaillement ont été calculées à partir des spectres de relaxation discrets et de la fonction d'amortissement, et ont été comparées aux données expérimentales. L'équation constitutive de type K-BKZ fournit une très bonne prédiction de l'ensemble des résultats expérimentaux.

**KEY WORDS:** poly (vinyl chloride), acrylonitrile butadiene rubber, time temperature superposition, miscible blend, shear viscosity, K-BKZ constitutive equation

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