

INFLUENCE OF MOLECULAR WEIGHT OF SAN ON RHEOLOGICAL AND MECHANICAL PROPERTIES OF ABS-PLASTICS

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ABSTRACT:

Rheological and mechanical properties of acrylonitrile-butadiene-styrene polymers (ABS) prepared via bulk polymerization depending on the molecular weight (Mw) of styrene-acrylonitrile copolymer (SAN) have been investigated. The tendencies of attaining the yield stress at steady-state shear flow and approaching to the "plateau" region of storage modulus at low frequencies in oscillatory tests were observed. Both these phenomena are induced by formation of the structural skeleton consisting of polybutadiene (PB) particles arranged in the SAN-matrix. Growth of Mw of SAN leads both to increase of the "plateau" value of storage modulus at low frequencies and the yield stress. This fact can be explained by the influence of Mw of SAN chains grafted onto PB particles on structure formation in ABS melts because of a redistribution of the ratio particle-particle / particle-matrix interactions. The elongational viscosity of ABS melts is a power function of Mw of SAN matrix. The power index of this function increases with the polymer straining that reflects orientation of SAN chains with their length increase. The strain-hardening index of ABS melts increases considerably with increase of SAN matrix Mw. However, it does not depend on presence of PB particles in the material. It means that the value of this index is governed by orientation effect in the SAN matrix. The impact strength of the investigated ABS samples is interrelated with rheological characteristics of ABS melts as well as Mw of SAN. The dependence of impact strength on Mw can be explained by increasing role of orientation effects of SAN chains with Mw increase in the copolymer fibrils connecting the walls of crazes formed at impact action.

ZUSAMMENFASSUNG:

Die rheologischen und mechanischen Eigenschaften von Acrylnitril-Butadien-Styrolpolymeren (ABS), die mittels Massepolymerisation hergestellt wurden, wurden in Abhängigkeit des Molekulargewichts (Mw) des Styrol-Acrylnitrilcopolymeren (SAN) untersucht. Es wurden die Tendenzen beobachtet, eine Fließgrenze in stationärer Scherströmung zu besitzen und einen Plateaubereich für den Speichermodul bei kleinen Frequenzen aufzuweisen. Diese beiden Phänomene werden durch die Bildung eines Strukturgerüsts verursacht, das aus den Polybutadien-(PB)-Partikeln in der SAN-Matrix besteht. Eine Erhöhung des Molekulargewichts von SAN führt zu einer Erhöhung des Plateauwertes bei niedrigen Frequenzen und der Fließspannung. Dieser Sachverhalt kann durch den Einfluss des Molekulargewichts der SAN-Ketten, die auf die PB-Teilchen aufgepropft worden sind, auf die Strukturbildung in der ABS-Schmelze unter Berücksichtigung der Umverteilung des Verhältnisses Teilchen-Teilchen/Teilchen-Matrix-Wechselwirkungen erklärt werden. Die Dehnviskosität der ABS-Schmelze ist eine Potenzfunktion des Molekulargewichts der SAN-Matrix. Der Exponent dieser Funktion steigt erheblich mit der Dehnung des Polymeren an, was die Orientierung der SAN-Ketten mit der Kettenlänge widerspiegelt. Der Dehnverfestigungsindex der ABS-Schmelze steigt erheblich mit erhöhtem Molekulargewicht der SAN-Matrix an. Dagegen hängt er nicht von den PB-Teilchen in dem Material ab. Dies bedeutet, dass der Index durch den Orientierungseffekt in der Matrix bestimmt wird. Die Schlagfestigkeit der untersuchten ABS-Proben wird mit den charakteristischen rheologischen Größen der ABS-Schmelze und dem Molekulargewicht von SAN in Beziehung gesetzt. Die Abhängigkeit der Schlagfestigkeit vom Molekulargewicht kann durch die erhöhte Bedeutung des Orientierungseffekts der SAN-Ketten mit erhöhtem Molekulargewicht in den Copolymerfibrillen erklärt werden, die die Ränder der beim Bruch gebildeten Crazes verbinden.

RÉSUMÉ:

Les propriétés mécaniques et rhéologiques de polymères de acrylonitrile-butadiène-styrène (ABS), préparés par polymérisation en masse en fonction de la masse moléculaire (Mw) du copolymère styrène-acrylonitrile (SAN), ont été étudiées. Les tendances à atteindre la contrainte seuil sous écoulement de cisaillement constant et à s'approcher du plateau du module élastique aux basses fréquences des tests oscillatoires, ont été observées. Ces deux phénomènes sont induits par la formation du squelette structural constitué de particules de polybutadiène (PB) organisées dans la matrice SAN. La croissance de la Mw du SAN conduit à une augmentation de la valeur du plateau du module élastique aux basses fréquences, ainsi qu'à l'augmentation de la contrainte seuil. Ce fait peut être expliqué par l'influence de la Mw des chaînes de SAN greffées sur les parti-

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local temperature increase in several tens of degrees depending on the rate of deformation [44, 45] and, perhaps, may bring about the local softening of the material.

Keeping in mind the direct correlation between J and M_w of SAN matrix of ABS studied, it is possible to give another explanation of this dependence. In this case M_w increase should promote the stretching and orientation of SAN chains in the fibrils connecting the craze walls. In its turn this should increase the rigidity of the fibrils and influence the impact strength value. Such orientation of SAN chains in the fibrils may be determined by both the adiabatic heating of craze walls and by the transition of SAN chains to the forced high elastic state because of decreasing of the potential barrier determining the mobility of polymer chain segments under the action of high stresses [2, 45]. This is agreement with the applicability of the Eyring activation equation for description of the kinetics of the craze formation [2, 45].

4 CONCLUSION

The considered results show that molecular weight of SAN influences considerably the rheological behavior and some mechanical properties of ABS. This influence appears in two different ways. On the one hand M_w of SAN influences the rheological behavior of ABS in the same way as in the case of homophase polymeric systems. That is an increase of M_w of SAN leads to the increase of viscosities both at shear and uniaxial extension. It also intensifies the orientational effects and rigidity of ABS melts at their stretching and thus influences their processing and the impact strength. In the last case the M_w increase should influence the craze development at ABS deformation. On the other hand the increase of M_w of SAN leads to the increase of the length of SAN chains grafted onto PB particles. It is believed that this facilitates the separation of PB particles from the SAN matrix and leads to their agglomeration with formation of denser structural network. This determines the flow mechanism of ABS and causes increase of their yield stress and the storage modulus in the low frequency plateau region.

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